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Silica removal pretreatment for effluent reuse in graphic paper production

Eliminación de sílice como pretratamiento para la reutilización de efluentes en la fabricación de papeles gráficos

MEMORIA PARA OPTAR AL GRADO DE DOCTORA

PRESENTADA POR

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ELIMINACIÓN DE SÍLICE COMO PRETRATAMIENTO PARA LA REUTILIZACIÓN DE EFLUENTES EN LA FABRICACIÓN DE PAPELES GRÁFICOS / SILICA REMOVAL PRETREATMENT FOR EFFLUENT REUSE IN GRAPHIC PAPER PRODUCTION

DOCTORAL DISSERTATION

Submitted to the Complutense University of Madrid for the degree of Doctor in Chemical Engineering by

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ÁNGELES BLANCO SUÁREZ Y RUBÉN MIRANDA CARREÑO, PROFESORA TITULAR Y PROFESOR CONTRATADO DOCTOR DEL DEPARTAMENTO DE INGENIERÍA QUÍMICA, RESPECTIVAMENTE, DE LA FACULTAD DE CIENCIAS QUÍMICAS DE LA UNIVERSIDAD COMPLUTENSE DE MADRID

INFORMAN

Que el trabajo de investigación titulado "ELIMINACIÓN DE SÍLICE COMO PRETRATAMIENTO PARA LA REUTILIZACIÓN DE EFLUENTES EN LA FABRICACIÓN DE PAPELES GRÁFICOS / SILICA REMOVAL PRETREATMENT FOR EFFLUENT REUSE IN GRAPHIC PAPER PRODUCTION", ha sido realizado bajo su dirección en el Departamento de Ingeniería Química, dentro del Grupo de Investigación de Celulosa y Papel de la Universidad Complutense de Madrid, y constituye la memoria que presenta Dña. Isabel Latour Romero para optar al Grado de Doctor.

Y para que conste a los efectos oportunos, firman la presente, en Madrid a 8 de octubre de 2015.

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ORIGINAL PUBLICATIONS LIST

I. **I. Latour,** R. Miranda, A. Blanco. Silica removal from newsprint mill effluents with aluminum salts. *Chemical Engineering Journal* 230 (2013) 522-531.

II. R. Miranda, **I. Latour**, A. Hörsken, R. Jarabo, A. Blanco. Enhanced silica removal by polyamine- and polyacrylamide- polyaluminum hybrid coagulants. *Chemical Engineering & Technology* (2015) DOI:.10.1002/ceat.201400604.

III. **I. Latour,** R. Miranda, R. Carceller, A. Blanco. Efficiency of polyaluminum nitrate sulphate-polyamine hybrid coagulants for silica removal. *Desalination and Water Treatment* (2015) DOI: 10.1080/19443994.2015.1091992.

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VI. R. Miranda, R. Nicu, **I. Latour**, M. Lupei, E. Bobu, A. Blanco (2013) Efficiency of chitosans for the treatment of papermaking process water by dissolved air flotation. Chemical Engineering Journal 231 (2013) 304-311.

VII. **I. Latour**, R. Miranda, A. Blanco**.** Silica removal in industrial effluents with high silica content and low hardness. *Environmental Science and Pollution Research* 21 (2014) 9832-9842.

VIII. **I. Latour**, R. Miranda, A. Blanco. Optimization of silica removal with magnesium chloride in papermaking effluents: mechanistic and kinetic studies. *Environmental Science and Pollution Research* (2015) DOI: 10.1007/s11356-015-5542-z

IX. **I. Latour**, R. Miranda, A. Blanco Silica removal with sparingly soluble magnesium compounds. Part I. *Separation and Purification Technology* 138 (2014) 210-218.

X. **I. Latour**, R. Miranda, A. Blanco**.** Silica removal with sparingly soluble magnesium compounds. Part II. *Separation and Purification Technology* 149 (2015) 331-338.

Articles in preparation

XI. R. Miranda, **I. Latour**, A. Blanco. Silica removal from an industrial effluent by adsorption onto calcined hydrotalcite.

XII. R. Miranda, **I. Latour**, A. Blanco. Silica removal from an industrial effluent onto activated alumina.

INDEX

SUMMARY

Although great efforts have been carried out during the last decades, the reduction of water use continues being a key issue for papermakers due to the stringent environmental legislation, the increase in water prices, the treatment costs, the development of sustainable processes, or simply due to the lack of water resources. Closure of water circuits by traditional internal treatments (e.g. dissolved air flotation) and reuse of the process waters is a common practice in paper mills; however, a high closure of the water circuits produces an exponential accumulation of dissolved and colloidal material (DCM) which affects the production process and the quality of the final product.

One of the most applied strategies to further reduce the fresh water consumption is the reuse of the final effluent after an advanced treatment, usually involving a final reverse osmosis (RO) step. In deinking paper mills, the reuse of the effluent is limited by silica fouling of RO membranes. If silica is not previously removed, the maximum recovery in RO membranes is limited to 20%. The main source of these high silica levels (150-250 mg/L SiO_2) is the sodium silicate used as process additive, which cannot be substituted due to its variety of functions and low price.

For an economically feasible process, the RO recovery must be increased from 20% to 60-80%. Consequently, it is necessary to find a silica removal technique that allows treating large volumes of water with high silica contents. Silica concentration should be reduced to around 20-60 mg/L while maintaining the conductivity increase at minimum, without causing side effects on the membrane and at low cost.

Silica removal is usually carried out by coagulation or during precipitative softening processes at high pH. These techniques have been successfully applied in waters with low silica levels and high hardness content. However, there are only a few studies in the literature focused on silica removal in waters with high silica and low hardness contents such as those from the paper industry. Therefore, the main objective of this doctoral thesis is to generate new knowledge on the applicability of these two techniques (coagulation-flocculation and silica removal during precipitative softening) in the waters from the paper industry. Moreover, the potential use of adsorption onto activated alumina and hydrotalcites for silica removal is also studied.

First, the use of polyaluminum chlorides for silica removal was optimized. Among the different coagulants, PAN-PA2, which is a hybrid coagulant formed by a combination of a polyaluminum nitrate sulphate (PANS) with a cationic quaternary polyamine (PA), was the most efficient and versatile coagulant. It removed 97% of silica at pH=10.5 and it was also very efficient (76% silica removal) at the initial pH of the effluent (pH=8.3). Due to the high efficiency of the hybrid coagulant for this application, the efficiency of several commercial inorganic-organic hybrid coagulants was studied. Results showed that the hybrids significantly increased both silica and chemical oxygen demand (COD) removal at all the pHs studied, being the PA modifications more efficient than PAM modifications.

Based on these results, the efficiency of newly tailor made hybrid coagulants was studied optimizing their formulation, i.e. organic polyelectrolyte content and its molecular weight. These coagulants were based on the combination of PANS with different concentrations of PA and PDADMAC of different molecular weights. PA hybrids were always more efficient than PANS,

especially at lower pHs, being 5% the optimum PA content. On the other hand, the efficiency of PDADMAC hybrids was close to that of PANS.

The use of chitosan and chitosan derivates as alternative biodegradable coagulants for silica removal was studied. However, results indicated that only minor silica removals could be obtained (<10%).

Silica removal during precipitative softening was also studied. The low hardness of deinking paper mill effluents made necessary the addition of magnesium compounds (soluble and sparingly soluble compounds). With soluble magnesium compounds, high silica removal rates (80-90%) were obtained at pH=11.5, however, an important increase in the conductivity of the treated waters occurred. Therefore, the use of sparingly soluble magnesium compounds was studied. At ambient temperature and low contact time, these compounds showed low efficiency (20-40%) due to their low solubility. With the aim of increasing silica removal, the pre-acidification of the sparingly soluble magnesium compounds was studied. After this pre-acidification, sparingly soluble magnesium compounds showed similar silica removal rates to those obtained with the soluble magnesium compounds but with the advantage of a lower conductivity increase of the treated waters.

The second strategy followed to favor the dissolution kinetics of the sparingly soluble magnesium compounds and thus the silica removal, was to increase the contact time and the operational temperature. These studies demonstrated that these compounds could be used directly with high silica removal efficiencies at temperatures > 35ºC. Silica removal rates > 90% were obtained with MgO at T>35ºC, 90 min contact time, without pH regulation and at low dosages (500 mg/L), which is a great achievement.

In the literature there is no consensus about which is the mechanism involved in the removal of silica during water softening. Different authors consider either adsorption into fresh precipitated $Mg(OH)_2$ or co-precipitation of silica to form magnesium silicates with different stoichiometries. In this thesis, the mechanism involved was clarified. The analyses of the solids demonstrated that the main silica removal mechanism is precipitation as magnesium silicates, being antigorite ($Mg_3Si_2O_5(OH)_4$) the most likely species to precipitate under these conditions.

Finally, the possibility of using activated alumina and calcined hydrotalcites as adsorbents for silica removal was also studied. Results obtained indicated that these techniques are viable to treat high silica loaded waters with a high efficiency (80-90% removal). However, the required dosages were high, especially in the case of activated alumina. Calcined hydrotalcites are a promising solution as the required dosage for high removal efficiencies was not high (around 2.5 g/L) and its regeneration was also possible. Some of the advantages of these treatments are the low conductivity increase (no pH regulation is required in this treatment) and the high COD removals (25%).

RESUMEN EXTENDIDO

Tradicionalmente la industria papelera ha sido uno de los mayores consumidores de agua, sin embargo, en las últimas décadas se han llevado a cabo grandes esfuerzos y la industria papelera se ha convertido en un referente en la gestión y reducción del consumo de agua, especialmente en España. Existen varias alternativas para reducir el consumo de agua en la fabricación de papel. La primera alternativa es el cierre de los circuitos de agua, practicada en mayor o menor medida por todas las fábricas, la cual implica la reutilización interna de las aguas de proceso, normalmente tras un tratamiento por flotación con aire disuelto. Mientras que los sólidos en suspensión son eliminados en los sistemas convencionales de clarificación, la eliminación de materia disuelta y coloidal (MDC) es prácticamente nula, por lo que se acumula exponencialmente en las aguas de procesos a medida que se reduce el consumo de agua de alimentación.

Cuando ya no se pueden conseguir mayores reducciones en el consumo de agua mediante el cierre interno de circuitos, hay que recurrir a otras fuentes alternativas de agua como la reutilización del efluente de la fábrica y/o la utilización de agua regenerada procedente de una depuradora de agua municipal. Mediante el tratamiento avanzado de estas aguas se obtiene agua de una calidad similar al agua potable, siendo posible su utilización en cualquier parte del proceso. Sin embargo, en las fábricas de papel destintado la reutilización del efluente está limitada por su alto contenido en sílice, que produce incrustaciones en las membranas de ósmosis inversa. Estas incrustaciones provocan problemas operacionales en la membrana como la disminución de la calidad del agua generada, un mayor consumo de energía y limitan el tiempo de vida útil de la membrana. Si la sílice no es eliminada previamente, el porcentaje máximo de recuperación al que se puede trabajar en la unidad de ósmosis inversa es de un 20%, lo cual limita la viabilidad económica y técnica de toda la cadena de tratamientos para la reutilización del efluente. El alto contenido en sílice del efluente (150-250 mg/L) procede de la utilización de silicato sódico como aditivo de proceso en las etapas de destintado y blanqueo de la pasta. Debido a la gran cantidad de funciones que posee este aditivo, normalmente asociadas a la consecución de las propiedades ópticas del producto final, y a su bajo precio, su sustitución es complicada por lo que es necesario eliminar la sílice antes de las membranas de ósmosis inversa.

Aunque existen diferentes técnicas para la eliminación de sílice, en la mayoría de los casos se realiza por coagulación a pH alto o durante el ablandamiento de aguas. En la mayoría de estudios existentes en la bibliografía, estas técnicas se han aplicado en el tratamiento aguas salobres, las cuales se caracterizan por un bajo contenido en sílice (10-40 mg/L) y alta dureza, lo cual hace que muchas de las conclusiones alcanzadas en estos estudios no sean extensibles al tratamiento de aguas industriales con alto contenido en sílice.

Por tanto, el objetivo principal de esta Tesis Doctoral es generar nuevo conocimiento en la utilización de las dos técnicas principales de eliminación de sílice (coagulación-floculación y eliminación de sílice durante el ablandamiento de aguas). Además, se estudiará la posibilidad de utilizar la adsorción con alúmina activada e hidrotalcitas como técnica novedosa para este tipo de tratamientos.

En primer lugar se estudió la eliminación de sílice con diferentes policloruros de aluminio comerciales. El producto que dio mejores resultados fue un coagulante híbrido formado por un

nitrato sulfato de polialuminio (PANS) y una poliamina (PA). Con este producto se consiguieron eliminaciones de sílice de un 97% a pH=10.5. También fue muy eficiente incluso a pH=8.3 (pH inicial del efluente) (76% de eliminación), lo cual haría innecesario el ajuste de pH, disminuyendo la conductividad del agua tratada y los costes de tratamiento.

Basándose en estos resultados, se profundizó en el estudio de coagulantes híbridos comerciales formados por PANS con diferentes contenidos de poliacrilamidas catiónicas (PAM) o PAs. Los coagulantes híbridos fueron muy efectivos tanto en la eliminación de sílice como de materia orgánica. Una vez más, las modificaciones con PA fueron más eficaces que las modificaciones con PAM.

A continuación, se desarrolló una nueva gama de coagulantes híbridos, preparados combinando PANS con 3 PAs de diferentes pesos moleculares para la optimización tanto del contenido en PA en el híbrido como su peso molecular. Los coagulantes híbridos fueron más efectivos que la sal de aluminio (PANS), especialmente a bajos pHs, siendo un 5% el porcentaje de PA que proporcionó los mejores resultados. La PA de mayor peso molecular mostró una mayor efectividad en la eliminación de demanda química de oxígeno (DQO).

Por otra parte, se estudió el uso en el tratamiento de aguas de proceso de diferentes biopolímeros derivados del quitosán, sin embargo, con estos compuestos se obtuvieron bajas eliminaciones de sílice (<10%).

La siguiente alternativa analizada fue la eliminación de sílice durante el ablandamiento. Debido a la baja dureza de las agua a tratar fue necesario añadir compuestos de magnesio, más eficaces que los compuestos de calcio en la eliminación de sílice. En primer lugar, se utilizaron compuestos solubles de magnesio: sulfato y cloruro de magnesio. Con estos compuestos, se obtuvieron altas eliminaciones de sílice (80-90%) pero a pH elevado (11,5), lo que provocaba un incremento importante de la conductividad en el agua tratada y una adición considerable de contra-iones a las aguas. Por esta razón, se estudió la posibilidad de usar compuestos de magnesio insolubles.

Los compuestos insolubles de magnesio (óxido de magnesio, hidróxido de magnesio y un carbonato-hidróxido mixto de magnesio) fueron poco efectivos (20-40% eliminación de sílice) cuando se probaron en las mismas condiciones de operación que las sales solubles (temperatura ambiente, 15 min de tiempo de contacto). La baja solubilidad de estos compuestos hace que haya poco magnesio disuelto en el agua bajo las condiciones de operación probadas y, en consecuencia, bajas eliminaciones de sílice. Con el objetivo de aumentar las eliminaciones de sílice se siguieron diferentes estrategias. En primer lugar, las suspensiones de los compuestos de magnesio se pre-acidificaron con ácido sulfúrico. Los compuestos de magnesio pre-acidificados mostraron eliminaciones de sílice similares a los de los compuestos solubles (80-90%) con la ventaja adicional de que el incremento en conductividad en las aguas tratadas era menor. La segunda estrategia consistió en aumentar la temperatura y el tiempo de reacción, con fin de favorecer la cinética de disolución de estos compuestos. En este caso, el MgO fue muy efectivo a temperaturas mayores de 35ºC, obteniendo eliminaciones del 90% de sílice con tiempos de reacción de 90 minutos, sin necesidad de regular el pH inicial del agua y a bajas dosis (500 mg/L). Esto hace que el MgO sea la opción de tratamiento ideal si el agua a tratar está a T > 35 ºC, mientras que la coagulación o el uso de sales solubles de magnesio son los tratamientos indicados cuando el agua está a temperaturas menores.

Aunque en la bibliografía existe consenso en que los compuestos de magnesio son más efectivos que los de calcio en la eliminación de sílice, no lo hay sobre si la sílice es eliminada por adsorción en $Mg(OH)_2$ o mediante la precipitación de silicatos magnésicos. En este sentido, en la presente Tesis Doctoral se ha clarificado el mecanismo de eliminación de sílice durante el ablandamiento de aguas. El principal mecanismo de eliminación de la sílice es por precipitación de silicatos magnésicos, siendo la antigorita ($Mg_3Si_2O_5(OH)_4$) la estequiometria del silicato magnésico más probable.

Finalmente, se estudió la adsorción como alternativa para la eliminación de sílice. En este caso se probaron dos adsorbentes: alúmina activada e hidrotalcitas. Esta técnica es muy novedosa para la eliminación de sílice y sólo existe un pequeño número de estudios donde se ha utilizado alúmina activada como sorbente, si bien la utilización de hidrotalcitas sería la primera vez que se utiliza con este fin. Los resultados obtenidos muestran que esta técnica es viable para tratar aguas con alto contenido en sílice. Las dosis de alúmina activada necesarias para obtener eliminaciones de sílice del 80-90% son demasiado altas (7.5-15 g/L). Sin embargo, los resultados obtenidos con las hidrotalcitas calcinadas son prometedores ya que se obtuvo un 80-90% de eliminación con dosis muy inferiores (2.5g/L) y, lo que es también muy importante, su eficacia sólo disminuía ligeramente tras varios ciclos de adsorción-desorción-regeneración. Adicionalmente, el aumento de conductividad en el agua tratada es mínimo, no es necesario realizar un ajuste de pH y consiguen también eliminaciones significativas de DQO.

1. INTRODUCTION

Nowadays, there is an increasing interest in environmental friendly manufacturing and sustainable production processes, driven not only by the regulations but also by customer perspective on environmental issues. Among the different industrial sectors, pulp and paper industry is one of the most sustainable in Europe. Paper is a renewable, recyclable and biodegradable material which can satisfy the demands of the current society. In fact, paper is the most recycled product in Europe, today 52% of the paper industry's raw material comes from recovered products and Europe is the global leader in paper recycling with a 72% recycling rate (CEPI, 2014).

Technological advances in pulping, deinking and bleaching have improved the quality of secondary fibres and now recovered paper can be used as raw material in many paper grades. Figure 1.1 shows the utilization rate of recovered paper, classified by type, for paper and board production for each sector in Europe in 2014. It can be observed that the production of corrugated board (case materials) and newsprint is almost exclusively based on recovered fibres. In the case of the production of newsprint, object of the present thesis, the utilization rate is one of the highest (93%) being old newspapers and magazines the most important raw materials for its production.

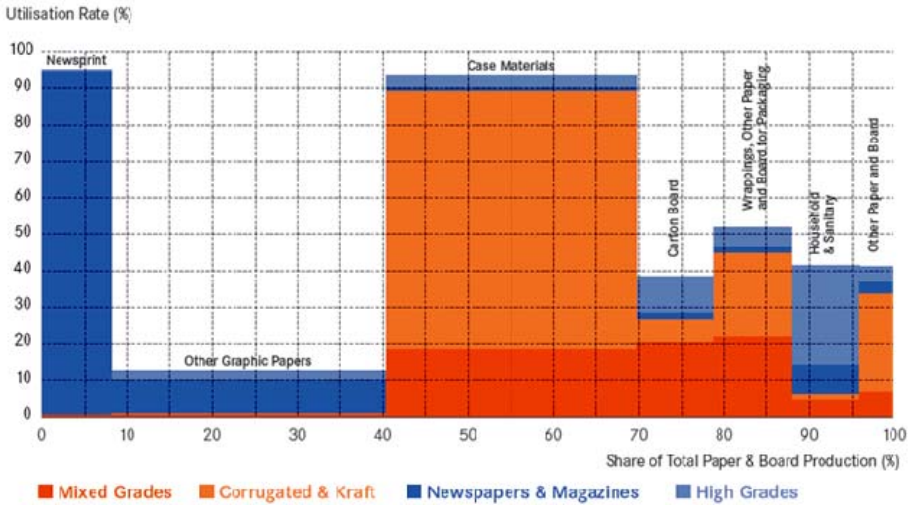

Figure 1.1. *Utilization of paper for recycling by sector in Europe in 2014 (CEPI, 2015).*

1.1. RECYCLED GRAPHIC PAPER MANUFACTURING

The recycled graphic paper manufacturing process involves two main stages: pulp manufacturing and paper formation. The configuration of the different operations depends on the specifications of the final product. For example, deinking is necessary for the production of graphic papers but it is not used for packaging grades. Figure 1.2, shows a general scheme of the main processes involved in the deinking line for graphic paper production. The deinking line starts in the pulper, where the paper is disintegrated and the ink is detached from the fibres with the addition of chemicals. Then, the pulp is cleaned and screened to remove contaminants such as staples and plastics. Subsequently, the pulp is subjected to deinking and bleaching processes to achieve the optical properties required for the final product. Once the pulp is obtained, the paper sheet is formed. In the paper machine, the paper is formed and it passes through the pressing and drying

sections to remove the excess of water. Finally, in the finishing section the appearance and properties of paper are enhanced by different treatments such as coating or calendering.

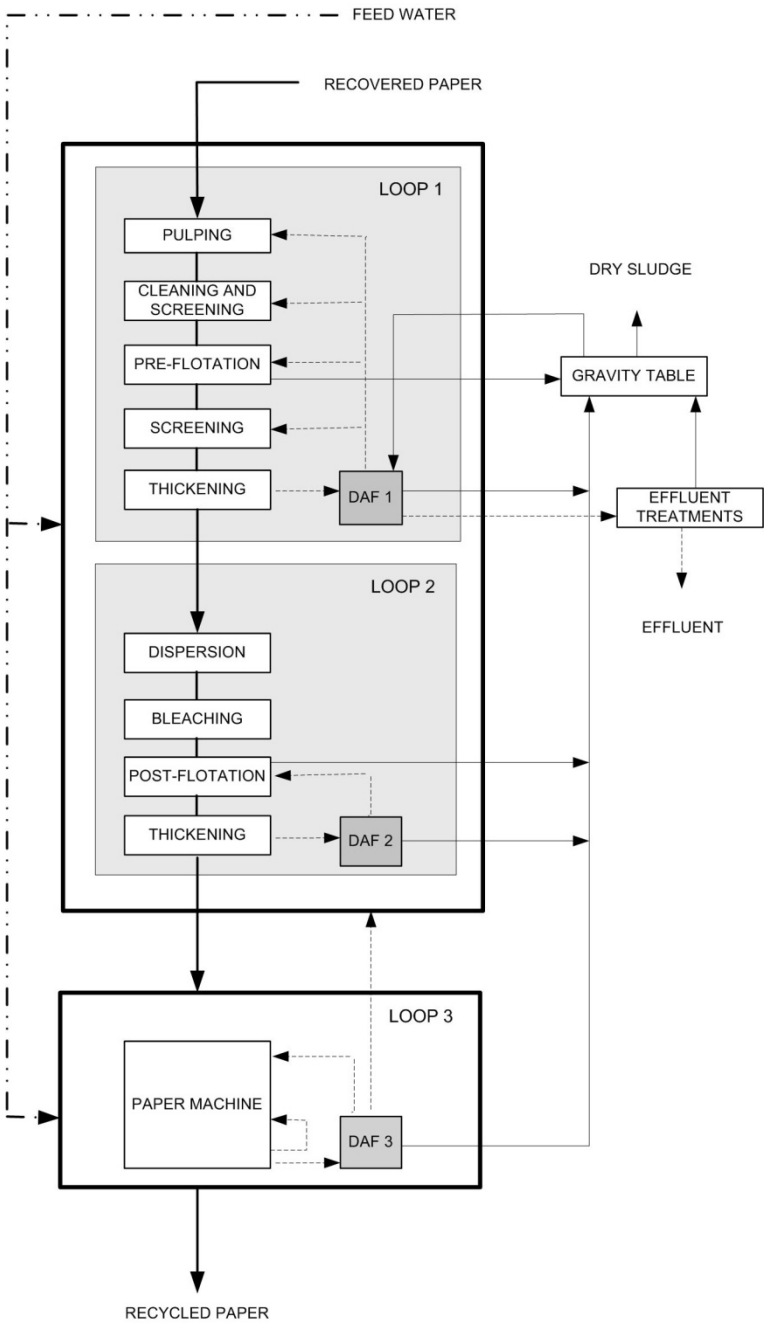

Figure 1.2. *Simplified scheme of the deinking line and water circuits for recycled graphic paper production.*

The operational conditions in the different process stages, including type and dosage of chemicals, are of great importance to achieve the required properties of the final product. Table 1.1 shows the typical chemical consumption in the different stages of the newsprint production process. Most of the chemicals used in the process are fairly standard such as caustic soda or hydrogen peroxide. On the other hand, some other complex products are used, e. g. surfactants used in flotation deinking and polyelectrolytes for water clarification or for sheet formation (Lassus 2000; Ferguson 1992a).

There are additives that have more than one role in the process. This is the case of the use of sodium silicate (Na_2SiO_3). It is added in both pulping and bleaching steps to achieve the optical properties required in the final product (Lassus 2000; Ferguson 1992a; Ferguson 1992b). In the pulping stage, sodium silicate enhances ink dispersion and facilitates its removal by flotation. In the bleaching process, sodium silicate acts as a peroxide stabilizer by chelating transition metals, controls corrosion, acts as a pH buffer and is a surface active agent. On the other hand, it causes relevant side effects. In this sense, sodium silicate increase silica concentration in the process water and in the effluent causing scaling problems (Le Fevre and Moran 1996) especially in high closed water circuits. However, due to its great variety of functions, good performance and low price, its substitution is still difficult (Akbarpour et al. 2013; Hamäläinen et al. 2007).

Table 1.1. *Typical chemical consumption in newsprint production (BAT pulp, paper and board 2015).*

Stage	Chemicals
Pulping	0.5-1.0% H_2O_2
	0.5-1.0 %NaOH
	1-2% Na_2SiO_3
Flotation I	0.3-0.6% soap
Flotation II	0.2-0.4% soap
	(NaOH + fatty acids)
Bleaching	1.0-2.0% H_2O_2
	0.5-1.2% NaOH
	1-1.8% Na_2SiO_3
	0.4-1% ditionite
	Up to 0.2% NaOH

* All chemicals consumption is expressed as 100 % effective chemicals and not as commercial solutions containing various amounts of water except for Na_2SiO_3 which is expressed as a commercial solution

1.2. WATER MANAGEMENT IN DEINKING PAPER MILLS. EFFLUENT REUSE

Traditionally paper industry was very intensive in terms of freshwater consumption (Thompson et al. 2001). Throughout the production process, water is used: as dispersion and transporting medium of fibrous raw materials and additives, as heat exchanger fluid, as sealant in the vacuum systems, for steam production, as lubricant agent and for other minor applications (Negro el al. 1995). The amount of water required in the process depends on the raw material, the final product and the technology used in the process. In the case of the newsprint paper production from recovered paper fresh water consumption ranges from 8 to 20 m^3/ t_{paper} (BAT pulp, paper and board 2015).

Nowadays, reduction of fresh water consumption is a key issue due to more restrictive legislation, the lack of water resources, and the increase of water prices and effluent disposal costs. As a big fresh water consumer, the paper industry has made great efforts and now it is one of the leading industries in water management and water reuse (Blanco et al. 2015).

Figure 1.2 shows a simplified scheme of the configuration of the water in a recycled graphic paper process. In this particular case, there are three water loops with dissolved air flotation (DAF) units

in each one. The number of loops and its configuration can vary depending on each particular case (Miranda et al. 2008; Blanco et al. 2015). The deinking line is divided into two loops to prevent contaminants accompany the pulp throughout the process. The third loop is located in the paper machine. In this third loop, the white water from the wet section of the process is treated obtaining three different quality water streams: cloudy, clear and superclear water. The clear and superclear water streams are used in the paper machine where the highest quality water is required, i.e. in the showers of the paper machine or for the dilution of the different chemicals.

Despite all the advantages, the closure of the water circuits has also some drawbacks. The main problem is that the reuse of the water in the process causes a considerable accumulation of dissolved and colloidal material (DCM). Although DAF units are able to remove 80-98% suspended solids, DCM is almost completely recirculated. This increase of the DCM affects both papermaking process and final product quality. Therefore, the level of closure of the water circuits is limited by the assumable DCM levels in water circuits (Miranda et al. 2009a; Miranda et al. 2009b).

Nowadays new and more advanced strategies, such as the use of reclaimed water from municipal wastewater treatment plants (WWTP) or the reuse of the effluent after an advanced water treatment, are being under study with the aim of obtaining new water sources with a similar quality than the fresh water, avoiding the accumulation of DCM in water circuits and thus being possible a practical zero liquid discharge or zero fresh water consumption (Ordoñez et al. 2011; Ordoñez et al. 2010). Currently, most of the reclaimed water is used for agricultural and urban irrigation; one of the main limitations of the use of reclaimed water is the lack of infrastructures to transport the reclaimed water from the WWTP to the facility. Therefore, one of the most promising solutions to continue reducing the use of water in papermaking is the reuse of the effluent in the plant after an advanced treatment with membrane technologies such as ultrafiltration (UF) and reverse osmosis (RO) followed by a disinfection stage by for example UV light (Negaresh et al. 2013; Ordoñez et al. 2010). These membrane technologies allow achieving similar or even better water quality than fresh water; however, membrane fouling caused by silica is limiting the implementation of these technologies in deinking paper mills. This limitation is due to the use of sodium silicate as process additive that produces effluents ranging from 50 to 250 mg/L as SiO_2 (Huuha et al. 2010).

Silica scaling is severe and once it is formed, is very difficult to remove, even by chemical cleaning (Badruzzaman et al. 2011; Stathoulopoulou and Demadis 2008; Zeng et al. 2007; Neofotistou and Demadis 2004; Weng 1995). It causes a decline in water production rates, low permeate quality, unsteady-state operation conditions, higher energy consumption and serious damages in the membranes that shorten its lifetime (Sheikholeslami and Zhou 2000). Moreover, if silica is not removed, it is not possible to work on the RO at recoveries higher than 20% (Ordoñez et al. 2010) limiting the technical and economic feasibility of the whole treatment (Alhseinat and Sheikholeslami 2012, Al-Rehaili 2003).

Silica scaling can occur through different mechanisms. First, deposition of silica compounds such as pure quartz scales, calcium silicate, magnesium silicate and aluminum silicate when their solubility is exceeded. Colloidal silica deposition can also be found. In this case colloids are formed in the bulk solution and then accumulate on the membrane surface blocking the pores. Finally, biogenic silica scaling caused by microorganisms can also appear on the membranes (Sheikholeslami and Bright 2002; Sheikholeslami and Tan 1999).

Previous studies treating an effluent with high silica concentration from a deinking paper mill showed that it is not possible to work at recoveries over 20% without silica scaling in the effluent reuse treatments (Ordoñez et al. 2010). At these recoveries the reclamation of the final effluent is not economically feasible.

Figure 1.3 shows silica concentration versus membrane recovery for a typical initial concentration in a deinking paper mill of 140 mg/L and at different silica removal rates. It can be observed that it is not possible to work at recoveries higher than 20% as silica solubility, which is around 100-150 mg/L L (marked with horizontal red lines in the figure), is exceeded. Therefore, to work at regular recoveries (60-80% for this application) it is necessary to remove at least 80% of the initial silica.

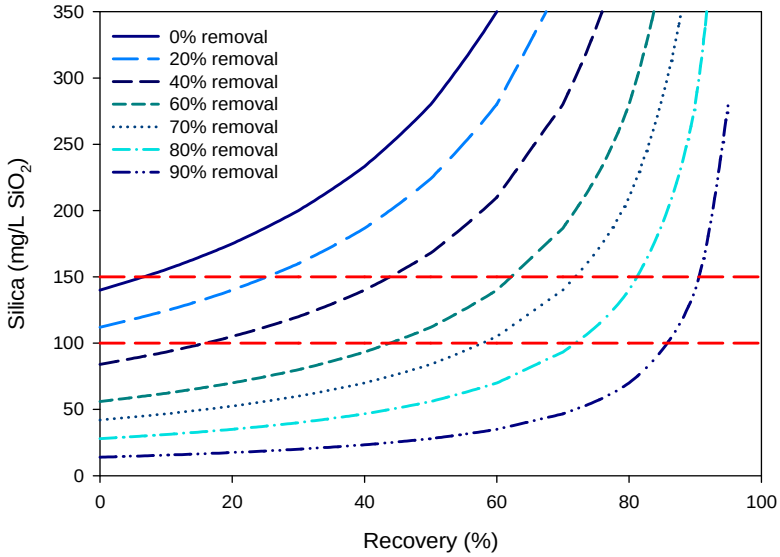

Figure 1.3.- *Silica concentration vs. membrane recovery at different silica removal rates (initial concentration 140 mg/L). A 100% SiO_2 RO rejection has been assumed.*

1.3. SILICA: TYPES AND ORIGIN

Silica and silicates derive from the orthosilicic acid which is a weak polyprotic acid with pKa values of 9.9, 11.8 and 12 (Ning 2002). Figure 1.4 shows the speciation diagram for the orthosilicic acid in pure water as a function of pH, where it can be observed that pHs higher than 8 are required in order to have silica ionized.

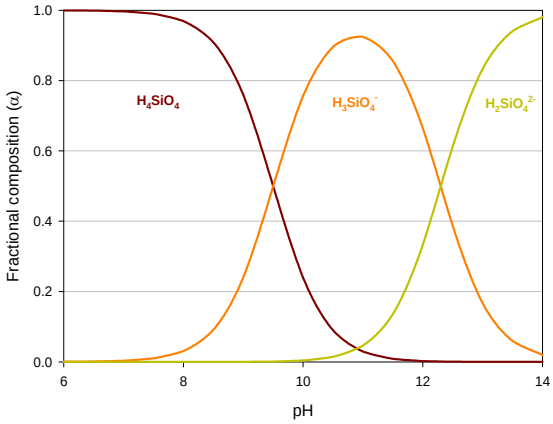

Figure 1.4. *Speciation diagram for the orthosilicic acid system in pure water as a function of pH.*

Orthosilicic acid only remains monomer at 25ºC when its concentration is lower than 2 mM (≈120 mg/L as SiO_2). It polymerizes at higher concentrations creating larger molecules than can reach a colloidal size. The rate of silicic acid polymerization is strongly pH-dependent. It is very fast in neutral and slightly alkaline solutions, and extremely slow at low pH values (pH=2-3) (Ning 2002). More complex colloids can also be formed by its combination with organic and inorganic compounds present in the water (Sheikholeslami and Tan 1999).

The most common classification of silica related species is based on their size. They can be classified as soluble, colloidal or particulate. Soluble silica includes orthosilicic acid, small molecules as dimers, trimers and oligomers. Colloidal silica is formed by more highly polymerized species or particles larger than 50 Å, although sometimes this denomination also includes species down to 10-20 Å, depending on the authors/source. This category includes the colloidal particles formed by the combination with organic and inorganic species (Sheikholeslami and Tan 1999). Finally, particulate silica is larger than colloidal size silica (>1µm).

Moreover, silica can be found in crystalline and in an amorphous form. Crystalline silica has very low solubility in water (6 mg/L as SiO_2) and it is more stable than amorphous silica, which shows a significantly higher solubility of 100-140 mg/L (as SiO_2) at 25ºC (Zaman et al 2015; Sheikholeslami et al. 2001). This solubility is also affected by chemical characteristics such as pH or the presence of organic and inorganic matter. The solubility of silica is essentially constant between the pH limits of 2 and 8.5, but increases rapidly near pH 9 (Le et al. 2015; Cornelis et al. 2011) (figure 1.5a). On the other hand, silica solubility is highly affected by temperature, increasing from 100-150 mg/L as SiO_2 up to 300 mg/L as SiO_2 at 70ºC (Le et al. 2015; Amjad et al. 1997) (figure 1.5b).

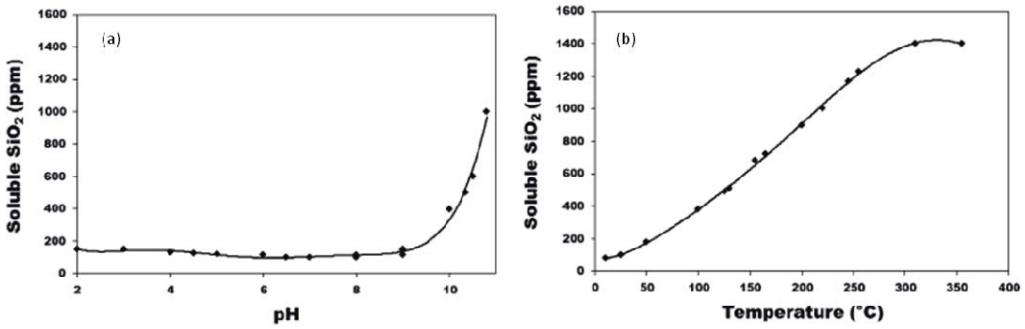

Figure 1.5. *Silica solubility vs. (a) pH (25 ºC), and (b) temperature (Source: Le et al. 2015).*

1.4. SILICA SCALING CONTROL TECHNIQUES

In order to control silica scaling, one strategy is to interact and modify silica to avoid deposition on the membranes without removing. For this purpose, there are different alternatives such as the use of antiscalants, dispersants or working at operational conditions of high silica solubility (high alkaline pHs) (Finster et al. 2015; Ning 2002; Ning 2001). From these techniques, the use of antiscalants is probably the most common one (Amjad et al. 2014; Neofotistou and Demadis 2004; Darton 1999), however, its efficiency in waters with high silica concentration is questionable. Besides, when the treated water is reused in other process stages, as the process conditions can change significantly, scaling problems could appear. Another alternative would be working at pH>10 (Ning RY 2001; White and Masbate 2001), which would increase silica solubility up to around 300-350 mg/L (figure 1.5); however, other species could precipitate extensively on the membrane, such as calcium carbonate which is present at high concentrations in deinking paper mills. Moreover, it would be necessary to use high pH resistant RO membranes and, similarly to what occurred with antiscalants when the treated water is reused, scaling problems could appear later.

The last approach is a pre-treatment of the water to remove silica before the RO unit. Although there are many techniques proposed in literature, silica removal is usually carried out during softening or by coagulation at high pH (Zhao et al 2015; Hermosilla et al. 2012; Huuha et al. 2010, Hsu et al. 2008, Chuang et al. 2006). These techniques are able to treat large volumes of water with high removal rates at low costs, which is a pre-requisite for its use in papermaking applications. Moreover, adsorption could be another option, with very limited research for silica removal, mainly based on synthetic solutions and focused on using activated alumina (Bouguerra et al. 2007).

Nevertheless, there are also specific treatments used for particular applications such as ultra-pure water production or geothermal water treatment. In addition to the previous techniques, electrocoagulation, electrodeionization or ion exchange with strongly based resins, have been reported in the literature (Subramani and Jacangelo 2014, Zeng et al. 2007). However, these techniques are not suitable for the treatment of large amounts of wastewater with high silica content as the case under study (150-250 mg/L as SiO_2). Furthermore, the cost of these treatments is usually higher than the ones previously mentioned.

1.4.1. Coagulation

Coagulation is widely recognized as an efficient silica removal technique. Coagulation is the process by which the components of a stable solution or suspension are destabilized by overcoming the forces that keep the suspension stable. Although in some cases flocculation is used as a synonym for coagulation both concepts have been standardized and flocculation means the process whereby the destabilized particles by coagulation form larger agglomerates (Aguilar et al. 2002).

The most commonly used coagulants for wastewater treatment are inorganic coagulants, particularly Fe(III) and Al(III) salts (Bache and Gregory 2007). For silica removal applications, aluminum based coagulants are the most effective ones (Hermosilla et al. 2012). Among aluminum coagulants, polyaluminum chlorides ($Al_n(OH)_mCl_{3n-m}$) offer several advantages compared to traditional ones such as alum ($Al_2(SO_4)_3$) or sodium aluminate ($NaAlO_2$). Polyaluminum salts are effective in a wider range of pHs and at low temperature, generate more compact and easily sedimentable flocs, are less likely to cause overdosage phenomena and also are less sensitive to water properties fluctuations (Ye et al. 2007; Aguilar et al. 2002).

Polyaluminum chlorides have been extensively used in the last decades for wastewater treatment. However, as chlorides can cause corrosion problems, sometimes chlorides are partially substituted by other species such as sulphates or nitrates, providing a new range of substituted coagulants: polyaluminum nitrates, polyaluminum sulphates or a combination of them, such as polyaluminum nitrate sulphate (PANS) (Lee et al. 2012; Miranda et al. 2009b; Pernitsky and Edzwald 2006). Furthermore, these products can also be modified with organic polymers to create inorganic-organic hybrids or composite coagulants which improve the coagulation performance of the inorganic salts alone due to the synergy between the individual components (Lee et al. 2012). Although there are different kinds of hybrid materials, inorganic-organic hybrids are probably the most developed combination for coagulation and flocculation purposes (Lee et al. 2012). The organic coagulants offer the advantage of lower dosages, broader pH operating range, and smaller sludge production (Miranda et al. 2009b; Nardi et al. 2008). Although these organic polymers are more expensive, considerable savings on coagulant dosage can be made when they are combined with inorganic salts for the same removal performance (Bolto and Gregory 2007)

The most commonly used organic polymers in hybrid coagulants are polyacryalamides (PAMs) and polydimethyldiallylammonium chloride (PDADMAC) (Lee et al. 2012; Wang et al. 2011; Tzoupanos and Zouboulis 2010). There are also other water soluble polymers families that have not been extensively studied yet. Some of these polymers are polyamines (PAs), polyimines, polyvinylpyridines, polyacrylic acid, polyvinyl sulphonic acid, polystyrene sulphonic acid and polyethylene oxide (Tripathy and De 2006). Due to their complexity, there is a need to improve the knowledge on their performance under different operational conditions and also on the flocculation mechanisms of these hybrid materials.

Polyaluminum coagulants are characterized by their aluminum content (expressed as $\%Al_2O_3$) and basicity which is related to the hydroxide content and quantify the hydrolysis grade of Al^{3+} (Equation 1.1).

$$\text{Basicity } (\%) = 100 \cdot \left(\frac{1}{3} \cdot \frac{[OH^-]}{[Al_T]} \right) \quad (1.1)$$

The effectiveness of coagulation with polyaluminum salts depends on the interaction between hydrolyzed aluminum and particles in the raw water. Al(III) is driven into various hydrolyzed Al species such as $Al(OH)^{+}$, $Al(OH)^{2+}$, $Al_2(OH)_2^{4+}$, $Al_3(OH)_4^{5+}$, $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$, ($Al_{13}$), and aluminum hydroxide ($Al(OH)_3$), which are governed by the basicity and the total aluminum content (Lin et al. 2008).

Coagulation-flocculation mechanisms

The main coagulation-flocculation mechanisms that may take place are (Blanco et al. 2001):

- Charge neutralization: this mechanism takes place when cations react chemically with negatively charged particles. Coagulation occurs in the isoelectric point of the system and it is reversible. Charge values higher than the isoelectric point have negatively effect on coagulation. This mechanism is commonly attributed to low dosages aluminum and ferric salts.
- Patch charge model: it takes place with cationic polyelectrolytes of low or medium molecular weight and high charge density. The patch formed changes the surface charge of the particle in the area where it is adsorbed. This mechanism produces “soft flocs” which are easily dispersed. Optimum flocculation occurs at 50% coverage of the particle surface.
- Bridging model: flocculation of colloidal particles by non-ionic or low medium charge density polyelectrolytes of high molecular weight is believed to take place by the formation of bridges between the particles. A flocculation maximum can be obtained under conditions very different from the iso-electric point. Flocs are more difficult to break down and to refloc.
- Sweep flocculation: it occurs when metal salts (e.g. aluminum or ferric salts) are added to water in concentrations sufficiently high. At these high dosages coagulants form a precipitate, as the solubility product is exceeded, which enmesh colloidal particles and settle with them. In the case of aluminum salt, aluminum precipitates as $Al(OH)_3$.

1.4.2. Silica removal during softening processes

Precipitation softening is a commonly used process to reduce raw water hardness, alkalinity, silica and other constituents. In this process, a chemical is added to promote the precipitation of the different dissolved species. Although there are many variations, the most extended process involves the addition of lime to increase the pH. This treatment can be complemented by the addition of Na_2CO_3 depending on the presence or not of carbonate hardness. During lime softening, dissolved calcium and magnesium precipitates as $CaCO_3$ and $Mg(OH)_2$, respectively. Moreover, silica concentration is also reduced during lime softening where calcium, magnesium concentrations are reduced (GE Power & Water 2013). Although both calcium and magnesium are proven functional for silica removal, the higher Mg/Ca ratios, at constant total hardness, the higher silica removal (Chen et al. 2006).

Silica removal during softening requires enough hardness present in the water to obtain high silica removal rates. In this sense, silica removal during softening has been used in waters with high magnesium hardness (>250 mg/L) concentration such as brackish or sea water and for relatively low silica concentration (<30 mg/L) (Chen et al. 2006; Al-Mutaz and Al-Anezi, 2004). When the water to be treated has high silica and low magnesium concentration, as occurs in deinking paper mills effluents, it is necessary to add an external hardness source, preferably magnesium compounds such as MgO or $MgCl_2$.

In the literature there is no consensus about which is the mechanism involved in the removal of silica during water softening (Demadis et al. 2012; Demadis 2010; Hsu et al. 2008; Parks and Edwards 2007; Chen et al. 2006; Sheikholeslami and Bright 2002). The two main mechanisms proposed are adsorption into fresh precipitated $CaCO_3$ and $Mg(OH)_2$ and co-precipitation of silica to form calcium and magnesium silicates with different stoichiometries.

1.4.3 Adsorption

In the recent years, there is an increasing interest on the use of inorganic materials for the adsorption of heavy metal and anions (Sharawy et al. 2013). Adsorption offers several advantages compared other techniques such as coagulation or softening at high pH: no increase in total dissolved solids, low sludge production and possible reuse of the adsorbent after regeneration (Bouguerra et al. 2007).

Milne et al. (2014) recently reviewed the adsorbents used for the removal of silica and classified them in: iron compounds (iron (III) hydroxide, ferrihydrite and goethite), aluminum compounds (activated alumina and aluminum hydroxide, calcium aluminate and other aluminates), zirconium compounds, manganese compounds, nickel compounds, cobalt compounds and others. In this application, adsorption onto aluminum compounds appears to give the best results. Activated alumina, for example, is a relatively well known adsorbent with reasonable good regenerability controlled by pH. The activated alumina, for example, has been previously used to remove fluoride, arsenic, selenium, boron and bromide as well as silica (Bouguerra et al. 2008; Su et al. 2008; Chubar et al. 2005; Goldberg, 1997). Adsorption onto iron compounds appears to occur more quickly, but leads to the formation of a hard, glass-like scale that is more difficult to remove (Milne et al. 2014).

Nowadays, the use of hydrotalcites as adsorbent is gaining importance in very different applications. Hydrotalcite is a type of layered doubled hydroxide derived from the brucite structure which can be described by the general formula $[Mg_{1-x}Al_x(OH)_2]^{x+}[CO_{3x/2}{\cdot}mH_2O]^{x-}$, formed by isomorphous substitution of the Mg^{2+} with Al^{3+} and forming layers with a positive charge. The carbonate anion is the counter-balanced charge of the layers. Hydrotalcites are known as anionic clays as the interlayer anions, most commonly carbonate, can be exchanged with other anions. Hydrotalcite can occur as a natural mineral or can be synthesized (Li et al. 2006). Hydrotalcites can be transformed into the mixed oxide type undergoing dihydroxylation and decarbonation by calcination, which increases its exchange capacity and surface area (Bellotto et al. 1996). The calcined product can rehydrate and incorporate anions in order to rebuild the hydrotalcite structure. Previous works with hydrotalcites have demonstrated a high efficiency as ion exchangers/adsorbents for the removal of fluoride (Das et al. 2003), anionic dyes (Orthman et al. 2003), dichromate (Das et al. 2004), phenol (Ulibarri et al. 1995), selenite and selenate (You et al. 2001) or thiocyanate (Li et al. 2006).

The possibility of using adsorption with activated alumina for silica removal is almost a new approach to remove silica from industrial effluents. The most comprehensive study was carried out by Bouguerra et al. in 2007. However, synthetic waters instead of complex industrial effluents, with a low silica concentration (50 mg/L SiO_2) and a narrow temperature range were studied (10-30 ºC). On the other hand, there are no references on the use of hydrotalcites for silica removal despite their high efficiency for the removal of other anions.

2. OBJECTIVES OF THE RESEARCH

Nowadays sustainable water management in paper mills is a must. One of the alternatives to improve the sustainability of the process is the reduction of fresh water consumption through the regeneration and reuse of the effluent after an advanced treatment, usually including a RO step (Negaresh et al. 2013). With this treatment, it is possible to obtain high quality water to replace fresh water used at critical points, such as in the high pressure showers of the paper machine, where the highest quality is required (Ordoñez et al. 2010). Nevertheless, the main bottleneck for the implementation of this technology is silica scaling on RO membranes (Salvador Cob et al. 2012, Hater et al. 2011, Koo et al. 2001). If silica is not previously removed, it is not possible to work on the RO at recoveries higher than 20% (Ordoñez et al. 2010), thus comprising the economic feasibility of the whole treatment chain. To increase the RO recovery up to 60-80% there is a need to find silica removal techniques to obtain high silica removal rates (80-90%) for the treatment of large volumes of water, with high silica content, as those typically found in deinking paper mills. Low cost, no side effects on the membranes and low conductivity increase to avoid the post-treatment of RO rejects are also desired.

Although there are different silica removal treatments the two most common are coagulation at high pH or during the precipitative softening processes (Hermosilla et al. 2012; Huuha et al. 2010; Parks and Edwards 2007; Zeng et al. 2007; Chen et al. 2006). In the literature, there are very few studies focused on silica removal in waters from the paper industry. Among them, Hermosilla et al. (2012) presented coagulation as a promising technique; however, the coagulant dosage and the final conductivity were prohibitive. On the other hand, silica removal during softening is mostly applied to treat brackish water, which has low silica content (10-40 mg/L SiO_2) and high magnesium hardness, which makes many of the conclusions reached not extensible for the treatment of industrial wastewater such as deinking paper mill effluents. On the other hand, the potential adsorption of silica onto activated alumina and hydrotalcites in high silica loaded waters has not been demonstrated yet. Moreover, there is a need of generating fundamental knowledge on the silica removal mechanisms involved in these three techniques.

Therefore, the main objective of the present PhD thesis is to optimize the silica removal techniques to treat water with high silica content and low hardness, making technically feasible the effluent reuse in the paper industry. According to the research needs listed above, the following specific objectives were defined for the three techniques studied (figure 2.1).

Coagulation:

1. To study the efficiency of different aluminum coagulants on silica removal optimizing the operating pH, the dosage and the pH regulator. First, commercial aluminum coagulants were studied **(Publication I)**. As a hybrid coagulant of PA showed the best performance, the next step was to analyze the efficiency of commercial hybrid coagulants with different dosages of PA and polyacrylamide (PAM) **(Publication II)** and to develop a new brand of tailor made hybrid coagulants optimizing the PA content **(Publication III).** PDADMAC hybrids were also tested but discarded.
2. To study the coagulation-flocculation mechanism of the different aluminum salts and hybrid coagulants used **(Publication I, II, III and V).**

3. To study the effect of suspended solids on the coagulant demand and silica removal mechanisms in different water streams to determine the optimal location of the coagulation treatment **(Publication IV and V).**
4. To study the efficiency of chitosan and chitosan derivates as alternative biodegradable coagulants for silica removal **(Publication VI).**

Silica removal during precipitative softening:

5. To optimize the use of soluble magnesium compounds in terms of: magnesium source, pH, temperature, contact time and dosage **(Publication VII and VIII).**
6. To optimize the use of sparingly soluble magnesium compounds in terms of magnesium source, pH, temperature, contact time and dosage **(Publication IX and X).**
7. To clarify the mechanism of silica removal during precipitative softening with magnesium compounds **(Publication VII- X).**

Adsorption:

8. To optimize the use of activated alumina and hydrotalcites as adsorbents for silica removal **(Publication XI, XII)**

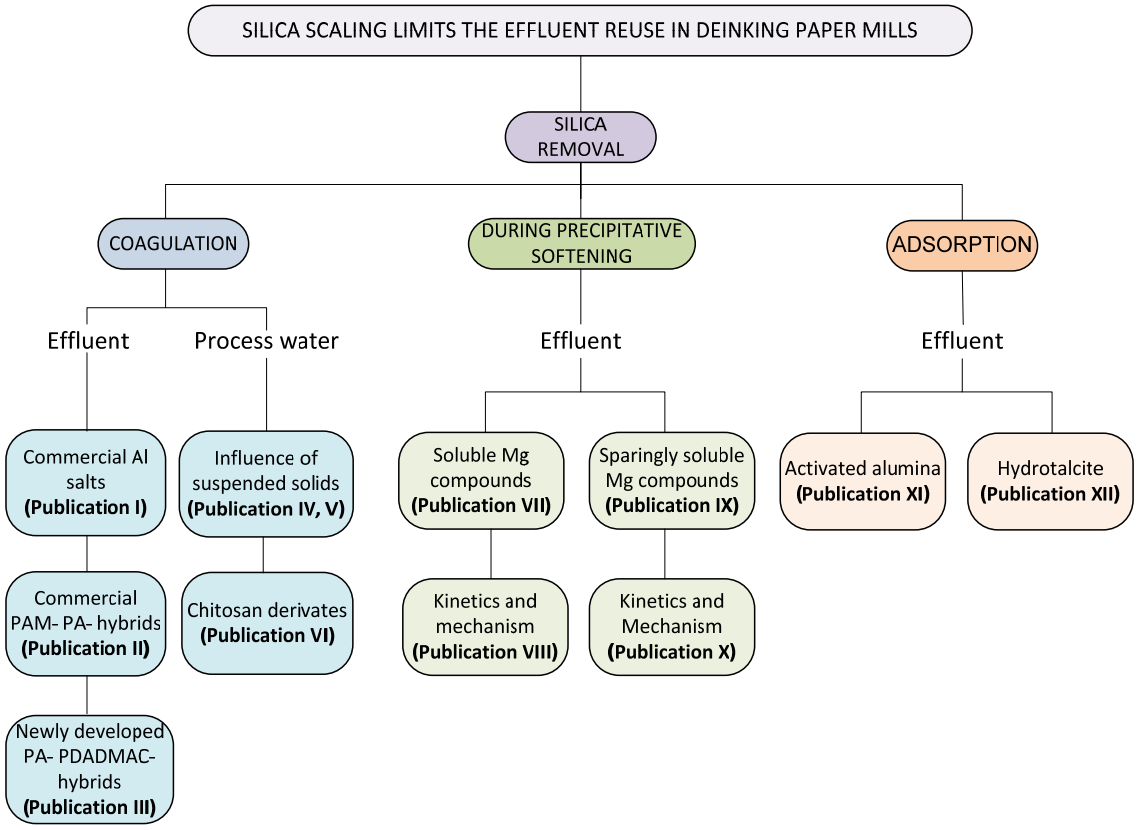

Figure. 2.1. *Scheme of the performed research to achieve the global objective of this thesis.*

3. MATERIALS AND METHODS

3.1. MATERIALS

3.1.1. Water samples

Wastewaters used in this PhD thesis were taken from a paper mill placed in Madrid. This mill produces newsprint from 100% recovered paper with a highly closed water circuits. The average fresh water consumption is 7.5 m^3/t which is below the BREF reference values (8-20 m^3/t) (BAT pulp, paper and board 2015). The water circuits in the mill are configured in three loops (figure 1.2), each one equipped with DAF units for the internal treatment of the process waters. Moreover, the mill has an integrated wastewater treatment plant before the discharge of the effluent. Specifically the effluent is treated in a DAF unit followed by a biological treatment in a moving bed bioreactor and a secondary dissolved air flotation, before its discharge.

Depending on the study considered, water samples were collected from the effluent before its discharge or from the inlet of two DAF units located in the water circuits of the pulp preparation stages, named DAF1 and DAF2. Water samples were stored at 4ºC during the tests and no sets of trials longer than five days were carried out.

The characterization of the effluent is shown in table. 3.1. The contamination load of the samples varied in time depending on the operational conditions in the manufacturing process and the programmed stops of the plant.

On the other hand, the main characteristics of the water samples taken from the two DAF units are shown in table 3.2. Additionally, figure 3.1 shows the chord size distribution of the waters measured by the focused beam reflectance measurement (FBRM) probe.

Table. 3.1. *Characterization of the paper mill effluent.*

Raw water	
pH	8.2-8.6
Conductivity (mS/cm)	1.5-3.5
COD (mg/L)	400-1000
BOD (mg/L)	150-300
Cationic demand (meq/L)	0.50-2.00
Total solids (mg/L)	1800-3150
Total suspended solids (mg/L)	80-180
Turbidity (NTU)	10-120
Total alkalinity (mg/L $CaCO_3$)	650-1000
Dissolved fraction	
Silica (mg/L SiO_2)	140-260
COD (mg/L)	250-550
Total solids (mg/L)	1900-3000
Sulphates (mg/L)	200-750
Chlorides (mg/L)	130-180
Calcium (mg/L)	30-60
Magnesium (mg/L)	3-7
Turbidity (NTU)	6-15

Table. 3.2. *Characterization of the DAF1 and DAF2 inlet water.*

Raw water	**DAF 1**	**DAF 2**
pH	6.9	7.7
Conductivity (mS/cm)	2.62	2.13
COD (mg/L)	3665	3610
Cationic demand (meq/L)	1.24	1.16
Total solids (mg/L)	5520	6590
Total suspended solids (mg/L)	1620	3350
Turbidity (NTU)	680	2400
Total alkalinity (mg/L $CaCO_3$)	856	1425
Dissolved fraction		
Silica (mg/L SiO_2)	273	240
COD (mg/L)	2600	2285
Total solids (mg/L)	3898	3240
Turbidity (NTU)	22	89

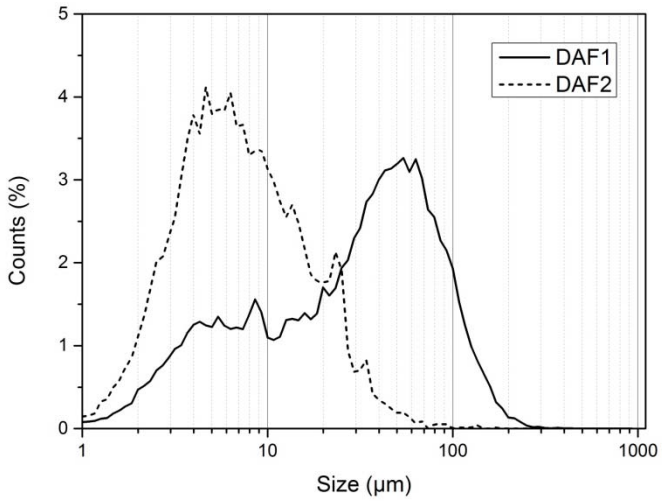

Figure. 3.1. *Chord size distribution of DAF1 and DAF2 waters measured by FBRM (Publication IV).*

3.1.2. Coagulants

The different coagulants described are grouped depending on their nature in: aluminum salts, commercial aluminum hybrid coagulants, newly developed aluminum hybrid coagulants and chitosans.

Commercial aluminum salts

Table 3.3 shows the main characteristics of alum and four polyaluminum based coagulants. One polyaluminum chloride with high basicity (PACl-HB) was supplied by Kemira Ibérica S.A (Spain); the other two polyaluminum chlorides with medium basicity, PACl-MB1 and PACl-MB2, were supplied by SERTEC-20 S.L. (Spain) and Sachtleben Wasserchemie GmbH (Germany) respectively. PANS was supplied also by Sachtleben Wasserchemie GmbH (Germany). Finally, alum (reagent grade) was supplied by Panreac.

Table. 3.3. *Characteristics of commercial aluminum salts.*

Coagulant	Chemical family	Al_2O_3 (%)	Basicity (%)	Dry content (%)	Charge density* (%)	pH
PACl-HB	Polyaluminum chloride	9.7	85	29.5	1.67	2.7
PACl-MB1	Polyaluminum chloride	10.0	65	35.0	1.27	2.6
PACl-MB2	Polyaluminum chloride	16.8	37	34.1	1.77	<1
PANS	Polyaluminum nitrate sulphate	10.2	46	21.7	0.8	2.6
Alum	Aluminum sulphate	15.3	-	-	-	-

** measured by colloidal titration.*

Commercial hybrid coagulants

Table 3.4 shows the characteristics of the commercial hybrid coagulants used. PANS is the same product included in table 3.3 and it was used as the base product to prepare five hybrid inorganic-organic materials with different active contents of PAM and PA. PANS-PAM1, PANS-PAM2 and PANS-PAM3 were obtained adding to PANS a high charge density and low molecular weight cationic PAM at different dosages. PANS-PA1 and PANS-PA2 were obtained by adding different dosages of a mixture of cationic quaternary PAs of high charge density and different molecular weights. The weight percentage of the organic polymer in the hybrid materials, or active content, varied depending on the product: PANS-PAM1 and PANS-PA1 were the products with the lowest active contents (1x). PANS-PAM2 had double active content (2x), PANS-PA2 had triple active content (3x) and PANS-PAM3 quadruple active content (4x).

Table. 3.4. *Commercial hybrid coagulants and PANS.*

Coagulant	Polymer	Al_2O_3 (%)	NO_3^- (%)	SO_4^{2-} (%)	Active content	Charge density* (meq/g)
PANS	-	10.2	17	3.	-	0.8
PANS-PAM1	Polyacrylamide	9.1	16	3.6	1x	1.13
PANS-PAM2	Polyacrylamide	8.3	16	3.3	2x	1.18
PANS-PAM3	Polyacrylamide	7.4	14	3.2	4x	1.20
PANS-PA1	Polyamine	8.8	16	3.2	1x	1.68
PANS-PA2	Polyamine	6.1	12	2.5	3x	2.57

** measured by colloidal titration.*

Newly developed hybrid coagulants

Different inorganic-organic hybrids were prepared using PANS as the base product and two types of organic polymers: PA and PDADMAC. First, PA hybrids were prepared by direct blending of PANS with three PAs of similar charge but different molecular weight at ambient temperature, their molecular weight following the order: PA1 < PA2 < PA3 (table 3.5). PANS and PA2 were supplied by Sachtleben Wasserchemie GmbH (Germany), while PA1 and PA3 were supplied by Kemira Oyj (Finland). Table 3.5 shows the main characteristics of these coagulants.

Table. 3.5. *Characteristics of the PAs and PANS used for the hybrid formulation.*

Coagulant	Charge density* (meq/g)	Molecular weight
PANS	0.8	-
PA1	3.2	Low
PA2	3.4	Medium
PA3	3.8	High

** measured by colloidal titration.*

For each PA type, four different addition levels were tested. These levels were 5, 10, 15 and 20 wt.% of commercial solutions (48-52% dry solids), the rest being PANS. Higher PA contents were also prepared but the blends were unstable as evidenced by the appearance of turbidity within 24 h after its preparation. Hybrids are noted as PANS-PAx-Z were PAx is PA1, PA2 and PA3 (depending on the PA used) and Z is the PA content by weight in the hybrid. The aluminum content and the cationic charge of these hybrid coagulants, grouped by the commercial PA solution content, are summarized in table 3.6.

Table. 3.6. *Characteristics of the hybrid coagulants.*

Coagulant	PA content (wt%)	Al_2O_3 (%)	Charge density* (meq/g)
PANS	-	10.2	0.8
PANS-PAx-5	5	9.8	0.9-1.0
PANS-PAx-10	10	9.4	1.1
PANS-PAx-15	15	8.9	1.2
PANS-PAx-20	20	8.3	1.3-1.4

** measured by colloidal titration.*

Moreover, two different PDADMAC of similar charge density (2.6-2.9 meq/g) and different molecular weight were used to prepare hybrids with PANS. PDADMAC1 and PDADMAC2 with low and medium molecular weight respectively were supplied by Kemira Oyj (Finland).

For each PDADMAC, three different addition levels were tested. These levels were 1, 3 and 5 wt.% of commercial solutions, being the rest PANS.

Chitosans and chitosan derivates

Four chitosan products were tested; two native chitosans and two quaternary derivatives whose main characteristics are shown in Table 3.7. The two native chitosans had very similar deacetylation degree and cationic charge density, but differ in their molecular weights: one had low molecular weight (Ch.LMW) and the other one medium molecular weight (Ch.MMW). They were both supplied by Sigma–Aldrich Co. The two quaternary derivatives (Quat.5 and Quat.10) were prepared from the low molecular weight chitosan (Ch.LMW) using N-(3-chloro-2- hydroxypropyl) trimethyl-ammonium chloride (Quat-188) as the quaternizing agent (details are given in Publication VI). Two quaternization degrees were tested, 1:5 for Quat.5 and 1:10 for Quat.10 (Table 3.7).

Table. 3.7. *Characteristics of chitosan products.*

Chitosan product	M_w x 10^5 (g/mol)	Charge density (meq/g) *	Deacetylation degree (%)	Quaternization degree (%)	pH stock solution (1 g/L)
Ch.MMW	2.375	5.8	86.5	-	4.05
Ch.LMW	0.768	5.4	85.7	-	4.00
Quat. 5	-	2.3	-	72	6.95
Quat. 10	-	2.1	-	86	6.95

** measured by colloidal titration.*

3.1.3. Magnesium compounds

To increase magnesium hardness five different magnesium compounds were used: two soluble and three sparingly soluble (Table 3.8). All magnesium compounds, analytical grade, were supplied by Panreac.

Table. 3.8. *Characteristics of magnesium compounds.*

Magnesium compound	Magnesium content (wt%)	Solubility 20ºC (g/L)
$MgCl_2 \cdot 6H_2O$	11.9	1670
$MgSO_4 \cdot 7H_2O$	9.86	710
MgO	60.30	0.086
$Mg(OH)_2$	41.68	0.012
$(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$	25.02	0.0375

3.1.4. Adsorbents

Activated alumina

A commercial boehmite type activated alumina (Catapal B®) was used. Its composition was: 72% Al_2O_3 and 0.002% Na_2O, C: 0.25%, SiO_2: 0.01-0.015%, Fe_2O_3: 0.005-0.015%, TiO_2: 0.01-0.20%. Table 3.9 shows the textural properties of Catapal B®.

Table. 3.9. *Properties of the activated alumina.*

Product	BET surface (m^2/g)	Pore volume (cm^3/g)	Average pore width (Å)
Catapal B ®	237.2	0.362	61

Hydrotalcite

Synthetic hydrotalcite, with the general formula $Mg_6Al_2(CO_3)(OH)_{16} \cdot 4H_2O$, was supplied by Sigma-Aldrich. According to the supplier, the weight ratio MgO/Al_2O_3 varied between 4.0 and 5.0, i.e. the atomic ratio Mg/Al was between 1.4-1.8 and the loss on drying is < 0.35%. XRF of the raw hydrotalcite and the calcined hydrotalcite gave the following Mg/Al molar ratios, 1.48 for raw hydrotalcite and 1.94 for calcined hydrotalcite. The raw hydrotalcite had a very low BET surface and pore volume (Table 3.10). Therefore, it was calcined at 450 ºC during 4.5 h. This treatment largely increased the BET surface up to 132 m^2/g and the pore volume to 0.162 cm^3/g.

Table. 3.10. *Properties of the raw and the calcined hydrotalcite.*

Product	BET surface (m^2/g)	Pore volume (cm^3/g)	Average pore width (Å)
Raw hydrotalcite	5.9	0.023	158
Calcined hydrotalcite	132.0	0.162	49

3.2. EXPERIMENTAL PROCEDURES

3.2.1. Coagulation-flocculation

Jar-tests

Jar-tests were carried out in a multiposition magnetic stirrer OVAN MulitMix Heat D. Figure 3.2 summarizes the methodology followed to study the efficiency of the different coagulation-flocculation treatments. A sample volume of 200 mL was used. First, when necessary, the pH of the samples was adjusted adding NaOH or $Ca(OH)_2$ (10 wt./vol.%), depending on the study. After 30 seconds of high speed mixing at 200 rpm, the coagulant was added to the sample from a 10% wt./vol. solution and mixed at high speed (200 rpm) during 2.5 min. Next, the flocculant was added from a 0.10% wt./vol. solution and was mixed 10 min at slow speed (40 rpm). An anionic PAM with high molecular weight and medium density charge was used as flocculant aid in all tests. Finally, the sample was allowed to settle during 60 minutes and the supernatant was characterized by pH, conductivity, cationic/anionic demand, alkalinity and turbidity. Furthermore, reactive silica, COD and turbidity were measured in the dissolved fraction of the supernatant.

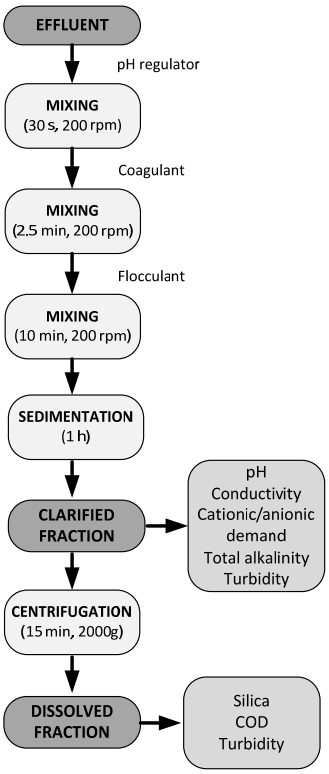

Figure. 3.2. *Jar-test methodology.*

Dissolved air flotation tests

DAF tests were carried out in a laboratory-cell model Flottatest FTH3 supplied by Orchidis Laboratories. The experimental protocol followed is shown in figure 3.3. A sample volume of 1 L was used in all the cases. In these tests, first the coagulant was added to the sample from a 10% wt./vol. solution in the case of aluminum salts and from a 1.0 wt./vol.% stock solution in the case of chitosan products. After 2.5 min of high speed mixing (180 rpm) the flocculant was added and mixed at slow speed (40 rpm) for 10 min. Finally, a 20% tap water (200 mL) saturated in air at 7 bar

was added, and after 10 min flotation time, samples were collected from the bottom of the jars. Both clarified and dissolved fractions were characterized.

A minimum of three blanks for each DAF waters were carried out without adding any chemical, to consider the dilution of the samples due to the addition of air-saturated water during flotation (20%) and the physical efficiency of the DAF (without any chemicals).

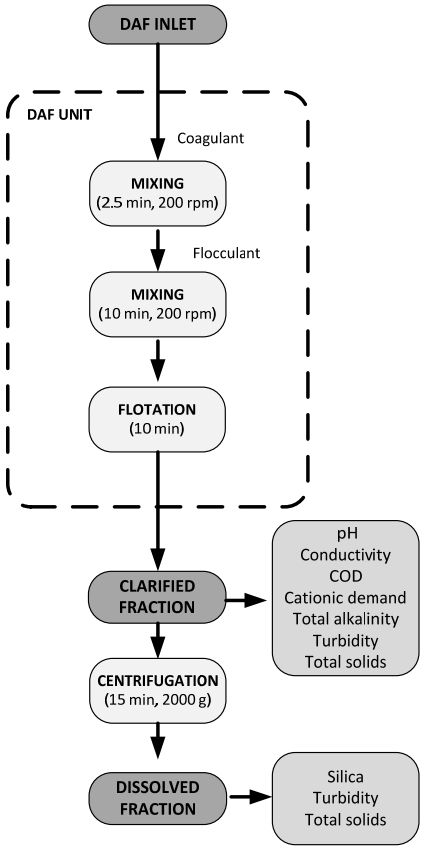

Figure 3.3. *Protocol for the lab-scale DAF experiments.*

On-line flocculation monitoring

FBRM is a very useful technique to monitor flocculation processes as allows assessing flocculation behaviour and flocculation mechanisms without the limitations of traditional methods (Rasteiro et al. 2008; Blanco et al. 2002a; Blanco et al. 2002b). The device generates a laser beam that is focused on a focal point that describes a circular path at high speed (2000 rpm). When particles intercept its path, the light is reflected and propagated back through the probe window to the detector. The time duration of the backscattered light pulse allows the particle chord length to be calculated. Thousands of chord length measurements are collected per second, producing a histogram in which the number of observed counts is sorted in several chord length channels over the measurement range. From these data, total counts, counts in specific size intervals, mean chord size, and other statistical parameters can be calculated.

The FBRM probe used in the tests was a D600L model (Mettler-Toledo), having a measurement range of 1 to 1000 µm. Two different flocculation studies were carried out: flocculation by successive coagulant additions and flocculation-deffloculation-reflocculation tests.

The flocculation by successive coagulant additions was carried out by the addition of increased dosages of the different coagulants to a sample of 250 mL while stirred at 200 rpm with the FBRM probe submerged on it. After 30 s of stabilization, the coagulants were continuously added to the sample e.g. 200 mg/L of coagulant were added each 10 s up to a final dosage of 8000 mg/L. When necessary, pH regulation was carried out before the coagulant addition.

In the flocculation-deflocculation-reflocculation tests, single dosages of coagulant were used. In these trials, the probe was also submerged into a 250 mL sample stirred at 200 rpm. After 30 s of stabilization time, the dosage of the coagulant was added. Then, the system was allowed to evolve for 2.5 min. After this time, the mixing speed was increased to 500 rpm and maintained during 2 min to break the formed flocs. Finally, the mixing speed was reduced to 200 rpm again and the system was monitored for other 5 min to analyze the reversibility of the flocs after the shear forces ended.

3.2.2. Silica removal during softening

Jar-tests

Figure 3.4 shows the jar-test methodology followed for the evaluation of silica removal during precipitative softening with magnesium compounds. Trials were carried out at 20ºC, 35ºC or 50ºC. First, the pH of the samples was adjusted by adding NaOH or $Ca(OH)_2$ (10 wt./vol.%) to 250 mL of sample. After 1 min of mixing at 200 rpm, the studied magnesium compound was added and mixed from a 10 wt./vol.% solution. Contact time varied between 15 min to 24 h depending on the study. Then the waters were allowed to settle for 1 h. Finally, the clarified waters and the dissolved fraction were characterized. Settled solids were also analyzed by FTIR spectrophotometry and SEM-EDX.

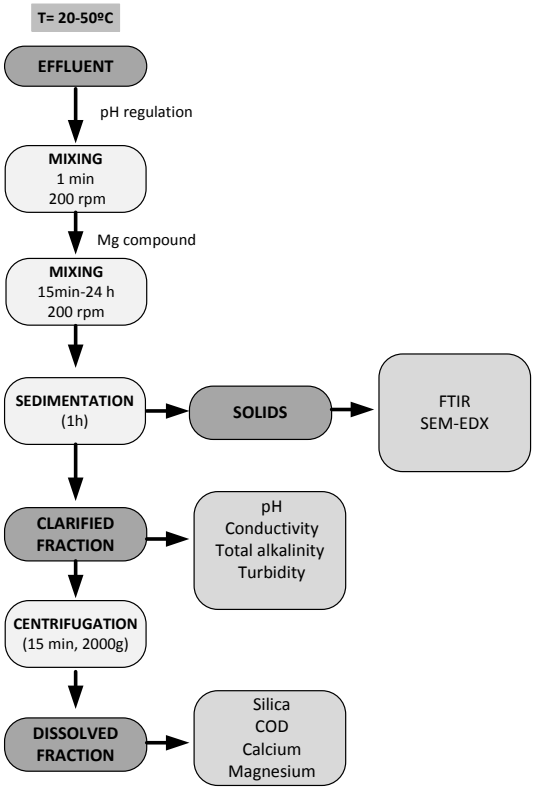

Figure 3.4. *Methodology for the evaluation of silica removal during softening.*

Optimization of the contact time

For the optimization of the contact time, kinetic studies were conducted. First, the pH regulation was carried out by adding NaOH or $Ca(OH)_2$ (10 wt./vol.%) and after one minute mixing, the magnesium compound was added. Samples were taken at different times and immediately filtered through 0.45 µm PTFE membrane filter. These samples were characterized in terms of silica and magnesium concentration.

3.2.3. Silica removal by adsorption

Equilibrium studies

Figure 3.5 shows the jar-test methodology followed to analyze silica removal by adsorption with activated alumina and hydrotalcite. Trials were carried out at 20ºC, 35ºC or 50ºC. First, the pH of the samples was adjusted by adding NaOH (0.1 M) or HCl (0.1 M) to 200 mL of sample. After 1 min of mixing at 200 rpm, the adsorbent was added. According to preliminary tests, contact time was fixed at 1h for Catapal B and at 2h for hydrotalcite. Then the waters were allowed to settle for 1 h, and the clarified waters and the settle solids were analyzed.

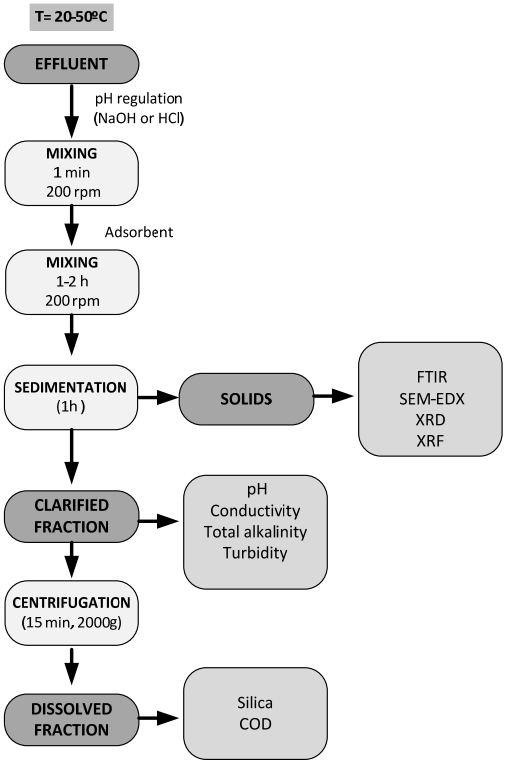

Figure 3.5. *Methodology followed to study silica removal by adsorption.*

Optimization of the contact time

Kinetic studies were carried out at different temperatures from 20-50ºC. After 1 min mixing, the adsorbent was added to 600 mL of the water to be treated. Samples were taken at different times and immediately filtered through a 0.45 µm PTFE membrane filter to stop adsorption. These samples were characterized in terms of silica content.

3.3. ANALYTICAL TECHNIQUES

3.3.1. Water characterization

The different treatments were evaluated in the clarified and dissolved fraction. The dissolved fraction was obtained after centrifugation of clarified waters at 2000 g during 15 min in an Universal 32 centrifuge (Hettich Zentrifugen GmbH). In all cases, the preservation of the samples, the analyses and the measurements described below were performed according to the Standard Methods for the Examination of Water and Wastewater (APHA-AWWA-WEF, 2005). All measurements were carried out by duplicate or triplicate. The average error between replicates was always under 5%. The results shown in the graphs correspond to the average value of the measurements.

pH was measured using a model GLP 22 (Crison Instruments, S.A), according to Method 4500-H^+- B-Electrometic. **Conductivity** was measured with a model GLP 31 (Crison, S.A.) according to the ISO 7888:1985 method. **Total solids and total suspended solids** were measured according to the Standard Methods 2450 B and 2450 D respectively. **Cationic/anionic demand** was measured by colloidal titration using a Charge Analyzing System (CAS) supplied by AFG Analytic GmbH and polydiallyldimethylammonium chloride (PDADMAC, 0.001 N) and polyethylene sulfonic acid sodium salt (PES-Na) (0.001 N) as titrants, depending on the sample charge, both supplied by BTG Instruments GmbH. **Turbidity** was measured with a LP 2000-11 nephelometer, supplied by Hanna Instruments, according to ISO 7027:2001. **Chemical oxygen demand (COD)** was measured was measured by the Nanocolor® COD 300 or COD 1500 methods from Macherey-Nagel GmbH, using an Aquamate Vis spectrophotometer (Thermo Scientific Inc.), according to ISO 15705:2003. **Alkalinity** was measured by titration with sulfuric acid 0.1 N using a pH electrode connected to an automatic titrator, model Compact I (Crison Instruments S.A.) to reach pH 4.5, according to EPA 310.1 (1983) method. **Sulphates** content was measured by turbidity development of the sample after adding $BaCl_2$ using Nanocolor® Sulphates 1000 and Nanocolor® Sulphates 200 test methods (Macherey-Nagel GmbH & Co) with PF-11 Filterphotometer (Macherey-Nagel GmbH & Co). Finally, **calcium and magnesium** were measured using a direct air-acetylene flame atomic absorption method according to ISO-7980:1986 in a SpectraAA 220 spectrophotometer supplied by Varian.

Silica

Silica species can be classified in terms of its reactivity. This reactivity refers to the staining with a molybdate based compound in a colorimetric technique used for the determination of silica in waters. The three categories are:

- **Reactive soluble:** polysilicic acid and small molecules such as dimers, trimers, oligomers.
- **Non-reactive soluble** (colloidal, not filterable) also referred as unreactive silica. More highly polymerized species or particles larger than about 50 Å, although sometimes down to 10-20 Å. This category includes the colloidal particles formed by the combination with organic and inorganic species, usually aluminium and calcium oxide.
- **Non-reactive insoluble** (particulate, filterable): also known as suspended, larger than colloidal and dissolved silica.

There are several techniques for the determination of silica: inductively coupled plasma method (ICP), atomic absorption spectrophotometry method (AAS) and colorimetric methods. The ICP

method is the only one that determines total silica. Atomic absorption determines soluble silica and part of the colloidal. Finally, colorimetric methods determine molybdate-reactive silica. Among the available techniques, the one selected in this thesis is the one based on the silicomolybdate and molybdenum blue reduction automated with flow injection analysis (FIA).

The equipment used in the measurements is a FIA Compact MLE model (figure 3.6). The measurement is made according to DIN EN ISO 16264: "Water quality-Determination of soluble silicates by flow analysis (FIA and CFA) and photometric detection (ISO 16264:2002)". As commented before, this method determines molybdate-reactive silica, which includes soluble silicates, monomeric silica, silicic acid and an undetermined fraction of colloidal silica.

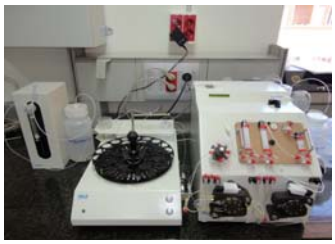

***Figure. 3.6**. FIA Compact MLE model for silica measurement.*

In some selected samples, total silica was measured by both ICP and the FIA colorimetric method. Silica concentration obtained by ICP (total silica) was almost the same than the ones obtained for reactive silica (silicomolybdate method), indicating that most of the silica present was in the dissolved form and as a consequence, this technique can be used to evaluate silica removal efficiency.

3.3.2. Solids characterization

SEM-EDX

Image analyses of the solids were carried out by scanning electron microscopy (SEM) in a JEOL JSM-6400 microscope. This SEM is configured with an energy dispersive X-ray analyzer (EDS system) which enables to perform compositional analysis. For SEM-EDX analyses samples were firstly dried and coated with a thin graphite layer.

FTIR spectrophotometry

FTIR analyses were carried out in a Nicolet Magna 750 spectrophotometer with a Spectratech IR-Plan Advantage Microscope. Spectra were recorded at 2 cm^{-1} resolution and 16 scans were taken for both the samples and the background. Samples were prepared with the same amount of sample and KBr, i.e. 0.6 mg of sample and 250 mg of KBr.

For the adsorption studies, FTIR analyses were carried out on KBr pellets (2 mg of sample and 98 mg of KBr). A Nicolet Nexus 670 spectrometer was used for recording the spectra (400-4000 cm^{-1}) at 4 cm^{-1} resolution. Four scans were taken for both the background and the sample.

Specific Surface (BET)

The specific surface area of the sample was determined by the N_2 adsorption/desorption method at liquid N_2 (77 K) using BET method in a Micromeritics ASAP 200 equipment. Micropores were studied by the t-plot method.

4. RESULTS

4.1. COAGULATION

4.1.1. Conventional coagulants

The efficiency of several aluminum salts under different operating conditions was analyzed, optimizing pH conditions and pH regulator. Four polyaluminum-based products and alum ($Al_2(SO_4)_3 \cdot 18H_2O$) were used. The polyaluminum-based coagulants were two polyaluminum chlorides (PACl-HB and PACl-MB1) and two commercial PANS-PA hybrids (PANS-PA1 and PANS-PA2). Characteristics of the coagulants are shown in table 3.3 and 3.4. For each coagulant five dosages were tested (from 500 to 2500 mg/L) at three different pHs: 8.3 (water initial pH), 9.5 and 10.5. The jar-test methodology followed is shown in figure 3.2. First, the best coagulants were selected using NaOH as pH regulator. Once the best coagulants were selected, the efficiency of NaOH and $Ca(OH)_2$ as pH regulators was compared.

As it was already mentioned, to work at regular recovery rates in RO membranes (60-80%), it is necessary to decrease silica level down to 20-60 mg/L. Thus, for an initial silica content of 140 mg/L SiO_2, it was necessary to achieve 60-85% silica removal.

All the coagulants achieved the required silica removal at pH 10.5. Without any doubt, PANS-PA2, is the product recommended for this application. PANS-PA2 had a great versatility as it achieved the highest silica removal efficiency (up to 97%, pH=10.5 and 2500 mg/L) but, even more important, it could achieve high enough silica removal rates even without pH adjustment of the water. Without pH adjustment, PANS-PA2 obtained a final silica concentration of 45 and 37 mg/L, with dosages of 2000 and 2500 mg/L, respectively. In these treatments, the conductivity increased only from 2.2 mS/cm up to 2.4-2.5 mS /cm, and the COD removal rates were at the same time, the highest of the product tested (26-28%). PANS-PA2 could be also used at pH 9.5 and dosages >1000 mg/L to achieve the required silica removal, which would reduce the cost of the coagulation treatment, but slightly decreasing the other additional benefits. At the same dosage, higher pH improves the silica removal. For example, at 2500 mg/L dosage, the pH adjustment to 9.5 increased the silica removal from 73% to 79% (compared to no pH adjustment). However, the conductivity increased from 2.5 mS/cm to 2.7 mS/cm and COD removal decreased from 28% to 22%.

High silica removal rates obtained with PANS-PA2 without pH regulation could be attributed to the high charge density of this product and the effect of the quaternary PA added to the polyaluminum salt, which is efficient even at pH 8.3. However, the dosage of PA in the coagulant must be high enough, as in the case of PANS-PA2, because at lower dosages of PA (PANS-PA1), only 53% removal was achieved at initial pH. The dosage of PA in PANS-PA2 was around three times higher than in PANS-PA1.

Alum was also a promising product for silica removal. Unlike PANS-PA2, maximum silica removals were not achieved at the highest dosage but the optimal range was 500-1000 mg/L. At this optimal range, silica removals achieved were 35% removal at pH 8.3, 58% at pH 9.5 and 73% at pH 10.5. It is important to notice that a fine control of alum dosage is required, as overdose can occur. This overdose reduces significantly silica removal rates and in, some cases, increasing the turbidity of the treated waters. For example, at pH 10.5, silica removal could decrease from 80% at 1000 mg/L

to 44% at 2000 mg/L. Other drawback is the limited COD removal achieved, around 3%, and the high conductivity of the treated waters, around 3.0 mS/cm.

The high efficiency of alum could be related to its high aluminum content, around 2.5 times higher than PANS-PA2 (the coagulant with the lowest aluminum content). The explanation why its efficiency decreases at higher dosages than 1000 mg/L is a combination of two facts, its high aluminum content and its 0% basicity, which caused the highest alkalinity consumption and an important pH decrease, which impairs the formation of the active species of the aluminum salts. Apart from the problems caused by the high pH decrease and conductivity increase when the waters were treated with alum, the increase in sulphates was also considered. Under conditions of maximum silica removal (500-1000 mg/L) sulphates increased from 200 mg/L to 430-560 mg/L.

Finally, lime was preferred to caustic soda as pH regulator. The silica removal efficiency with both pH regulators was about the same. However, using lime, the conductivity of the treated waters was lower due to its low solubility, the COD removal was 10% higher and the sedimentation rates were faster. In addition, lime is considerably cheaper than caustic soda.

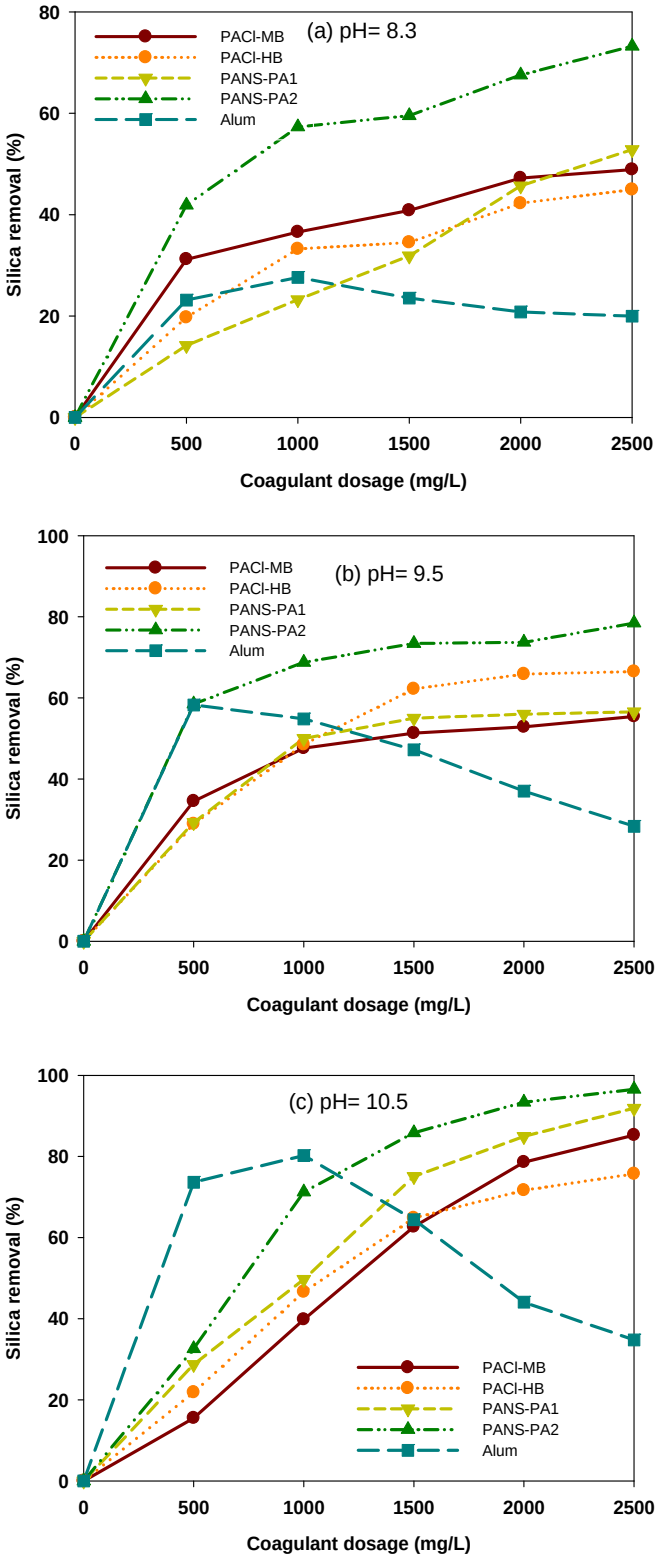

Figure. 4.1 Silica removal vs. coagulant dosage at different initial pHs: (a) pH=8.3; (b) pH=9.5; (c) pH= 10.5 (Publication I).

4.1.2. Commercial hybrid coagulants

In section 4.1.1 it was demonstrated that coagulation with aluminum salts is effective for silica removal on deinking paper mill effluents (Publication I). Although the results obtained were better than the previous results from Hermosilla et al. (2012), it is still necessary a further reduction of the required dosages and pHs. Among the different coagulants, the most promising product was PANS-PA2. Based on that, the efficiency of commercial hybrid inorganic-organic coagulants (with different dosages and charges of the polyelectrolytes) was studied at several conditions, optimizing the operating pH and the dosage.

The studied hybrids are based on the combination of the reference PANS with a cationic PAM and a PA at different proportions. Table 3.4 shows the coagulants used in this study and their main characteristics.

Coagulants were tested at four dosages (500, 1000, 2500 and 5000 mg/L), together with 10 mg/L of the flocculant (an anionic PAM of high molecular weight and medium charge), at three initial pHs: pH 8.3, which is the effluent pH (no pH regulation), pH 9.5 and pH 10.5. Flocculation monitoring was carried out by FBRM.

Results showed a higher efficiency of hybrid coagulants for silica removal compared to traditional coagulants such as PANS, especially at low pHs, which would avoid pH regulation before coagulation. From the hybrids tested, PA derivatives were more efficient than PAM derivatives, even at lower active contents, independently of the initial pH.

It was observed that several options were possible to reduce silica content in the effluent to avoid silica scaling in RO membranes working at 60-80% recoveries. At all the initial pHs tested, this objective was achieved. At initial pH 8.3, simultaneous high silica removal (75-80%) and COD removal (45-50%) can be obtained with PA hybrids, compared to 50% silica removal and 45% COD removal with PANS. As demonstrated by these results, the inverse relationship between silica and COD removal can be overcome with PA hybrids.

Regarding the flocculation mechanisms, PANS primary flocculation mechanism was sweep flocculation, due to the high dosages and pHs tested. PA hybrid coagulants developed a combination of sweep flocculation (due to PANS) (Tzoupanos and Zouboulis. 2011) and patches formation (Gao et al. 2007), which evolved to a partial interparticles bridges formation at high pHs. PAM hybrids behavior was a combination of sweep flocculation and interparticles bridges formation (Tzoupanos and Zouboulis 2011), independently of the pH tested.

Flocculation monitoring by FBRM measurements justified conclusions obtained by the jar-tests, although the differences observed between PANS-PA1 and PANS-PA2 by FBRM technique were larger than those observed in the jar-tests. In most of the cases, hybrids reduced the MCS (mean chord size) of the particles and increased the TNC (total number of counts), indicating different degrees of DCM destabilization (figure 4.2). However, the base product, PANS, increased the MCS and increased only slightly the number of particles, which indicates a limited destabilization of DCM. The product inducing the highest DCM destabilization, demonstrated by an important increase in the TNC and a parallel decrease in the MCS, was PANS-PA2. The predominant flocculation mechanism of PA hybrids, patches formation, was more efficient than both sweep flocculation and interparticles bridging for destabilizing anionic contaminants of high surface charge as silica and organic colloids. The MCS decrease observed with the hybrids was lower at

higher pHs while the increase in the TNC was generally higher at high pHs, thus indicating a higher destabilization of DCM at the highest pHs, as observed in jar-tests. FBRM data also justified that the main differences among the coagulants occur at initial pH 8.3, these differences being lower at higher initial pHs.

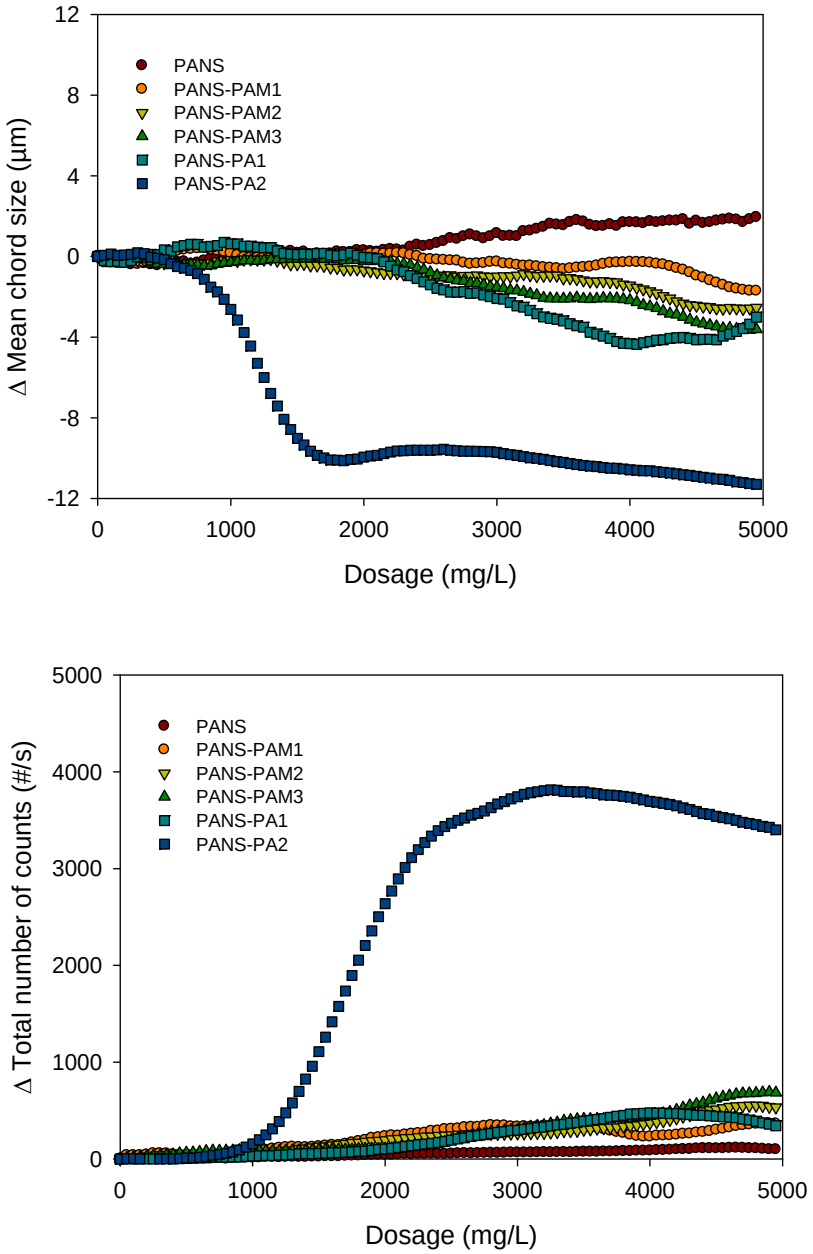

Figure. 4.2. *Evolution of (a) Δ Mean chord size and (b) Δ Total number of counts vs. coagulant dosage at initial pH = 8.3 (Publication II).*

4.1.3. Newly developed hybrid coagulants

PA hybrids

Based on previous results (section 4.1.2) and due to the high cost of hybrid products compared to conventional polyaluminum chlorides, the objective was to obtain a new brand of hybrids reducing the active content and the dosage needed and thus the cost of the treatment. For this purpose, the percentage of PA in the hybrid and the type of PA (different molecular weights) was optimized. These tailor made coagulants were prepared combining the reference product (PANS) with three commercial PAs of different molecular weights in different ratios (5-20 wt.% of PA). Tables 3.5 and 3.6 show the characteristics of the coagulants.

The different hybrids were tested at five dosages (500-2500 mg/L) at the initial pH of the effluent (pH=8.4) and pH=10.5, which was the pH allowing the highest silica removal rates. All the hybrids and PANS were tested in combination with the same flocculant: an anionic PAM of high molecular weight and medium charge.

Figure 4.3 shows silica removal rates obtained with the different hybrid coagulants at initial pH 8.4 and 10.5. At initial pH 8.4, all coagulants were more effective than the reference (PANS). As a general trend at initial pH 8.4, it was observed that silica removal increased mainly at the lower dosages while remained almost constant at the highest dosages. This could be explained because at initial pH 8.4 only part of total silica was ionized thus only a certain fraction of silica could be removed by coagulation. The higher alkaline pH, the higher ionization of silica, and hence higher removal rates could be achieved (Huuha et al. 2010). Very efficient products, such as the hybrids tested, removed most of silica ionized at low dosages. On the contrary, with a less efficient product such as PANS, silica removal was increased continuously with the dosage, even at the highest dosage tested. It was also observed that silica removal decreased with increasing PA content at the lower dosages. One of the factors affecting this behavior could be the lower aluminum content in the hybrid coagulant. In this sense, with the highest dosage of the hybrid coagulant (2500 mg/L), where the aluminum content was high enough, the removal rates obtained with the hybrids were very similar. It was also observed that at lower dosages the higher molecular weights of the PA were better for silica removal.

The synergy between PA and PANS allowed achieving similar silica removal rates with 500 mg/L than with 2500 mg/L of PANS, and only with a 5% content of PA in the hybrids. Another advantage of using hybrid coagulants is that maximum 50% silica removal can be achieved compared to 30% with PANS, at 2500 mg/L dosages.

Trends observed at initial pH 10.5 were very different to those obtained without pH regulation. At initial pH 10.5, higher silica removal could be obtained (90%), however, differences between hybrids and PANS were lower than at initial pH 8.4. In this case, the molecular weight of the PA or the increase in the percentage of PA in the hybrids did not have a significant effect. Moreover, at initial pH 10.5, silica removal continuously increased with the coagulant dosage. This could be explained by two simultaneous factors. First, at this pH silica is ionized in a larger extent, therefore more silica could be removed by coagulation. Second, aluminum coagulants have more alkalinity available to form the different aluminum hydroxides which are the active species in coagulation. As observed in previous studies, at higher pH levels the differences in efficiency of the coagulants are minor than at lower pHs (Publication I). The use of the hybrid coagulants would not be justified at initial pH 10.5, since the marginal increase in silica removal would not compensate the cost

increase in the treatment. This is completely different to what occurred at pH 8.4, where the use of hybrid coagulants it is clearly recommended. At initial pH 8.4, silica removal did not increase by increasing the PA content in the hybrid, showing the best results with 5% active content, which is also very beneficial to the treatment costs.

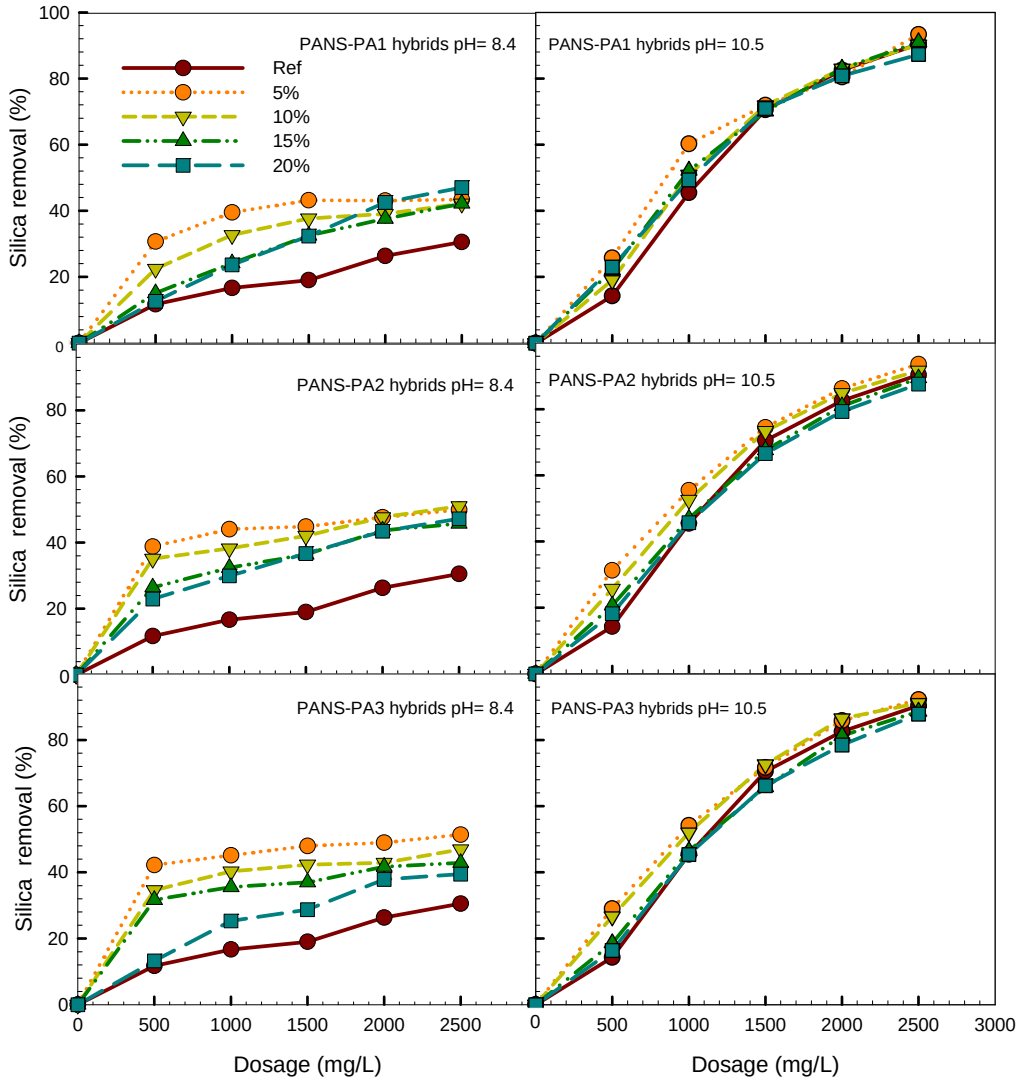

Figure 4.3. *Silica vs. PA hybrid coagulant dosage at different initial pHs (Publication III).*

Although the most critical parameter for effluent reuse in this paper mill is silica content, COD is also of interest to minimize the possible organic fouling on the membranes. Previous studies have demonstrated that there is a competition between COD and silica removal for a fixed dosage of coagulant, therefore silica and COD removals usually show opposite trends (Hermosilla et al. 2012, Publication I and II). Figure 4.4 shows the COD removal vs. dosage at initial pH 8.4 and 10.5. Opposite to silica, COD removal was lower at higher initial pH. At initial pH 8.4, the maximum COD removal was obtained at the highest dosage tested (2500 mg/L) for all the hybrids. As it is observed in figure 4.4, hybrid coagulants were also more efficient for COD removal than PANS, 51% vs. 37% at initial pH 8.4 and 31% vs. 4% at initial pH 10.5. PAs of higher molecular weight were more efficient for COD removal. Therefore, the use of PA of high molecular weight is recommended for the formulation of PANS-PA hybrids.

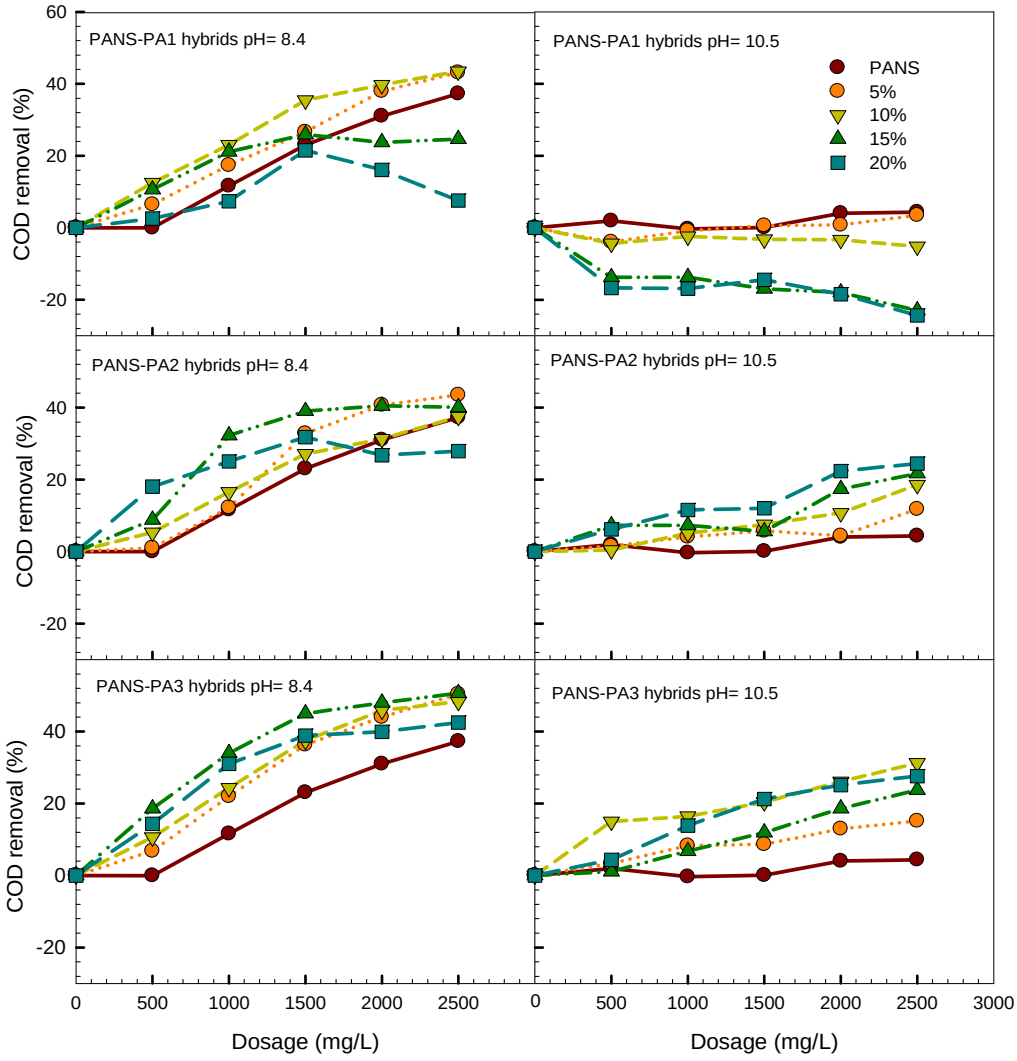

Figure 4.4. *COD vs. PA hybrid coagulant dosage at different initial pHs (Publication III).*

PDADMAC hybrids

Based on the results obtained with PA hybrids, a new range of PDADMAC hybrids was studied. Although, these hybrids has been tested in the literature, to our best knowledge they have not been applied for silica removal.

PANS-PDADMAC hybrids were prepared in the laboratory by direct blending the reference product (PANS) with two PDADMAC of similar charge density and different molecular weights in several ratios (1-5% wt.% of PDADMAC). Hybrids were tested at five dosages (500-3000 mg/L) at the initial pH of the effluent (pH=8.4) and 9.5. All the hybrids and PANS were tested in combination with the same flocculant: A-PAM of high molecular weight and medium charge.

In contrast to PA hybrids, at initial pH 8.4 no significant differences in silica removal were observed with the different hybrids and PANS. Maximum silica removal achieved with PANS and the hybrids was around 50%. Slightly, higher removal rates (≈5% difference) were obtained with the hybrids with the lower PDADMAC content (1%) for both PDADMAC tested. At initial pH=9.5, silica removal was improved around 10% with 1% of PDADMAC1. Maximum silica removal achieved with this product was 70% vs. 60% obtained with PANS. On the other hand, no differences were observed between PANS and PDADMAC2 hybrids. Therefore, these hybrids were discarded for silica removal.

4.1.4. Selection of the optimal treatment point and coagulation mechanism

Previous studies demonstrated that silica removal in the effluent requires high dosages of coagulants and high pHs to achieve high silica removal rates (>80%) in the effluent (Publication I-III). Since the effluent has low suspended solids, the rate of precipitation of $Al(OH)_3$ may be improved at higher concentration of small suspended solids and colloids which could act as nuclei for the formation of $Al(OH)_3$ precipitates. Therefore, the approach was to remove silica using two existing DAF units in the paper mill with different concentrations and size of suspended solids to achieve lower levels of silica in the effluent.

Four polyaluminum-based products and alum ($Al_2(SO_4)_3 \cdot 18H_2O$) were used as coagulants. PANS-PA1, PANS-PA2, one polyaluminum chloride with high basicity (PACl-HB) and another one with medium basicity (PACl-MB2). Characteristics of the coagulants are shown in table 3.3 and 3.4. All the coagulants were tested in combination with the same anionic PAM of high molecular weight and medium charge used as flocculant.

In waters from DAF1 the dosages of the coagulants varied from 25 to 250 mg/L Al_2O_3. As for the same aluminum dosage, the dosages of the coagulants in terms of commercial products were very different, in the study with waters from DAF2, all the products were tested at the same dosage of commercial products (100-1250 mg/L), independently of their aluminum content. DAF trials were carried out without pH regulation as an alkaline pH adjustment would produce pH "socks" when water was reused. The methodology followed is shown in figure 3.3.

Without chemicals or using only flocculant, the removal of contaminants was almost negligible in DAF units, especially in DAF2, due to the small size of the suspended solids. In DAF1, the pH decrease after coagulation was the most critical factor for silica removal, therefore, PACl-HB and PANS-PA2 (<0.3 pH units decrease) were the recommended treatment options. PACl-HB was selected when the most important contaminant was silica (40% silica removal, 6% soluble COD removal) (figure 4.5), while PANS-PA2 was recommended for high silica removals together with high turbidity and COD removals (35% silica removal, 20% soluble COD removal).

In DAF2, the most efficient products in silica removal were those with the highest aluminum content (figure 4.5), i.e. alum, PACl-MB2 and PANS-PA2. However, the use of alum was not recommended as it largely increases the conductivity of the waters and produces the largest pH suppression. Therefore, the use of PACl-MB2 and PANS-PA2 was the recommended treatment options. For DAF2 waters, PACl-MB would be used if the most important requirement was silica removal (35% silica removal, 24% soluble COD removal) and PANS-PA2 if high silica removals were necessary, but high turbidity and COD removals (30% silica removal, 28% soluble COD removal).

Results obtained indicated that the coagulant demand for silica removal in the effluent could be reduced significantly by treating the inlet of DAF units, especially in DAF2. The coagulant demand (mg/L coagulant per mg/L silica removed) could be reduced down to 35-50% for the coagulants with the highest aluminum contents (alum and PACl-HB) and around 20% with PANS, PANS-PA1 and PANS-PA2. Besides, the early removal of silica would contribute to have cleaner water circuits compared to silica removal on the effluent.

Depending on the initial silica content and the objectives of the treatment (direct discharge or effluent reuse treatments with RO membranes), a post-treatment in the effluent for silica removal could be necessary. The most important finding of this study was that silica could be removed in

the DAF units used as internal treatments for process waters, avoiding as much as possible the removal of silica from the effluent, where higher requirements of coagulants per mg/L of SiO_2 removed were necessary.

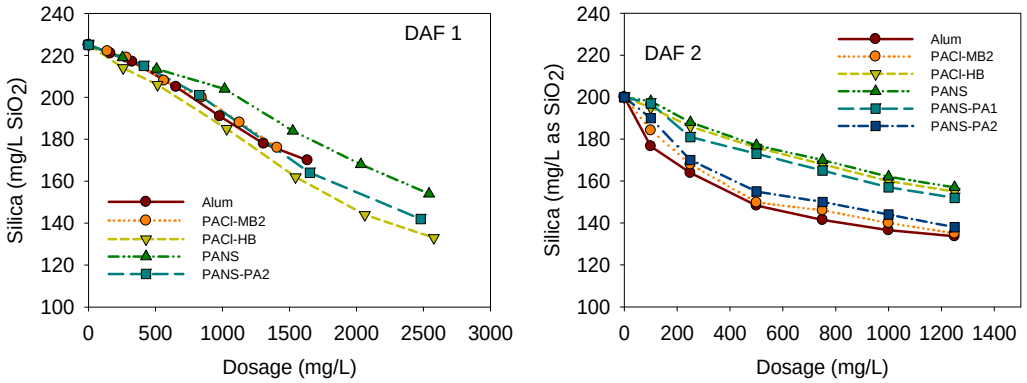

Figure 4.5. *Silica of clarified waters from DAF1 and DAF2 vs. coagulant dosage (Publication IV).*

Flocculation mechanism in the DAF units

The objective of this study was to analyze the flocculation behavior and flocculation mechanisms of the most promising products (Publication I and II). Five aluminum-based coagulants were tested (tables 3.3 and 3.4).

The flocculation mechanism was studied through the addition of successive coagulant dosages and the flocculation-deflocculation-reflocculation tests. For the successive additions trials a total dosage of 1000 mg/L Al_2O_3 was added through successive steps of 25 mg/L each 30 s. In the flocculation-deflocculation-reflocculation tests, single additions from 25 to 250 mg/L Al_2O_3 were used.

From these tests, the strength or breakage factor (SF) and recovery or re-growth factor (RF) were calculated using Ec. 4.1 and 4.2, where: MCS1 is the maximum MCS value before the flocs breakage, MCS2 is the MCS value when the flocs were broken after intensive stirring and MCS3 is the maximum MCS value for the flocs re-growth after the intensive stirring (Wei et al.2010; Yukselen and Gregory 2004).

$$SF = \frac{MCS_2}{MCS_1} \qquad [Eq. 4.1]$$

$$RF = \frac{MCS_3 - MCS_2}{MCS_1 - MCS_2} \qquad [Eq. 4.2]$$

Figures 4.6 shows and example of the curves obtained to study the strength of the flocs and reversibility of the flocs formed with the different treatments. Based on those flocculation-deflocculation-reflocculation curves, the strength factor (figure 4.7) and the recovery factor (figure 4.8) were calculated.

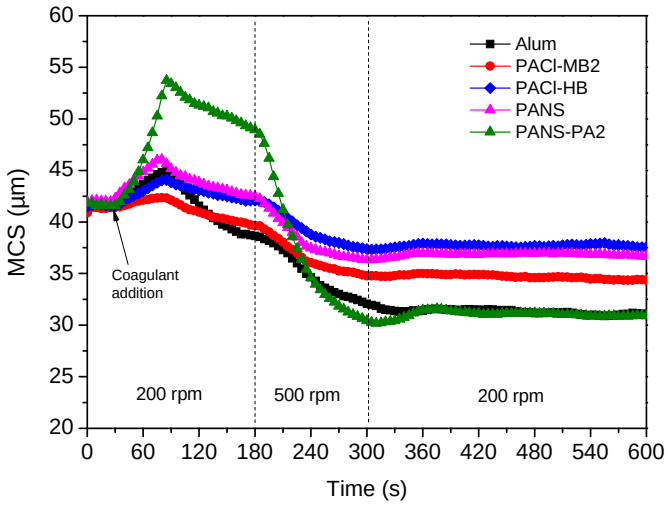

Figure 4.6. MCS at 250 mg/L Al_2O_3 coagulant vs. time in flocculation deflocculation-reflocculation studies (Publication V).

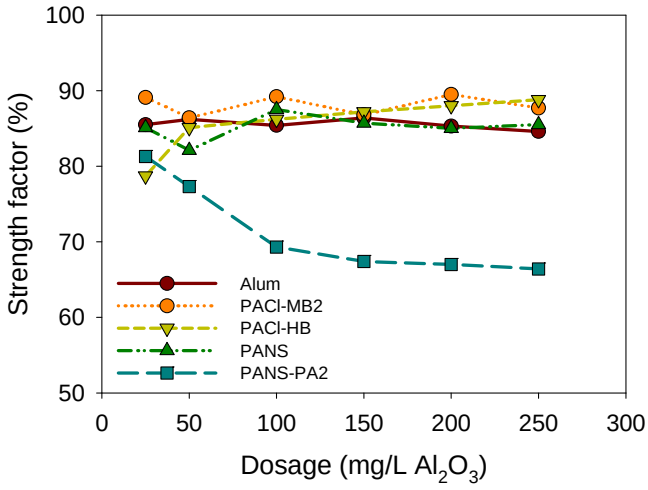

Figure 4.7. *Recovery factor for the different coagulants and dosages used* (Publication V).

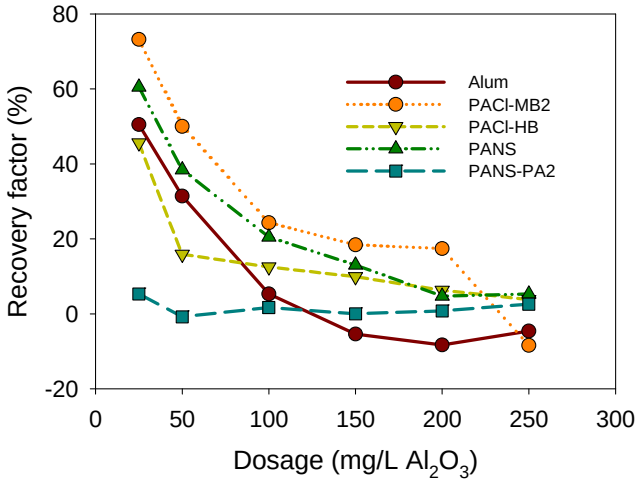

Figure 4.8. *Strength factor for the different coagulants and dosages used* (Publication V).

The strength factor of the flocs formed by the pure aluminum coagulants was very similar and high (85-90%), independently of the dosage tested. The strength factor of the hybrid coagulant was much lower than those of the other coagulants, and decreased with the dosage from 81% (at 25 mg/L) to 66% (at 250 mg/L). The larger flocs obtained during flocculation with PANS-PA2 was probably the cause for a reduced strength factor as larger flocs are usually also the weakest. The possible flocculation mechanism of PA by the formation of patches (with very low shear resistance) is in agreement with the results obtained.

The recovery factors for the pure aluminum coagulants decreased with the dosage, from 46-73% (at 25 mg/L) to 0% (at 250 mg/L). At the lowest dosages, the contribution of charge neutralization was still important and there were high recovery factors (in pure charge neutralization mechanisms the refloccualtion should be almost total). As the dosage of the coagulant increased, sweep flocculation (irreversible flocs) became predominant, and there was a parallel decrease in the strength factor of the formed flocs. In the case of PANS-PA2, the recovery factor was always close to zero, independently of the dosage. This behavior would be explained by interparticles bridges formation instead of patches formation at the reflocculation conditions, where the high concentration of small solids after breakage of the flocs promoted interparticles bridges formation instead of patches formation.

At low dosages of coagulant (25-50 mg/L), the main flocculation mechanism for the coagulants was charge neutralization, while at high dosages the contribution of sweep flocculation became predominant. The hybrid coagulant had rather different behavior. The PA in PANS-PA2 enhanced patches formation during flocculation and interparticles bridges formation during reflocculation.

Efficiency of chitosan derivatives on silica removal

Based on the growing interest on environmental friendly alternatives to synthetic additives, this study analyzed the efficiency of different chitosans and chitosan derivatives in the treatment of papermaking process water by DAF, with emphasis in their possible use for silica removal.

Two native chitosans with different molecular weights and two quaternary chitosan derivatives were tested (table 3.7). Moreover, the use of the native chitosans in combination with anionic bentonite microparticles was also considered. Chitosan were tested at different dosages from 25 mg/L to 250 mg/L. In dual systems, the bentonite was added in a fixed ratio chitosan: bentonite of 1:2 (wt./wt.).

Regarding silica, results obtained indicated that only minor silica removals could be obtained with these treatments, always lower than 5–10%. Differences among the treatments could not be clearly assessed as these differences were very close to the experimental error of the silica measurement method.

Although chitosan derivatives were not effective for silica removal, they show a good performance on the removal of organic matter. Native chitosans showed high efficiency at intermediate dosages and furthermore, their efficiency was enhanced by the combined addition of bentonite. For an equivalent removal of contaminants, the required dosage of chitosan was about half that the dosage required in absence of bentonite. In this case, quaternary derivatives did not improve the efficiency compared to the native chitosans.

The optimum treatment would be 50 mg/L of native chitosan and 100 mg/L of bentonite. This treatment is able to remove of 83–89% turbidity (residual turbidity 210–320 NTU), 68–71% dissolved turbidity (residual dissolved turbidity of 22–24 NTU), 18–22% total solids (residual total solids of 2750–2900 mg/L) and 19–23% COD (1440–1525 mg/L). In all the tests, the low molecular weight native chitosan was more efficient than the medium molecular weight chitosan.

4.2. SILICA REMOVAL WITH MAGNESIUM COMPOUNDS

4.2.1. Silica removal with soluble magnesium compounds

Selection of the magnesium compound, pH and dosage

Two soluble magnesium compounds ($MgCl_2 \cdot 6H_2O$ and $MgSO_4 \cdot 7H_2O$) were used to increase water hardness and thus silica removal efficiency during softening. The dosage, the operating pH and the pH regulator were optimized. Moreover, the combination of $MgCl_2 \cdot 6H_2O$ with and aluminum coagulant was also studied as suggested by previous studies (Zeng et al. 2007).

For each magnesium compound, five dosages were tested (from 250 to 1500 mg/L) at three different initial pHs: 10.5, 11.0 and 11.5. Figure 3.4 shows the methodology followed. In the present study, the contact time and the operational temperature were 15 min and 20ºC, respectively. First, the best magnesium compound was selected. Then the pH regulator was optimized, comparing the efficiency of NaOH and $Ca(OH)_2$. Finally, the effect of the polyaluminum coagulant (PANS-PA2, table 3.4) on the softening treatment with the most efficient magnesium salt was assessed. The coagulant dosage used was 125 mg/L.

Silica removal increased with the pH and the magnesium compound dosage (figure 4.9). High silica removal rates (80-90%) could be obtained by adding soluble magnesium compounds (1500 mg/L) at high pH (11.5.) These silica removal rates allow working in RO membranes at high recoveries (75-85%) without silica scaling phenomena.

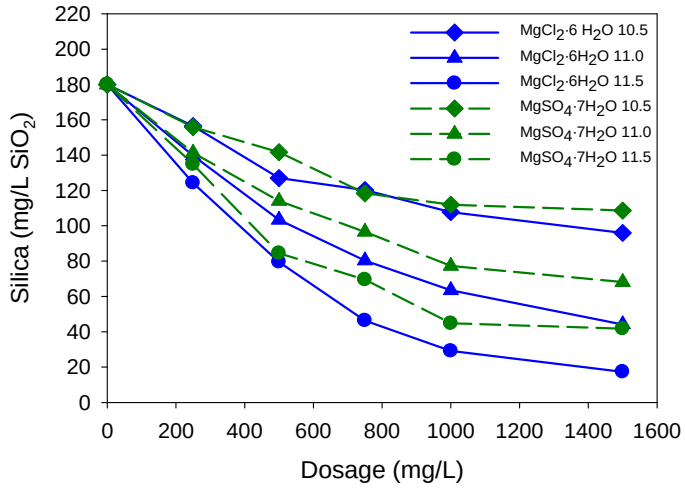

Figure 4.9. *Silica vs. dosage of $MgCl_2 \cdot 6H_2O$ and $MgSO_4 \cdot 7H_2O$, at different initial pHs* (Publication VII).

Figure 4.10 shows the mmol of silica removed per mmol of initial magnesium contents. This ratio was almost the same for both magnesium species, which would explain the lower silica removal rates obtained with $MgSO_4 \cdot 7H_2O$ than with $MgCl_2 \cdot 6H_2O$. The reason is the lower magnesium content of $MgSO_4 \cdot 7H_2O$ (9.9 wt.%) compared to $MgCl_2 \cdot 6H_2O$ (12.0 wt.%). Therefore, $MgCl_2 \cdot 6H_2O$ was preferred to $MgSO_4 \cdot 7H_2O$ because it was more effective on silica removal in terms of mg/L of silica removed per mg/L of Mg compound and, in the specific case of this paper mill, there is a discharge concentration limit of 1000 mg/L for sulphates.

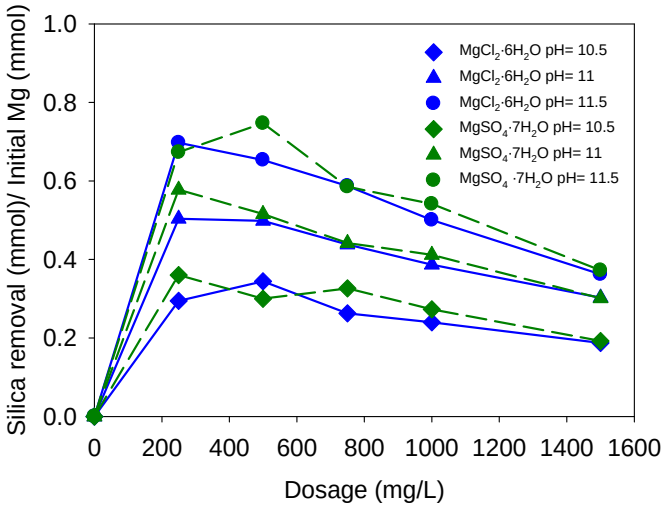

Figure 4.10. mmol of silica removed per mmol of initial magnesium at different initial pHs with $MgCl_2 \cdot 6H_2O$ or $MgSO_4 \cdot 7H_2O$ (Publication VII).

The high pHs required to obtain high silica removal rates were directly translated into a high conductivity increase of the treated waters. It is important to take into account that in coagulation tests the highest pH tested was 10.5 in all the cases. During softening with magnesium soluble salts, silica removal was very low at pHs lower than 10.5, this is the reason why higher pHs were tested in this case. The problem of high final conductivities could be partially solved with the use of $Ca(OH)_2$ as pH regulator (final conductivity around 3.0 mS/cm). Additionally, the use of $Ca(OH)_2$ compared to NaOH, as mentioned in section 4.1.1.) has the advantage of a lower cost, lower settling time required, higher silica removal (2-10% depending on the initial pH) and COD removal (additional 15% COD removal) rates obtained.

The combination of $MgCl_2 \cdot 6H_2O$ with PANS-PA2 did not improve silica removal significantly. A maximum increase of 10%, compared with the trials carried out without coagulant addition, was achieved. On the other hand, COD removal was not affected by the addition of coagulant and still the conductivity increased. Therefore, in this case, the combined use of a magnesium salt and coagulant is not recommended.

Optimization of the contact time and temperature

In the previous section it was found that the use of soluble magnesium compounds was a promising solution to obtain high silica removal rates at ambient temperature and short contact times (15 min). Among them, $MgCl_2 \cdot 6H_2O$ was the most efficient compound, achieving 90% silica removal at pH=11.5 and 1500 mg/L. In this study, the effect of the operational temperature and contact time were analyzed, aiming to the generalization of the results obtained to other cases.

The optimization of the operational temperature was carried out at three different pHs (10.5, 11.5 and 12.0), at three temperatures (20, 35 and 50ºC) using $MgCl_2 \cdot 6H_2O$ at five dosages (from 250 to 1500 mg/L). $Ca(OH)_2$ was selected as pH regulator as it was found in the previous section to be more advantageous than caustic soda. Methodology followed is shown in figure 3.4, in this case the effect of the reaction time was studied (up to 150 min).

High silica removal rates (>80%) could be obtained with different combinations of high pH and high temperature at different dosages of $MgCl_2 \cdot 6H_2O$. In each particular application, it is necessary to evaluate the optimal combination of pH and temperature to be used. For example, at 20ºC, it would possible to obtain high silica removal rates (80%) with 1500 mg/L of $MgCl_2 \cdot 6H_2O$ working at high pHs (11.5-12.0). Higher operational temperatures increased silica removal up to 80% at pH=10.5 and to 90% at pH 11.5-12.0, using 1500 mg/L of $MgCl_2 \cdot 6H_2O$. Finally, 90% removal could be achieved by decreasing the dosage down to 750 mg/L at pH=12.0, but increasing the operation temperature to 50ºC.

Figure 4.11 shows the evolution of silica removal with time at the different temperatures and pHs tested. Silica removal process was fast even at ambient temperature (20ºC), achieving >80% of the total silica removal with contact times lower than 30 min. Process kinetic were improved at higher temperatures, achieving 85% of the total silica removal in 20 min at T=35ºC and 15 min at T=50ºC, respectively.

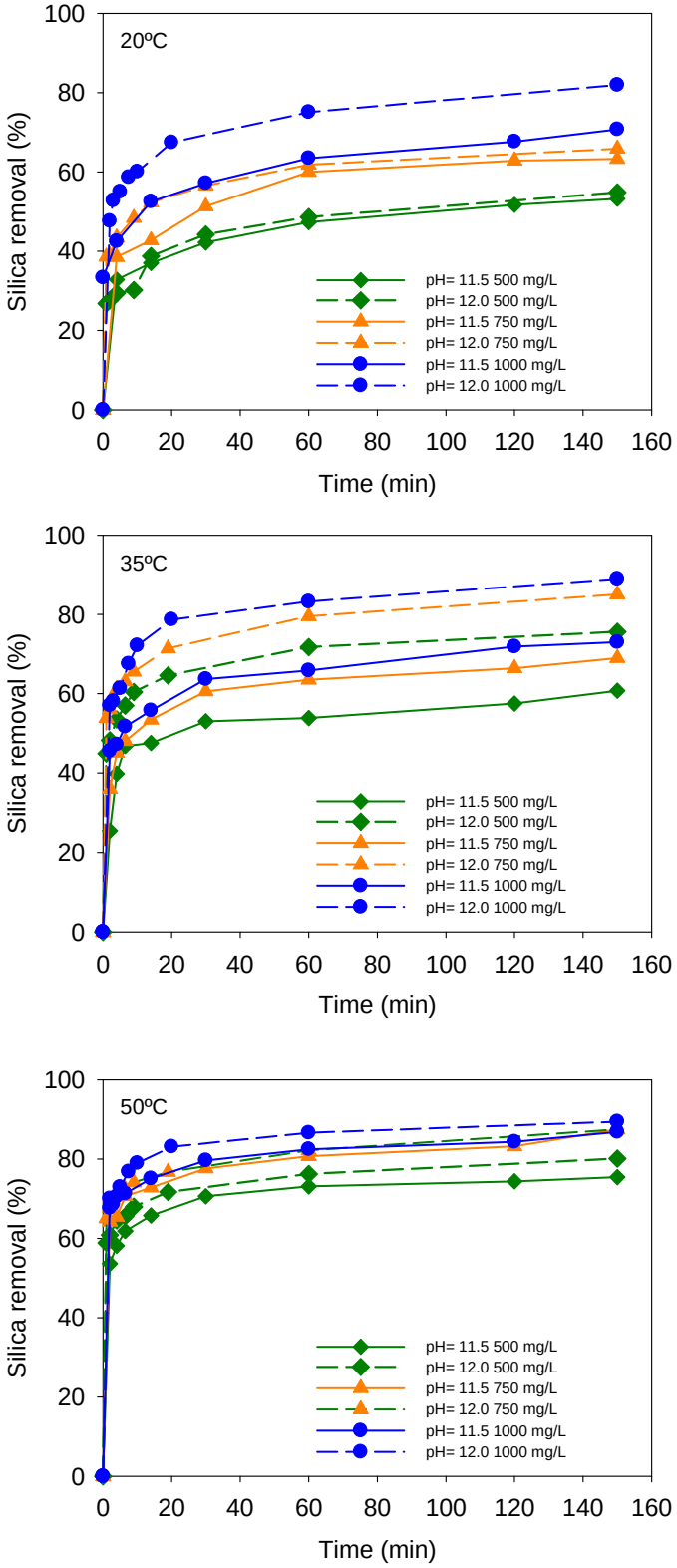

Figure 4.11. *Silica removal vs. time at different initial pHs and temperatures: 20ºC, 35ºC and 50ºC (Publication VIII).*

4.2.2. Silica removal with sparingly soluble magnesium compounds

Silica removal with soluble magnesium compounds allows obtaining high silica removal rates (80-90%). However, the high operational pH required (>11.5) and the counter-ions added to the water are directly translated into a high conductivity of the treated water. This can cause operational problems in the RO and a make necessary the post-treatment of RO brines before their discharge. Although this problem could be partially solved using $Ca(OH)_2$, another approach would be the use of sparingly soluble magnesium compounds, especially MgO, which has been traditionally used in "hot softening".

The use of different sparingly soluble magnesium compounds (MgO, $Mg(OH)_2$ and $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$) was studied. For each magnesium compound, six dosages were tested (from 250 to 1500 mg/L) at 3 different pHs: 10.5, 11.0 and 11.5. Figure 3.4 shows the methodology followed. In these experiments, the tests were also carried out at ambient temperature (20ºC) and 15 min contact time.

At these conditions, a maximum of 40% silica removal was obtained with 1500 mg/L of MgO at pH 11.5. With $Mg(OH)_2$ and $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$, removal rates lower than 20% and 10% were achieved, respectively. The low removal rates obtained with the three products were caused by the low solubility of the magnesium compounds and, consequently, the low concentration of dissolved magnesium that was available to react and precipitate either as fresh $Mg(OH)_2$ or magnesium silicates of different stoichiometries (Publication VIII; Parks and Edwards 2007). The higher efficiency in silica removal by MgO was due to its higher solubility (0.086 g/L), which was translated into around 52 mg/l of dissolved magnesium at equilibrium, and the higher magnesium content (60.3 wt.%).

Two different strategies were studied to increase dissolved magnesium and thus silica removal:

a) To increase the dissolved magnesium by pre-acidifying the magnesium compound slurries before use.
b) To increase the working temperature and/or the contact time to kinetically favour the dissolution of the magnesium compounds.

Silica removal with pre-acidified sparingly soluble magnesium compounds

A controlled pre-acidification of the slurries with sulphuric acid of the sparingly soluble magnesium compounds was carried out. Pre-acidified slurries were tested again at 20ºC and 15 min contact time. The same six dosages (from 250 to 1500 mg/L) and three pHs (10.5, 11.0 and 11.5) used when the slurries were not pre-acidified were selected for comparison purposes. Moreover, the pH regulator was optimized using the most efficient magnesium compound (NaOH and $Ca(OH)_2$).

Table 4.1 summarizes the main characteristics of the 10 wt./vol.% slurries with and without pre-acidification. Pre-acidification of the slurries was carried out at a dosage of 57.6 g of commercial H_2SO_4/L of slurry (Publication IX).

Table. 4.1. *Characteristics of the slurries with and without pre-acidification.*

Magnesium compound	pH	Conductivity (mS/cm)	Dissolved magnesium (g/L)	SO_4^{2-} (g/L)
MgO	11.5	0.2	4.9	0.0
p.a. MgO	9.8	20.4	10.9	54.2
$Mg(OH)_2$	10.3	0.5	5.6	0.0
p.a. $Mg(OH)_2$	9.5	31.3	19.4	54.0
$(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$	9.9	0.4	0.87	0.0
p.a.$(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$	8.3	25.6	15.2	54.3

** p.a. means pre-acidified slurry.*

Figure 4.12 shows silica removal with magnesium compounds with and without pre-acidification. Silica removal was significantly increased using the pre-acidified slurries, especially at the highest pHs. Maximum removal rates with the pre-acidified slurries were obtained at the highest pH (11.5) and dosage (1500 mg/L): 86% for both MgO and $Mg(OH)_2$ and around 80% for $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$.

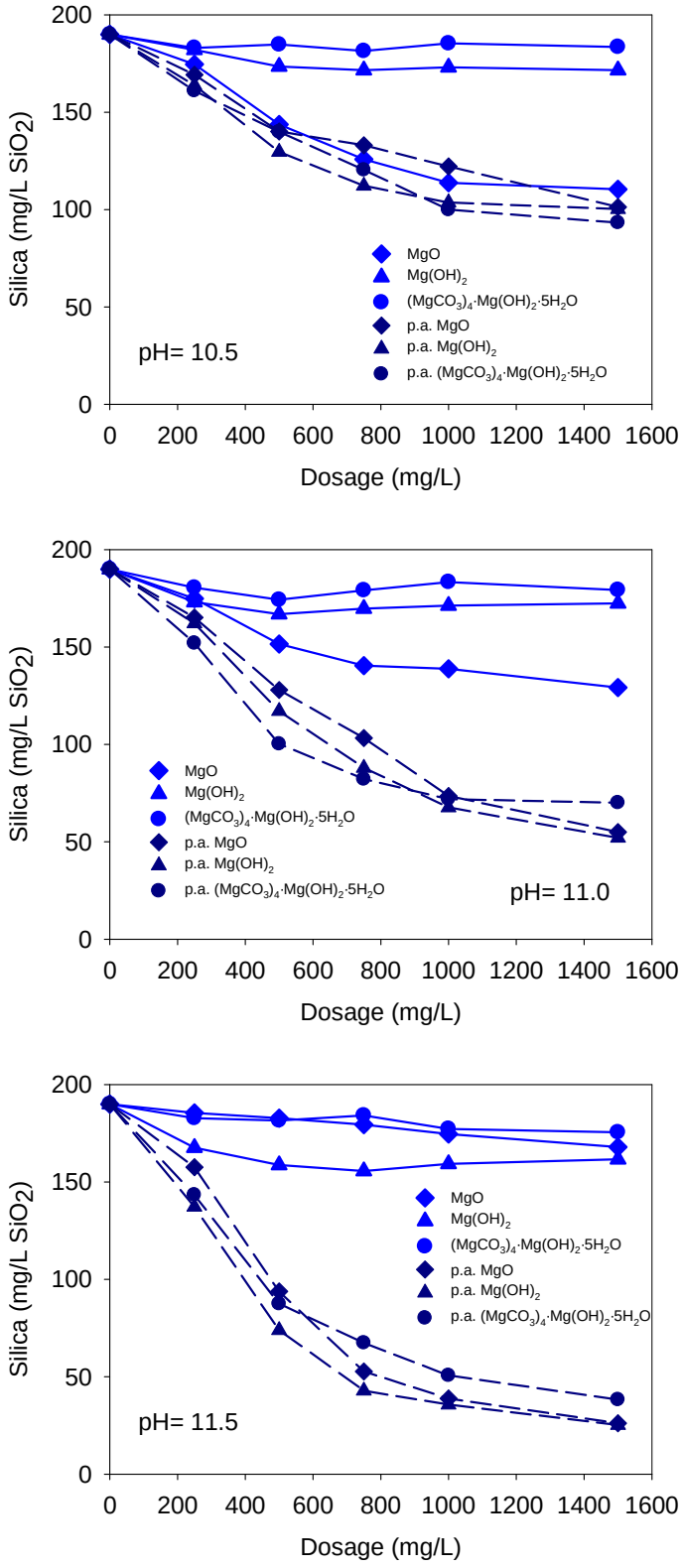

Figure 4.12. *Silica removal vs. dosage of magnesium compound at pH= 10.5, 11.0 and 11.5 (p.a. means pre-acidified slurry).*

Although pre-acidification increased the conductivity of the treated waters compared to the direct use of the sparingly soluble compounds, this problem was solved by using $Ca(OH)_2$ as pH regulator instead of NaOH. In the most favourable conditions (pH 11.5 and 1500 mg/L of pre-acidified MgO), final conductivity of the treated water was 4.6 mS/cm with caustic soda but only 2.4 mS/cm with lime milk for an initial conductivity of the waters of 2.2 mS/cm. The use of lime milk as pH regulator had the additional advantage of increasing to 25% COD removal compared to the 15% obtained with NaOH. As showed in the study, the use of pre-acidified MgO with $Ca(OH)_2$ as pH regulator allows obtaining high silica removal rates with a low increase in conductivity and at low cost, even at ambient temperature. In this way "cold softening" with pre-acidified MgO could be an interesting option for silica removal.

Moreover, maximum silica removal rates were similar to the ones obtained in previous studies with soluble magnesium compounds such as $MgCl_2 \cdot 6H_2O$ (90% silica removal) without adding chlorides to the system, and higher than $MgSO_4 \cdot 7H_2O$ (77% silica removal). Additionally, the conductivity of the treated waters was lower.

These aspects make the softening a competitive technique compared to other silica removal techniques such as coagulation, even at ambient temperature (Publication VII).

Optimization of the temperature and contact time

To increase dissolved magnesium concentration and thus silica removal, the effect of the operational temperature and contact time was studied using MgO, which was the most efficient sparingly soluble magnesium compound.

The efficiency of MgO was tested at different dosages (150-10000 mg/L), pH values (8.2-9.5) and temperatures (25-50ºC). Figure 3.4 shows the methodology followed and in these experiments reaction time was 24 hours. Moreover, a kinetic study at different temperatures was carried out.

As it can be observed in figure 4.13 and 4.14, silica removals higher than 95% were obtained with 500 mg/L of MgO without pH regulation even at 20ºC, minimizing the conductivity increase after the treatment to less than 0.5 mS/cm (final conductivity= 2.2 mS/cm). This is a clear improvement over the previous studies using both soluble and pre-acidified soluble magnesium compounds.

Initial pH regulation had no significant effect on silica removal using MgO as magnesium source at high contact times (t= 24 h) or temperatures (T> 35ºC). MgO dissolution itself (Ec. 4.3 and 4.4) increased OH^- concentration to reach a pH of around pH=11.5 which is optimum for both silica ionization and removal.

$$MgO\ (s) + H_2O \rightleftharpoons Mg^{2+} + 2\ OH^- \quad \text{(Eq 4.3)}$$

$$Mg^{2+} + 2\ OH^- \rightleftharpoons Mg(OH)_2\ (s) \quad \text{(Eq 4.4)}$$

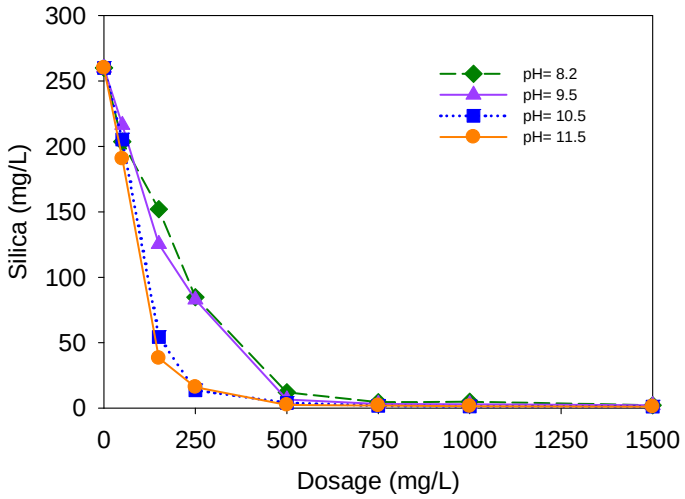

Figure 4.13. Silica removal vs. dosage at 25ºC and different initial pHs.

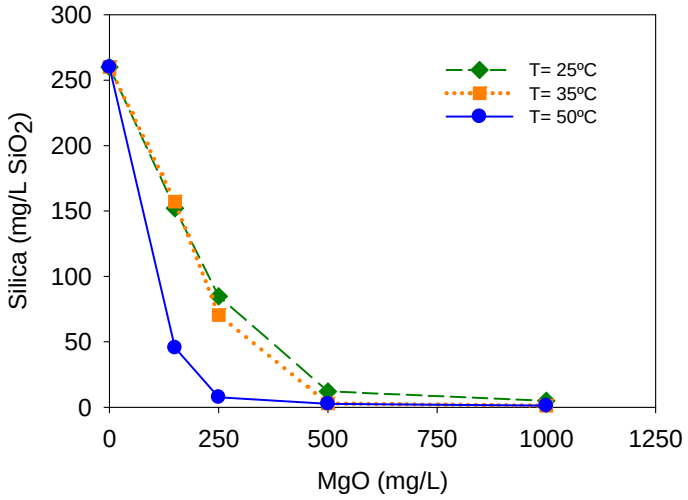

Figure 4.14. Silica removal vs. MgO dosage at initial pH 8.2 and 3 different temperatures.

Figure 4.15 shows the evolution of silica concentration with time at four initial pHs (8.2-11.5) and three temperatures (25-50ºC). Operational temperature and reaction time had strong effect on silica removal as MgO solubility is limited at temperatures lower than 35ºC. At T<35ºC silica removal involved three stages, one fast corresponding to the precipitation of magnesium silicates, one slow corresponding to further MgO dissolution and another fast stage until the achievement of the equilibrium concentration. At T> 35ºC, 80-90% silica removal could be achieved after 2-3 hours contact time. At 25ºC and dosages >500 mg/L silica removals of 80-90% could also be obtained, however, it would be necessary 24 h contact time.

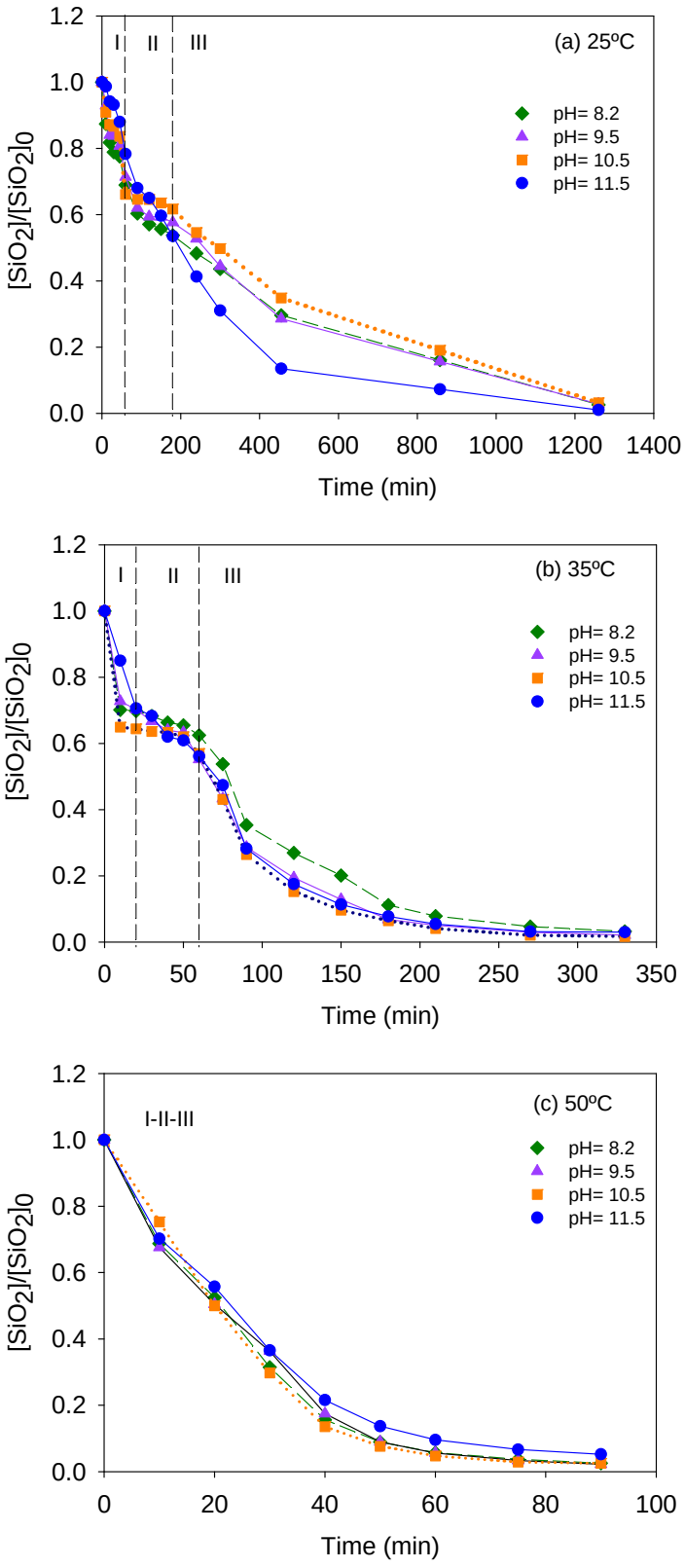

Figure 4.15.- *Silica concentration vs. time at different initial pHs and temperatures: (a) 25ºC, (b) 35ºC and (c) 50ºC (Publication X).*

4.2.3. Silica removal mechanism.

SEM-EDX analyses of the solids obtained during the tests were carried out for the identification of the silica removal mechanism. The analysis of the Si/Mg atomic ratio gave very valuable information about the different silica removal mechanisms, i.e. co-precipitation or adsorption, and the involved species, which is still unclear in the literature (Demadis et al. 2012; Demadis 2010; Hsu et al. 2008; Parks and Edwards 2007; Chen et al. 2006; Sheikholeslami and Bright 2002).

If adsorption on magnesium hydroxide was the main mechanism involved, the Si/Mg ratio observed in the solids would be very low, as the magnesium required to remove a certain amount of silica was considerably higher in adsorption than in co-precipitation. In this sense, Chen et al. (2006) and Hsu et al. (2008) reported a molar ratio Mg/Si 22:1 for adsorption on $Mg(OH)_2$ compared to ratios varying from 0.5 to 1 if the main silica removal mechanism is through the formation of magnesium silicates. Although there are many possible magnesium silicates with different stoichiometries, the literature indicated that the most common would be Mg_2SiO_4 (forsterite, pK_{ps}= 26.9), $Mg_3Si_2O_5(OH)_4$ (antigorite, pK_{ps}= 34.5) or $MgSiO_3$ (enstatite, pK_{ps}= 16.9) (Parks and Edwards 2007).

Figure 4.16 shows some SEM images of the solids obtained under different operational conditions using $MgCl_2 \cdot 6H_2O$ and table 4.2 shows the EDX analysis of these solids. The solids were mainly composed by Mg, Si, O and Ca. Atomic Si/Mg ratios varied between 0.5 and 1, which supported the precipitation of a mixture of forsterite (Mg_2SiO_4), enstatite ($MgSiO_3$) and antigorite ($Mg_3Si_2O_5(OH)_4$). Besides magnesium silicates, due to the addition of lime milk as pH regulator, particles with high calcium concentration were also detected which were compatible with $CaCO_3$, $Ca(OH)_2$ or calcium silicate (table 4.2).

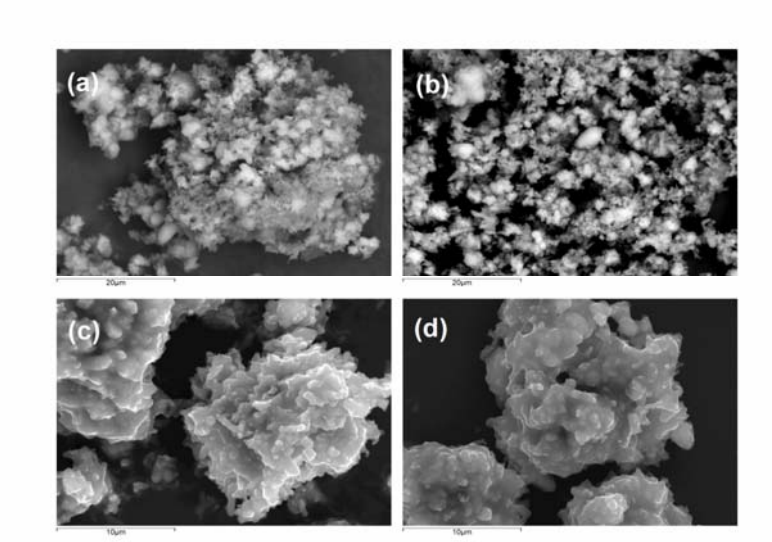

***Figure 4.16.**- SEM-EDX images of the typical solids obtained after the treatment at: (a) pH= 11.5, 250 mg/L and 20ºC, x2000; (b) pH= 11.5, 750 mg/L and 20ºC, x2000; (c) pH= 12.0 250 mg/L and 20ºC, x4000; (d) pH=12.0 750 mg/L and 20ºC, x4000 (Publication VIII).*

Table 4.2. -Composition of the of the solids obtained after precipitation.

	Mg (Atomic %)	Si (Atomic %)	Ca (Atomic %)	Si/Mg (Atomic/atomic)
(a)	0.62	0.41	19.41	0.66
(b)	4.47	3.21	18.80	0.72
(c)	1.76	1.67	25.94	0.95
(d)	1.47	0.73	24.97	0.50

Figure 4.17 shows Si (atomic %) vs. Mg (atomic %) of the solids analyzed by EDX at different operational conditions of dosage, pH and temperature. It could be observed that the Si/Mg atomic ratio for the different solids was very similar, independently of the operational conditions. A linear fit of the data obtained an average 0.69 atomic Si/Mg ratio, which is very close to the atomic Si/Mg ratio of the antigorite ($Mg_3Si_2O_5(OH)_4$, Si/Mg=0.67). This result is in agreement with Gunnarsson et al. (2005), who obtained also a Si/Mg=0.7 when studying the precipitation of magnesium silicate in synthetic water under different operational conditions of pH and temperature. Although, the average Si/Mg ratio was 0.69, particles with ratios from 0.5 to 1 were also observed (table 4.2 and figure 4.17). These lower ratios, could be attributed to other magnesium silicate stoichiometries (e.g. forsterite, Si/Mg = 0.5) or to the presence of other magnesium compounds such as $Mg(OH)_2$ or $MgCO_3$. Higher Si/Mg ratios could be associated to the presence of polymeric silica or magnesium silicates with higher Si/Mg stoichiometries (e.g. enstatite, Si/Mg = 1).

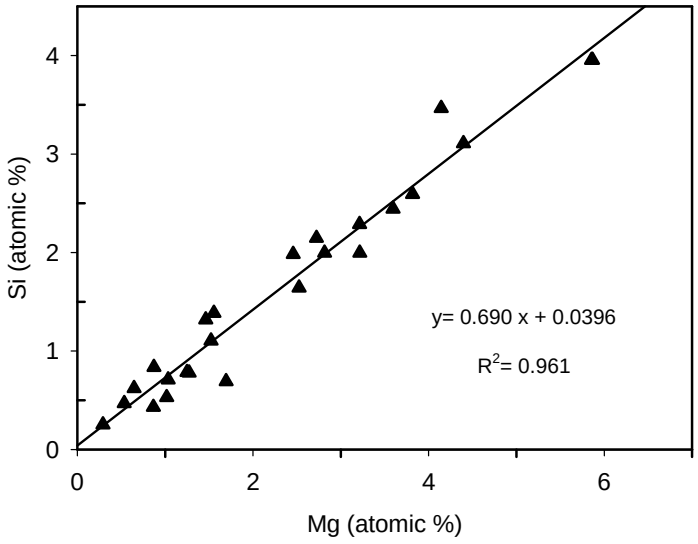

Figure 4.17. Si (atomic) vs Mg (atomic) of the solids obtained under different operational conditions (Publication VIII).

Based on the constant Si/Mg atomic ratio obtained and the large values of Si removed per Mg removed, it could be ascertained that the main silica removal mechanism is the precipitation of antigorite. If adsorption on fresh formed magnesium hydroxide was the main mechanism involved, the Si /Mg ratio observed in the solids would be much lower. The fast kinetics of the process also suggests that precipitation is favoured versus adsorption, at these experimental conditions.

SEM-EDX analysis of the solids obtained using MgO also supported the hypothesis of silica removal by precipitation of magnesium silicates. In the case of using MgO as magnesium source, it is important to take into account that it is a sparingly soluble compound and the unreacted MgO would contribute to decrease the ratio Si/Mg in the analyzed solids, especially at the highest dosages, where the excess of unreacted MgO is higher. Si/Mg molar ratio obtained at the lowest MgO dosages (150-250 mg/L) of by SEM-EDX was around 0.5-1, which is in agreement with the precipitation of a mixture of magnesium silicates such as forsterite (Mg_2SiO_4) and antigorite ($Mg_3Si_2O_5(OH)_4$). At higher dosages (≥500 mg/L), the ratio Si/Mg increased steadily, due to the presence of unreacted MgO and to the precipitation of $Mg(OH)_2$.

FTIR results carried out were consistent with the precipitation of magnesium silicates as the main silica removal mechanism. In all the FTIR spectra there was a Si-O band characteristic of magnesium silicates after the treatment with both magnesium compound (MgO and $MgCl_2{\cdot}6H_2O$). Peaks corresponding to calcium carbonate and $Mg(OH)_2$ were also detected. In the case of MgO, unreacted MgO was present.

Figure 4.18 shows a simplified diagram of the main reactions involved in the silica removal process by softening with magnesium compounds. Silica, which derives from the orthosilicic acid, could react with Mg^{2+} and precipitate as magnesium silicates. For the precipitation of magnesium silicates OH^- are consumed. These hydroxyl groups could be supplied by the pH regulator (NaOH or $Ca(OH)_2$) or by the magnesium compound in the case of MgO. Silica may also react with Ca^{2+} from the lime used as a pH regulator to yield calcium silicates. The use of lime would also introduce additional hydroxyl groups to the water which may be consumed in the precipitation of different magnesium silicates and magnesium hydroxide. On the other hand, silica polymerization could also occur, especially at high temperatures; however, at the conditions of basic pH and magnesium concentration tested, the precipitation of silicates was favored compared to polymerization (Sheikholeslami et al. 2001).

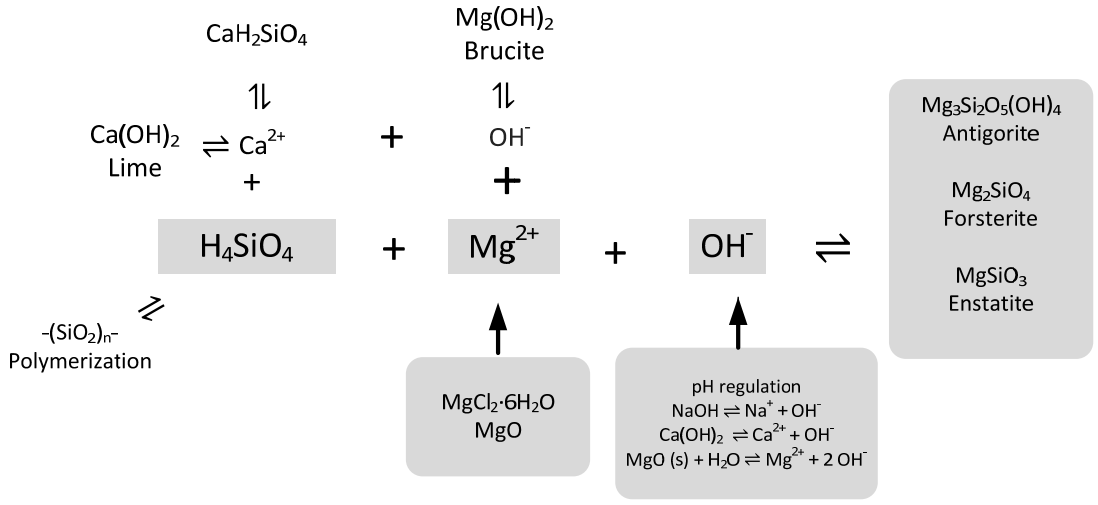

Figure 4.18. *Simplified scheme of the reactions that occur during silica removal.*

4.3. ADSORPTION

4.3.1. Silica removal with activated alumina

A commercial boehmite type activated alumina (Catapal B®) was used as adsorbent for silica removal (table 3.9). Dosage, operational pH and temperature were optimized.

The activated alumina was tested at nine dosages (from 1.5 to 20 g/L) and three different temperatures (20ºC, 35ºC and 50ºC). Silica removal was studied at 8 pHs from pH 5 to 12. During the adsorption process, the pH was maintained constant (± 0.2 pH units) by the addition of 0.1 M HCl or 0.1 M NaOH solutions.

Figure 3.5 shows the methodology followed. According to the preliminary tests, the contact time was fixed to 1 h. First, the effect of the operational temperature and contact time were studied. Then, the operational pH was optimized.

Figure 4.19 shows silica removal as a function of adsorbent dosage at different operational temperatures without any pH adjustment. As observed, silica removal increased with the dosage reaching an equilibrium value beyond which there was a negligible change in residual silica concentration. At ambient temperature, silica removal was 80% at an adsorbent dosage of 15 g/L, which is equivalent to a q=11 mg/g, for an initial concentration of around 200 mg/L SiO_2. As shown in figure 4.19, higher silica removal rates were obtained at higher temperatures, especially at 50 ºC. Equilibrium isotherms were fitted to Langmuir and Freundlich models, the fit to Freundlich model being slightly better than Langmuir model.

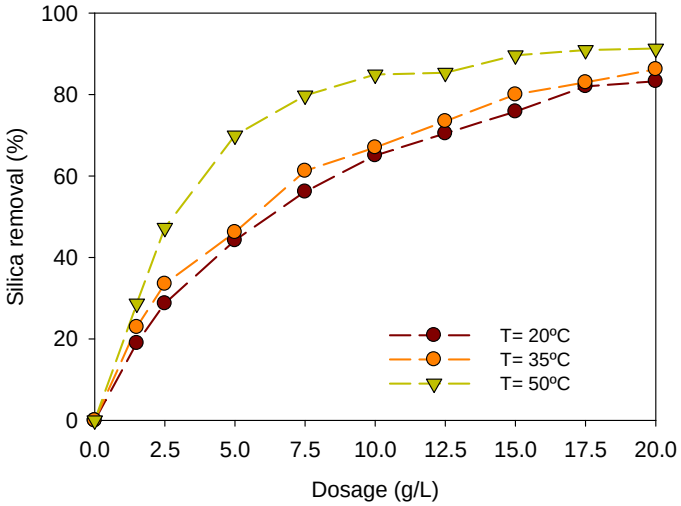

Figure 4.19. *Silica removal vs. activated alumina dosage at different temperatures (unpublished results).*

pH is one of the most important factors at the water-adsorbent interfaces. Therefore, the removal of silica on activated alumina was studied as a function of pH, from pH 5 to 12 (figure 4.20). When pH is controlled during the adsorption process, there was a clear pH range for optimum silica removal, from pH 8 to 10, which fitted well with the initial pH of the raw waters (pH 8.5). The optimum pH found in this study was similar to that found in the only previous work studying silica adsorption onto activated alumina of W. Bouguerra et al. (2007). In this case, maximum adsorption

of silica was achieved in the pH range of 8.0-8.5, using a synthetic wastewater of 50 mg/L. These results indicate that for optimum silica removal it would not be necessary a previous pH adjustment of the wastewater, which means a reduction of treatment costs and no conductivity increase in the treated waters.

At basic pHs, the silica is transformed to negative ionic forms which are more suitable to be removed by coagulation and co-precipitation. Since the point of zero charge for different types of alumina is around 8.7-9.0 (Bouguerra et al. 2007), the surface of activated alumina is positively charged at pHs lower than pH of zero charge. The anionic species would therefore stronger interact with activated alumina and produce a higher silica removal. The decrease in silica adsorption at high pHs could be explained by several reasons. Bouguerra et al. (2007) suggested that this decrease was caused by the electrostatic repulsion between adsorbent and adsorbate resulting from the generation of negative surface sites at these pHs. On the other hand, Bond et al. (2007) argued that the lower adsorption of silica at high pH was due to the competition of hydroxyl ions for anion adsorption sites of the activated alumina.

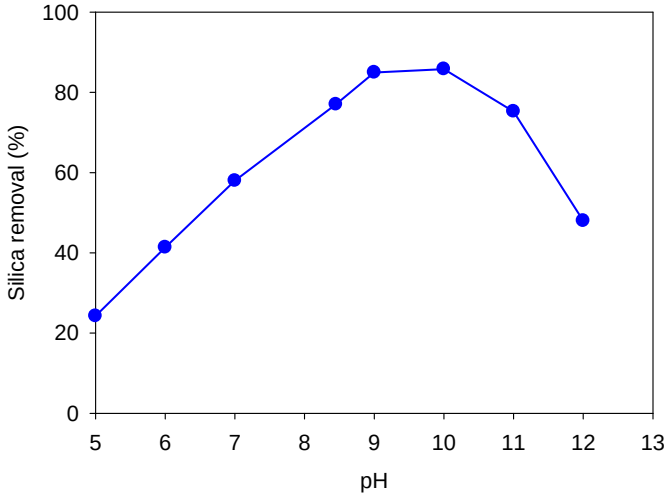

Figure 4.20. *Silica removal with activated alumina vs. pH (10 g/L, 20 ºC) (unpublished results).*

Results obtained indicate that adsorption with activated alumina is feasible to remove high silica concentration. However, the dosage required is relatively high. Optimum conditions are around 7.5-15 g/L without pH adjustment (initial pH around 8.5), the higher dosage when the treatment is carried out close to ambient temperature (20ºC) and the lower dosage when the treatment is carried out at 50 ºC. At these conditions, the removal of silica was around 80-90% (< 50 mg/L SiO_2) in the treated waters, which would be enough for effluent reuse at reasonable recovery rates in RO membranes or its direct discharge in the countries with more severe legislation on silica content in the effluents (50 mg/L SiO_2).

A kinetic study was also carried out, which shows that silica adsorption following a second order reaction. The kinetics was very rapid, with 1 h being time enough to achieve 80-90% of equilibrium silica adsorption.

4.3.2. Silica removal with hydrotalcite

Silica removal efficiency of hydrotalcite (HT) and calcined hydrotalcite (HCT) (450ºC, 4h) was studied (table 3.10). Based on the results obtained, silica removal was optimized in terms of dosage, pH and temperature, including both equilibrium and kinetic studies. Moreover, regeneration studies were also carried out.

HT and HTC were tested at dosages from 0.75 to 40 g/L at 20ºC and without pH regulation. Based on the results obtained, HTC was studied in detail. HTC was tested at eight pHs from pH 5 to 12. For the optimization of the operational pH two sets of experiments were carried out. In the first, the pH was adjusted at before the addition of HTC. In the second, the pH was maintained constant (± 0.2 pH units) by the continuous addition of 0.1 M HCl or 0.1 M NaOH solutions. HTC was also tested at three different temperatures (20, 35 and 50ºC). According to preliminary tests, the reaction time was fixed to 2 h. Methodology followed is shown in figure 3.5. and the kinetic study was carried out following the procedure described in section 3.2.3.

As it can be seen from figure 4.21, the efficiency of HTC is much higher than that of HT. With HTC, silica removal increased rapidly with the dosage, reaching an equilibrium value beyond which there was a negligible change in silica removal. From dosages of 5 g/L is possible to obtain removals higher than 95%. In contrast, the efficiency of HT is considerably lower, i.e. around 10% at 5 g/L dosage. Although silica removal continuously increased with the dosage, efficiencies higher than 50% were never obtained even using extremely high dosages (40 g/L).

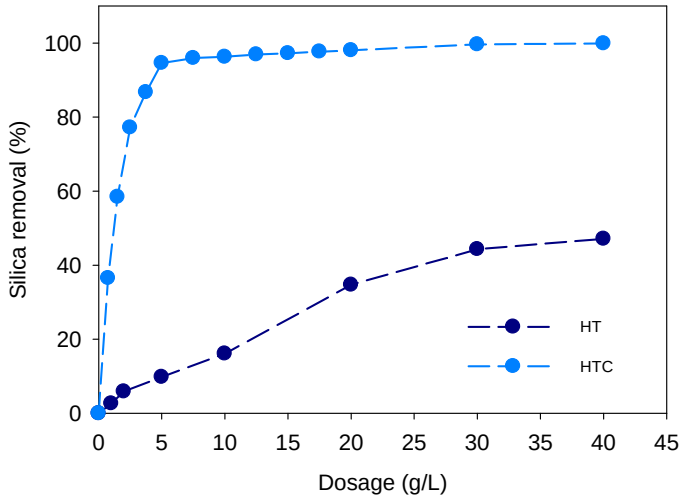

Figure 4.21. Silica removal vs. HT and HTC dosage *(unpublished results).*

HTC was found to be a suitable adsorbent for the removal of silica from water. The adsorption was only slightly affected by pH when the regulation is carried at before adding HTC. A maximum 90% SiO_2 removal could be achieved at pH 8.0-8.5.

Kinetic and equilibrium experiments were conducted at 20ºC, 35ºC and 50 ºC. The maximum adsorption capacity did not varied significantly with the temperature. The regression analysis of equilibrium data indicated that the Langmuir model fit better than Freundlich model. This suggests that the adsorption process is a monolayer sorption onto a surface with a finite number of identical sites. Furthermore, the adsorption processes followed the second order kinetics.

With all these data, optimum conditions for silica removal (80-90% removal) were around 2.5 g/L at 20ºC without any pH adjustment (initial pH around 8.5). Under these conditions, the adsorption kinetics was fast achieving 80-90% of equilibrium silica adsorption after 2 h (figure 4.22).

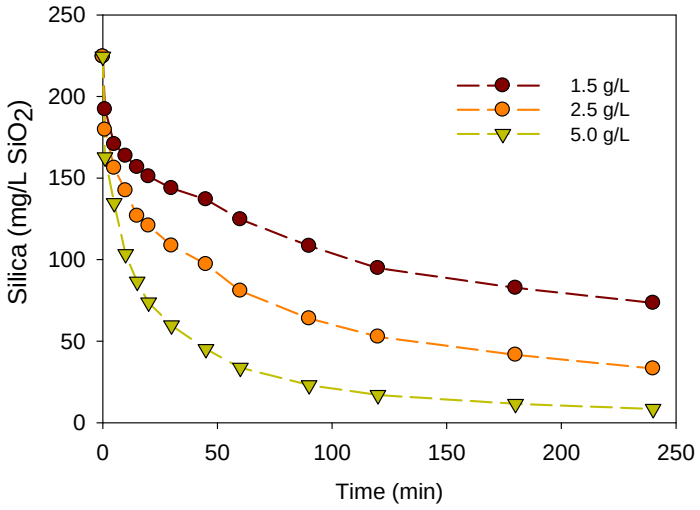

Figure 4.22 .*Silica concentration vs. time at 20ºC and different HTC dosages (unpublished results).*

Regarding the regeneration of HTC, several strategies were tested: a) desorption with saline and alkaline solutions (NaOH, Na_2CO3 and NaCl), b) regeneration by calcination at 450 ºC during 3 h, and c) a combination of desorption (NaOH and NaCl) and regeneration (450 ºC, 3h). Results obtained indicates that at least four regeneration cycles are possible with only small losses in its efficiency. In fact, after these four regeneration cycles, the accumulated q (mg/g) through the cycles reached 300 mg/g SiO_2, which represents a great achievement.

5. CONCLUSIONS

The work carried out in this doctoral thesis has generated new knowledge on the mechanisms and applicability of different silica removal techniques for treating wastewaters of high silica and low hardness contents. Specifically, the thesis has focused on making technically and economically feasible the effluent reuse in deinking paper mills by removing silica to avoid scaling in RO membranes at regular recoveries of 60-80%. However, the results obtained are also of interest for other different types of wastewaters.

The main findings for silica removal obtained by the different techniques are the following:

Coagulation

- Conventional aluminium coagulants (alum, PACls) are able to achieve high silica removal rates (>80%) but only at high pH (10.5) and dosages (2500 mg/L), which is translated into a high conductivity increase in the treated water and high costs.
- Hybrid aluminum-based coagulants (based on PANS) are able to achieve reasonable silica removal efficiencies avoiding the need of a previous pH adjustment of the waters and with a lower conductivity increase after the treatment. PA modification of a polyaluminum salt (PANS-PA2) is the most efficient one. It is able to remove 97% silica removal at the optimal conditions (2500 mg/L, pH 10.5), and it is still very efficient (76% silica removal) without pH adjustment, which means an important cost reduction and the minimization of the conductivity and pH increase of the treated waters. Furthermore, a significant COD removal (≈25%) is obtained. A 5% content of PA in the hybrids is the optimum. Coagulation with hybrid coagulants is, however, an expensive treatment. Although PAM hybrids and PDADMAC hybrids were also tested, they are not as efficient as PA hybrids.
- Chitosan and chitosan derivatives are not efficient in removing silica (<10%).
- Regarding the flocculation mechanisms, PANS primary flocculation mechanism is sweep flocculation due to the high dosages and pHs required. PA hybrid coagulants develop a combination of sweep flocculation (due to PANS) and patches formation, which evolves to a partial interparticles bridges formation at high pHs. PAM hybrids behavior is based on a combination of sweep flocculation and interparticles bridges formation, independently of the pH tested.
- Silica removal on the process waters is preferred to that in the effluent as the coagulant demand without pH regulation (mg/L coagulant per mg/L silica removed) is 20-50% lower, especially in DAF2. This is justified by the high amount of suspended solids and their smaller size, which act as nuclei and promotes the precipitation rate of $Al(OH)_3$.

Precipitative softening

- High silica removal rates (80-90%) can be achieved adding soluble magnesium salts such as $MgCl_2 \cdot 6H_2O$ and $MgSO_4 \cdot 7H_2O$ at high pH (11.5) with dosages of 1500 mg/L at ambient temperature and 15 min contact time. This high pH level needed is directly translated into an important increase in the conductivity of the waters. However, this problem could be partially solved with the use of $Ca(OH)_2$ instead of NaOH as pH regulator.
- Sparingly soluble magnesium compounds are not effective at ambient temperature and 15 min contact time (20-40% silica removal) but obtain similar efficiencies (≈80%) to soluble

magnesium compounds after pre-acidification, while the conductivity is slightly lower than using soluble magnesium salts.

- Dissolution kinetics of sparingly soluble magnesium compounds can be enhanced at higher temperatures avoiding the need of pre-acidification. At T>35ºC dissolution kinetics are fast enough to achieve high silica removal rates (>90%) at reasonable contact times (90 min). Silica removals higher than 95% can be obtained with 500 mg/L of MgO even without pH regulation, minimizing the conductivity increase after the treatment to less than 0.5 mS/cm.
- SEM-EDX and FTIR analysis of the solids obtained confirms that silica is removed through the formation of magnesium silicates. The EDX analysis showed that, independently of the operational conditions, the atomic Si/Mg ratio is around 0.69 which may indicate that the precipitated species is mainly antigorite.

Adsorption

- Results obtained indicate that adsorption with activated alumina and calcined hydrotalcite are feasible to remove high silica concentrations as those typically found in deinking paper mill effluents at ambient temperature and low contact times (1-2 h). Additional advantages of these treatments are that pH adjustment is not required, the small increase in conductivity and a significant decrease of soluble COD.
- High silica removal rates (80-90%) can be obtained with using activated alumina, however the required dosages are considerably higher compared to calcined hydrotalcites. Optimum conditions are around 7.5-15 g/L and the equilibrium adsorption is q=25-35 mg/g, depending on the temperature.
- With calcined hydrotalcites, similar silica removal rates are obtained (80-90%) but with significantly lower dosages (around 2.5 g/L). In this case, the equilibrium adsorption is around q=100 mg/g.
- As the results obtained with calcined hydrotalcites are very promising, regeneration studies were also carried out. A minimum of four cycles of adsorption - desorption – regeneration are possible without significant decrease of silica adsorption, thus increasing the equilibrium adsorption after 4 cycles of use to q = 300 mg/g. Optimum conditions for regeneration are: desorption of silica with 5% NaOH and 10% NaCl and next calcination at 450 ºC during 4 h.

Table 5.1 summarizes the best silica removal conditions for the different approaches followed for the treatment of a newsprint mill effluent with high silica content (150-250 mg/L) and low magnesium hardness (2-7 mg/L). These treatments are able to achieve >90% silica removal, thus allowing the effluent reuse by membrane technologies at reasonable recoveries without scaling problems.

Table 5.1.- Characteristics of the treatments to achieve high silica removal rates (90%) for the treatment of waters with high silica (150-200 mg/L) and low hardness (2-7 mg/L) contents.

CRITERION	COAGULATION (Aluminum salts)	SILICA REMOVAL DURING PRECIPITATIVE SOFTENING		ADSORPTION
Additive	Hybrid coagulant (PANS-PA2)	Soluble Mg compounds ($MgCl_2 \cdot 6H_2O$)	Sparingly soluble Mg compounds (MgO)	Calcined hydrotalcite (HTC)
Minimum temperature	Ambient temperature	Ambient temperature	≥ 35ºC	Ambient temperature
pH	10.5	11.5	8.5	8.5
Dosage	2500 mg/L	1500 mg/L	500 mg/L	2500 mg/L
COD removal	↑↑	↑	↑	↑↑
Final conductivity	↑↑	↑↑↑	↑	↑
Sludge generation	↑↑	↑↑↑	↑↑	↑
Cost	↑↑↑	↑↑	↑	↑↑

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Silica removal from newsprint mill effluents with aluminum salts

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HIGHLIGHTS

- Silica coagulation is necessary for the viability of RO treatments in paper mills.
- Silica removal is favored at high pH and dosages, the drawback is the conductivity increase.
- Polyamine modification of a polyaluminum salt is the most efficient coagulant.
- PANS-PA2 is able to reduce 97% silica concentration at pH 10.5 and 2500 ppm.
- Even without pH regulation, a 76% silica removal is obtained with PANS-PA2.

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ABSTRACT

The main obstacle for the implementation of reverse osmosis (RO) in a treatment chain to reuse the effluent of a newsprint mill as fresh water is the high silica content of the water, which produces severe scaling on the membrane, thus, limiting its recovery. Coagulation is one of the preferred methods to reduce silica concentration. Five aluminum based coagulants have been tested at five dosages (500–2500 ppm) and three pHs (8.3, 9.5 and 10.5). All products showed their best efficiency at the highest dosage and pH, with the exception of alum, that was more efficient at intermediate dosages. A combination of a polyaluminum nitrate sulfate with a cationic quaternary polyamine (PANS-PA2), was the most efficient and versatile coagulant. It removed 97% of silica (5 ppm residual silica) at the optimal conditions (pH 10.5, 2500 ppm) and it was very efficient (76% silica removal) at pH 8.3, avoiding the need of any pH adjustment, and minimizing the conductivity and pH increase of the treated waters as well as obtaining some removal of the organic colloidal matter (≈25%).

1. Introduction

Sustainable water use in the paper industry requires the closure of the water system without affecting paper machine runnability and product quality [1], which can be achieved by reusing the mill effluent after its advanced membrane treatment [2] and/or by the use of reclaimed water [3], depending on the availability of alternative water sources.

In deinking paper mills the closure of the internal water circuit is limited by the accumulation of recalcitrant organic colloidal matter that alters the process and the paper quality [1]. On the other hand, the reuse of the final effluent is limited by the reverse osmosis (RO) membrane fouling caused by silica. Thus, causing a decline in water production rates, low permeate quality, unsteady-state operation conditions, higher energy consumption and serious damages on the membranes that shorten their lifetime, by doing so compromising the technical and economic feasibility of the whole treatment chain. If silica is not removed the RO recovery is of only around 20% [2].

The main source of silica in deinking paper mills is sodium silicate, used as process additive. It has a variety of functions within the process. In the pulping stage, sodium silicate enhances ink dispersion and facilitates its removal by flotation. In the bleaching process, sodium silicate acts as a peroxide stabilizer by chelation of transition metals and a pH buffer, it controls corrosion and is a surface active agent. Although some attempts have been carried out to reduce the use of sodium silicate during deinking [4], it is still a necessary additive.

Silica can be found in crystalline and amorphous forms, being the first one more stable than the second. The difference of solubility is 6 ppm (as SiO_2) for crystalline silica vs. 100–140 ppm (as SiO_2) for amorphous silica, both at 25 °C [5]. Solubility depends on many factors such as pH or the presence of organic and inorganic matter. The solubility of silica polymorphs, both crystalline and amorphous, is essentially constant between pH 2 and 8.5, but increases rapidly from pH 9 onwards [6]. On the other hand, silica solubility is highly affected by temperature, increasing from

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100 to 140 ppm at ambient temperature up to 300 ppm at 70 °C [7].

There are different methods to control silica scaling, which can be grouped in preventive, corrective and cleaning. Prevention and correction of scaling are those preferred as it is very difficult to clean silica deposits. Preventive methods interact and modify silica so as not to allow it to deposit on membranes but they do not remove it. The use of antiscalants is probably the most common method [8,9], although their efficiency in highly contaminant waters is low. Besides, when treated water is reused in other process stages, as the process conditions can change significantly, scaling problems could appear once again. Regarding corrective methods, there are many silica removal techniques proposed in the literature, but these are usually carried out during softening processes or by coagulation at high pH [10,11]. These techniques enable the treatment of large volumes of water with high removal rates at low costs, which is a prerequisite for its use in papermaking applications.

When silica removal is carried out during a softening process it is necessary to ensure that there is enough hardness present in the water, especially magnesium hardness. On the other hand, several studies have been carried out with traditional coagulants such as alum, or ferric chloride, to treat pulp and paper mill effluents [12]. In this case, coagulation with alum has been proved to be more effective for silica removal than ferric chloride. Coagulation and ultrafiltration (UF) have been also successfully used in brackish water RO treatment to avoid silica problems [13,14]. Alum, ferric chloride and sodium aluminate were also studied to improve silica removal rate in a lime-soda ash process with brackish water [15].

Polyaluminum chlorides are effective at low temperatures in a wider range of pHs, they generate compact flocs easily sedimentable, they are less likely to cause overdosage phenomena and they are less sensitive to water properties fluctuations [16,17]. As chlorides can cause corrosion problems, sometimes they are partially substituted by other species such as sulfates or nitrates, providing a new range of products: polyaluminum nitrates, polyaluminum sulfates or a combination of them, such as polyaluminum nitrate sulfate. The main differences between these products are their basicity, strength and the content of other species such as silica, calcium or even organic compounds [18–20]. Although the silica removal mechanism of polyaluminum coagulants is not well understood [17,21], there is a consensus in that they act by two primary coagulation mechanisms [18,22]: (1) charge neutralization of the negative particles by adsorption of positively charged dissolved aluminum species, and (2) enmeshment of particles in precipitated $Al(OH)_3$.

Previous studies have demonstrated that coagulation with aluminum salts is effective for the treatment of deinked paper mill effluents; however, the required dosages and the conductivity of the treated waters were very high [10]. Therefore, the process was neither economically nor chemically feasible. To avoid these drawbacks, this paper studies the efficiency of new coagulants under several conditions, optimizing the operating pH and the pH regulator. The final objective is to increase RO recovery from 20% to 60–80%, making the effluent reuse process technically and economically feasible.

2. Materials and methods

2.1. Water samples

This research was carried out with the effluent of a Spanish paper mill using 100% recovered paper to produce newsprint. The mill has an integrated wastewater treatment plant consisting of a primary treatment by dissolved air flotation and a secondary treatment based on an aerobic digestion of the waters on a moving bed bioreactor followed by a dissolved air flotation for sludge separation. Water samples were taken before their discharge to an urban waste water treatment plant. Samples were stored at 4 °C for a maximum of 5 days. Table 1 summarizes the effluent characteristics.

Table 1
Characteristics of the paper mill effluent.

Raw water	
pH	8.3
Conductivity (mS/cm)	2.20
COD (ppm)	635
BOD (ppm)	300
Cationic demand (meq/L)	0.50
Total solids (ppm)	1830
Total suspended solids (ppm)	125
Turbidity (NTU)	63
Total alkalinity (ppm $CaCO_3$)	790
Dissolved fraction	
Silica (ppm SiO_2)	140
COD (ppm)	560
Sulfates (ppm)	200
Chlorides (ppm)	161
Calcium (ppm)	55
Magnesium (ppm)	2.7
Turbidity (NTU)	15

2.2. Chemicals

Alum ($Al_2(SO_4)_3{\cdot}18H_2O$) and four polyaluminum-based products were used as coagulants. The polyaluminum-based coagulants were two polyaluminum chlorides and two polyaluminum nitrate sulfates-based products. One of the polyaluminum chlorides has a high basicity (PACl-HB) and was supplied by Kemira Ibérica S.A. (Spain); the other has a medium basicity (PACl-MB) and was supplied by SERTEC-20 S.L. (Spain). The polyaluminum nitrate sulfate-based coagulants, named PANS-PA1 and PANS-PA2, were supplied by Sachtleben Wasserchemie GmbH (Germany). These products are obtained from the blending of a polyaluminum nitrate sulfate (PANS) with increased dosages of a cationic quaternary polyamine (PA), with a 17% charge density. Alum, reagent grade, was supplied by PANREAC. Table 2 summarizes their main characteristics. An anionic polyacrylamide with high molecular weight and medium charge density was used as flocculant aid in all tests (supplied by SERTEC-20 S.L., Spain). Two different pH regulators were used: NaOH and $Ca(OH)_2$, both of analytical grade supplied by PANREAC. Coagulants were prepared at 20 wt%, flocculant at 0.1 wt% and pH regulator at 10 wt% with ultrapure water on a daily basis.

2.3. Methodology for jar-tests

For each coagulant, 5 dosages (from 500 to 2500 ppm) were tested, those selected according to preliminary tests [23]. These dosages were tested at 3 different basic pHs: 8.3 (water initial pH), 9.5 and 10.5, as basic pHs are the most effective for the removal of silica by coagulation [11,24] and pH 10.5 is enough for almost complete removal of silica for this application [23]. First, the best coagulants were selected using NaOH as pH regulator, then, pH regulator was optimized, comparing the efficiency of NaOH and $Ca(OH)_2$.

Fig. 1 summarizes the jar-test methodology followed to study the efficiency of the different coagulation treatments. The comparison between different pH regulators was carried out following the same "jar-test" methodology but, in this case, the study was only

Table 2
Characteristics of the coagulants used in this study.

Coagulant	Chemical family	Formula	Al_2O_3 (%)	Basicity (%)	Dry content (%)	Charge density (meq/g)	pH
PACl-HB	Polyaluminum chloride	$Al_n(OH)_x(Cl)_y$	9.7	85	29.5	1.67	2.7
PACl-MB	Polyaluminum chloride	$Al_n(OH)_x(Cl)_y$	10.0	65	35.0	1.27	2.6
PANS-PA1	Polyaluminum nitrate sulfate	$Al_n(OH)_x(NO_3)_y(SO_4)_z$	8.8	46[a]	21.7	1.68	2.0
PANS-PA2	Polyaluminum nitrate sulfate	$Al_n(OH)_x(NO_3)_y(SO_4)_z$	6.0	46[a]	20.4	2.57	3.0
Alum	Aluminum sulfate	$Al_2(SO_4)_3{\cdot}18H_2O$	15.3	–	–	–	–

[a] Basicity of the polyaluminum nitrate used as base in these products.

focused on the most efficient coagulant according to previous results. Three different dosages (500, 1500 and 2500 ppm) of PANS-PA2 were tested with the two pH regulators and using the same flocculant with the same dosage as before. In addition, sedimentation rates were also considered in the comparison of the pH regulators.

Mixing was carried out in a multiposition magnetic stirrer OVAN MulitMix Heat D. All trials were carried out at room temperature (20 °C ± 2 °C) by duplicate, and the average error between replicates was always under 5%. The pH was measured using a model GLP 22 (Crison, S.A), according to Standard Method 4500 [25], and the conductivity was measured with a model GLP 31 (Crison, S.A.), according to the ISO 7888. Reactive silica was measured by flow analysis and photometric detection through silicamolybdate and reduction to molybdenum blue, using a FIA Compact (MLE GmbH) according to DIN EN ISO 16264 and expressed as ppm of SiO_2. COD was measured according to the Standard Method 5220-D [25]. Cationic demand was measured by colloid tritation with poly-diallyldimethylammonium chloride (PDADMAC) using a CAS Charge Analyzing System supplied by AFG Analytic GmbH to measure the end point. Alkalinity was measured by titration with 0.1 N H_2SO_4 according to EPA 310.1 method. Sulfate content was measured using Nanocolor® sulfates method (Macherey–Nagel GmbH). Calcium and magnesium content were measured using a direct air-acetylene flame atomic absorption method according to ISO-7980:1986. Finally, turbidity was measured with a LP 2000-11 nephelometer, supplied by Hanna Instruments, according to ISO 7027.

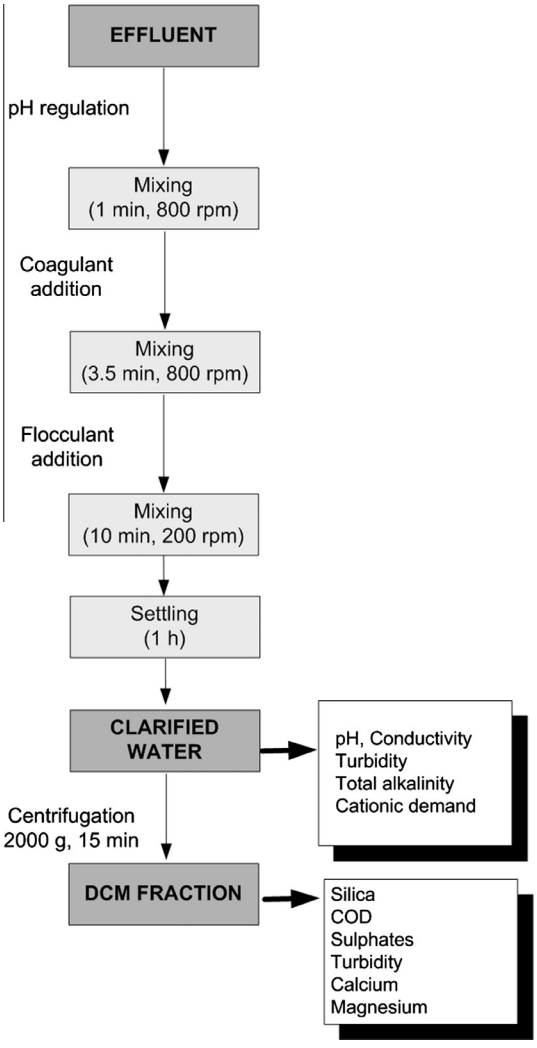

Fig. 1. Jar-test protocol followed to study the efficiency of different coagulants.

2.4. Methodology for monitoring flocculation behavior

The coagulation process was studied using a M500L Focused Beam Reflectance (FBRM) probe manufactured by Lasentec (Mettler Toledo, United States). The device generates a laser beam that is focused on a focal point that describes a circular path at high speed (2000 rpm). When particles cross the trajectory of the focal point, the detector measures the time duration of the backscattered light from this particle. This period of time is proportionally related to the size of the particle intercepted under the focal point. Thousands of chord lengths between 1 μm and 1000 μm, which are the detection limits of the device, are collected per second. From these data, the total number of counts (TNC), counts in a specific size region, mean chord size (MCS) and other statistical parameters can be calculated. The use of FBRM technique to monitor flocculation has been thoroughly described previously by the authors [26,27]. In a typical trial, the probe is submerged into a 100 ml and the stirring speed was fixed at 200 rpm. A continuous addition of coagulant was tested: 200 ppm of coagulant were added each 10 s up to a final dosage of 8000 ppm. Whenever necessary (pH 9.5 and 10.5), pH adjustment was carried out by the addition of NaOH 10 wt.% just after the 30 s stabilization time, the coagulant started to be added after 30 s of adding the caustic soda.

3. Results and discussion

3.1. Selection of pH and coagulant dosage

For all the coagulants but alum, silica was reduced by increasing the coagulant dosage and the pH (Fig. 2). In the case of alum, higher pHs also improved its efficiency but the most efficient dosage was found to be around 500–1000 ppm. Comparing all products, PANS-PA2 was clearly the most efficient. At the highest dosage, silica removal ranged from 73% (pH 8.3) to 78% (pH 9.5) and 97% (pH 10.5), achieving a residual silica of only 5 ppm at the best conditions. One important difference between this product and the others was its efficiency at pH 8.3: a 73% silica removal could be achieved at 2500 ppm, and even with a dosage of 500 ppm, 42% silica removal could be obtained. The other coagulants yielded very similar

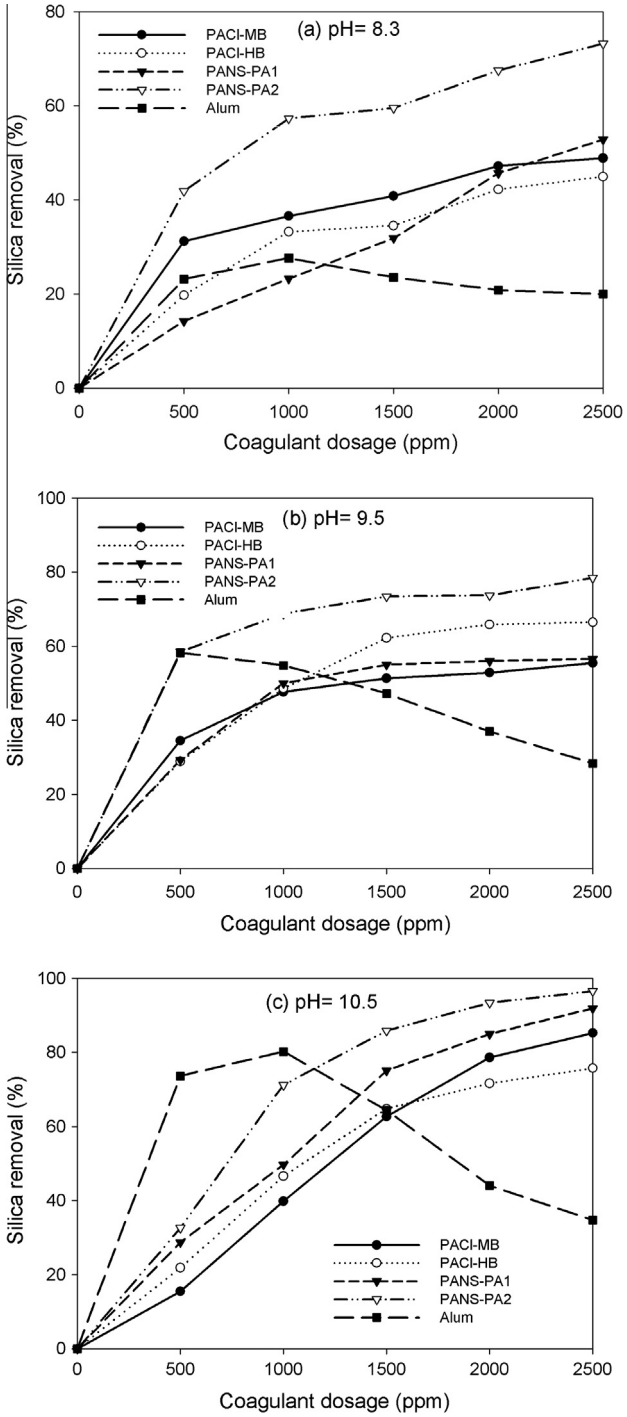

Fig. 2. Silica removal vs. coagulant dosage at different initial pHs: (a) pH = 8.3; (b) pH = 9.5; and (c) pH = 10.5.

efficiencies, with only slight differences related to their different nature, aluminum content and final pH after the treatment (governed by their aluminum content and basicity). PACl-MB removed around 50% silica at the highest dosage and pHs 8.3 and 9.5, and an important increase in efficiency was observed at pH 10.5 (85% removal). The same high increase of efficiency at pH 10.5 was observed with PANS-PA1. In this case, the removal efficiency at 2500 ppm increased from 50% to 55% at pH 8.3 and 9.5 to 92% removal at pH 10.5. Removal efficiencies obtained with the highest dosage of PACl-HB varied largely from pH 8.3 (45% removal) to the highest (72% removal). Finally, the use of alum at the optimal dosages (500–1000 ppm) achieved a 35% removal at pH 8.3, 58% at pH 9.5 and 73% at pH 10.5. Although the removal efficiencies of alum can be higher than those of PANS-PA2 at pH 10.5, only with PANS-PA2 high efficiencies can be achieved without any pH adjustment. Probably because of its high charge density and the effect of the quaternary polyamine added to the polyaluminum salt, which is efficient even at pH 8.3. However, the dosage of polyamine in the coagulant must be high enough, as in the case of PANS-PA2, because at lower dosages of polyamine (PANS-PA1), only 53% removal was achieved at initial pH. The dosage of polyamine in PANS-PA2 was around three times higher than in PANS-PA1. On the other hand, the high efficiency of alum could be related to its high aluminum content, around 2.5 times higher than the coagulant with the lowest aluminum content (PANS-PA2). The explanation for why its efficiency was decreased at higher dosages than 1000 ppm is a combination of two factors, its high aluminum content and the 0% basicity of the product, which caused the highest alkalinity consumption and an important pH decrease, making the formation of the active species of the aluminum salts difficult. In summary, PANS-PA2 and alum were found to be the most promising treatment options.

Although the most critical parameter in this application was silica removal, COD removal has to be considered as well since it contributes to the organic fouling of the membranes. First, it is important to note COD removal followed just the opposite trend to silica removal: it was higher at lowest pH (8.3) than at the highest pHs (pH 9.5 and 10.5) (Fig. 3). This fact can be explained by the competition between silica and the organic matter (mainly anionic) for the neutralizing capacity of the coagulant. This reverse relationship has also been described by Hermosilla et al. [10]. Higher dosages of the coagulants were always more efficient in COD removal, however, the effect of high dosages on COD removal was more evident at pH 8.3 and 9.5, while at pH 10.5 it was less significant. In general, the effect of dosage on COD removal was higher at the lowest dosages of the coagulant and remained almost constant at the highest (1500–2500 ppm).

PANS-PA1 was the most efficient product in COD removal, independently of pH and dosage. At pH 8.3, the maximum COD removal was obtained (39%), and the removal decreased to 30% at pH 9.5 and to 18% at pH 10.5. Alum was the second most efficient product removing COD, with very similar efficiency than PANS-PA1 at the highest dosages, but slightly lower efficiency at the lowest dosages. Maximum removal rates with alum were 36%, 32% and 20% at pH 8.3, pH 9.5 and pH 10.5, respectively. PACl-MB and PACl-HB were the least efficient products removing COD: at pH 8.3 the highest removals were 25–27%, and at pH 10.5, were 8%. PANS-PA2 showed an intermediate efficiency, its removal efficiency varying from 27% at pH 8.3 to 23% at pH 9.5 and 11% at pH 10.5. Although there was an inverse trend in the removal efficiencies of silica and COD, PANS-PA2 was able to maintain an intermediate COD removal while being the most efficient product in silica removal.

Another important parameter in coagulation processes is the water cationic demand. The neutralization capacity of the different aluminum-based products is mainly governed by the charge density of the products, which varies depending on the characteristics of the water (pH, conductivity, cationic demand, etc.). The initial cationic demand of water samples is higher at higher initial pHs because of the higher content of hydroxide ions and, in a lower extent, due to the ionization of species such as carboxylic or fatty acids.

PANS-PA2 is the coagulant with the highest charge density and the most efficient product reducing the cationic demand of waters. At the three studied pHs, the highest dosages (2000–2500 ppm) achieved complete neutralization of waters. Alum and PANS-PA1 obtained very similar neutralization efficiencies. Alum achieved complete neutralization at 2000–2500 ppm dosages at pH 8.3,

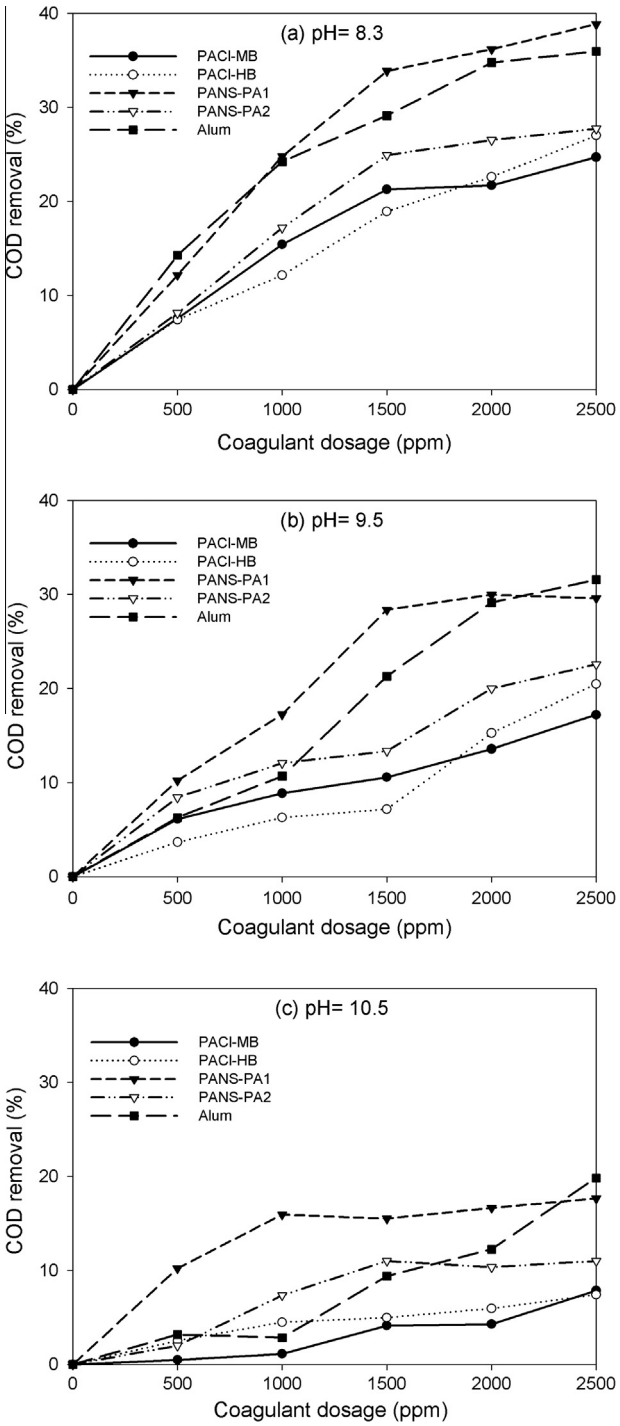

Fig. 3. COD removal vs. coagulant dosage at different initial pHs: (a) pH = 8.3; (b) pH = 9.5; and (c) pH = 10.5.

almost neutralization at pH 9.5 and 2500 ppm (0.02 meq/L), and an important decrease at pH 10.5 and 2500 ppm (0.14 meq/L). On the other hand, PANS-PA1 obtained almost complete neutralization at pH 8.3 and 9.5 (0.03 meq/L) and 0.34 meq/L at pH 10.5 and 2500 ppm dosage. Finally, PACl-MB and PACl-HB had similar efficiencies. At pH 8.3, 9.5 and 10.5 and 2500 ppm dosage, PACl-MB reduced, respectively, the cationic demand to 0.12, 0.19 and 0.41 meq/L; and PACl-HB to 0.21, 0.30 and 0.48 meq/L.

Although the reduction in cationic demand is beneficial for the removal of contaminants by coagulation, its effect must be addressed together with the main flocculation mechanisms involved. If the removal of contaminants takes place by charge neutralization, the maximum removal rate is close to the isoelectrical point and overdose is possible (restabilization occurs at charge reversal). However, with high dosages of aluminum salts, the main flocculation mechanism can be "sweep flocculation", where the contaminants are removed by enmeshment in the fresh precipitated flocs of $Al(OH)_3$. In this case, optimum dosage of coagulant does not occur at the isoelectric point and there will not be overdose phenomena although reaching charge reversal [17]. It is very interesting to notice that although higher cationic demand removals are beneficial to obtain higher removal efficiencies, a direct relationship between silica removal and cationic demand does not occur in all the cases. In some of them, reverse charge occurred, but silica removal efficiency even increased in these conditions. Therefore, flocculation by sweep flocculation predominates.

Aluminum reacts with hydroxyl groups to form different aluminum hydroxides, which are the active species in coagulation. The required alkalinity in the media is directly related to the dosage, aluminum content and basicity of the coagulants [28]. The results show that all coagulants had the same tendency. Alkalinity of the water decreased with the coagulant dosage and increased at higher initial pHs due to pH adjustment. Alkalinity of the treated waters was similar for all products but alum. At the highest dosage (2500 ppm), the final alkalinity was around 500 ppm $CaCO_3$ at pH 8.3, 600 ppm $CaCO_3$ at pH 9.5 and 750 ppm $CaCO_3$ at pH 10.5. The consumption of alkalinity for 2500 ppm dosage was around 300 ppm $CaCO_3$ at pH 8.3, 350 ppm $CaCO_3$ at pH 9.5 and 550 ppm $CaCO_3$ at pH 10.5. The highest decrease in alkalinity was in parallel with a higher silica removal at the highest pHs, especially at pH 10.5. Another factor influencing alkalinity consumption is the precipitation of calcium carbonate. For all the coagulants but alum, calcium in the treated waters remained in the 45–55 ppm range at pH 8.3 and 9.5 and decreased to around 10 ppm at pH 10.5, which is in agreement with the highest consumption of alkalinity at this pH 10.5 due to calcium carbonate precipitation. On the other hand, alum caused the highest alkalinity consumption. At 2500 ppm dosage, alkalinity of the treated waters was 0 ppm $CaCO_3$ at initial pH, 30 ppm $CaCO_3$ at pH 9.5 and 300 ppm $CaCO_3$ at pH 10.5. This is explained because this product was the one with the highest aluminum content and the lowest basicity (0%); therefore, alum was the product consuming more alkalinity from waters and, as described next, the one causing the highest pH decrease after the treatment.

To avoid any pH "shock" when mixing the tested water with process waters which could cause scaling phenomena and organic deposit formation, the treated waters must have a pH of 7.5 ± 1.0. Besides, according to the discharge limits of the newsprint mill, the RO rejects should have a pH between 6.5 and 9.5 to avoid the need of a final pH-adjustment. Final pH was determined by two factors: the pH adjustment before coagulation and the pH decrease caused by the alkalinity consumption of the coagulants.

PANS-PA2 was the product least affecting the pH of treated waters, while alum was the one causing the highest pH decrease, due to its highest aluminum content and lowest basicity. Without pH adjustment (pH 8.3) at the highest dosage (2500 ppm), pH of treated waters with PANS-PA2 decreased from 8.3 to 8.2, while in the case of alum, decreased to 4.3. The other three coagulants showed a similar trend, decreasing the pH from 8.3 to around 7.4. Their differences in aluminum content and basicity were not so large to observe important differences among them. When initial pH of waters was adjusted to pH 9.5 and using 2500 ppm dosage, the final pH of the water was in the range 7.7–8.3 for all the products but alum (pH 4.6). At initial pH 10.5 and 2500 ppm dosage, the final pH of treated waters was around 9.3–9.4 for all the coagulants but alum (pH 6.9).

The conductivity of the treated waters is also important as it affects the performance of RO membranes and the need to treat the RO rejects, which is a determinant factor in the economic feasibility of the full treatment chain. As regular recoveries in RO systems for this application are usually in the 60–80% range, the conductivity of RO rejects will be from 2 to 4 times higher than the inlet to the RO membranes. The boundary condition in this case is that it cannot exceed 7.5 mS/cm which is the limit for direct effluent discharge to the sewage system without post-treatment.

Conductivity of the treated waters was always higher than before the treatment, being the initial pH adjustment and the nature and dosage of the coagulants the two most determining effects. The increase in conductivity caused by the pH regulation was around 0.19 mS/cm to achieve pH 9.5 and 0.41 mS/cm for pH 10.5. In these studies, caustic soda was the pH regulator. The coagulation treatment also affects the conductivity of the waters, therefore, some differences were observed depending on the coagulant used. At the three pHs tested, alum was the product causing a higher increase in the conductivity of the waters, between 0.4 and 0.6 mS/cm at 2500 ppm dosage (excluding conductivity increase by pH adjustment). With PACl-MB and PACl-HB, this increase was 0.3–0.5 mS/cm. On the other hand, PANS-PA1 and PANS-PA2 are the coagulants causing the smallest increases in the conductivity (around 0.2 mS/cm for both products).

Apart from the problems caused by the high pH decrease and conductivity increase when the waters were treated with alum, the increase in sulfates content was also a factor to be considered. In this case, high sulfate concentration can cause calcium sulfate scaling on the RO membranes; in addition, sulfate content is limited to 1000 ppm for direct discharge of the RO rejects without any pre-treatment. Although PANS-PA1 and PANS-PA2 have sulfates in their composition a very small increase of sulfates was observed in the treated waters (from 200 to 230–250 depending on the initial pH). However, when alum was used, the concentration of sulfates increased up to 1050–1150 ppm. These levels cause scaling phenomena in RO membranes.

Finally, the turbidity of the waters decreased from 63 NTU (raw water) to 9 NTU (86% removal) with all the products at the three pHs at the maximum dosage. On the other hand, the dissolved turbidity of the waters was reduced from 15 NTU (raw water) to 3 NTU (80% removal). The same 3 NTU could be achieved with alum, however only at the optimal dosage of 1000–1500 ppm. At higher dosages than those, the turbidity increased up to 35 NTU (at 2500 ppm).

3.2. Selection of the best pH regulator

To improve the coagulation process, the convenience of using lime instead of caustic soda as pH regulator was studied. The main advantages of lime are that it is cheaper and could help to reduce the conductivity of the treated waters (as it is a sparingly soluble salt). Both pH regulators were tested in the same conditions: three different dosages (500, 1500 and 2500 ppm) of the most efficient coagulant (PANS-PA2) and two pHs as previously tested (pH 9.5 and 10.5). First of all, the dosages required for pH adjustment were determined. To achieve pH 9.5 140 ppm NaOH or 312 ppm $Ca(OH)_2$

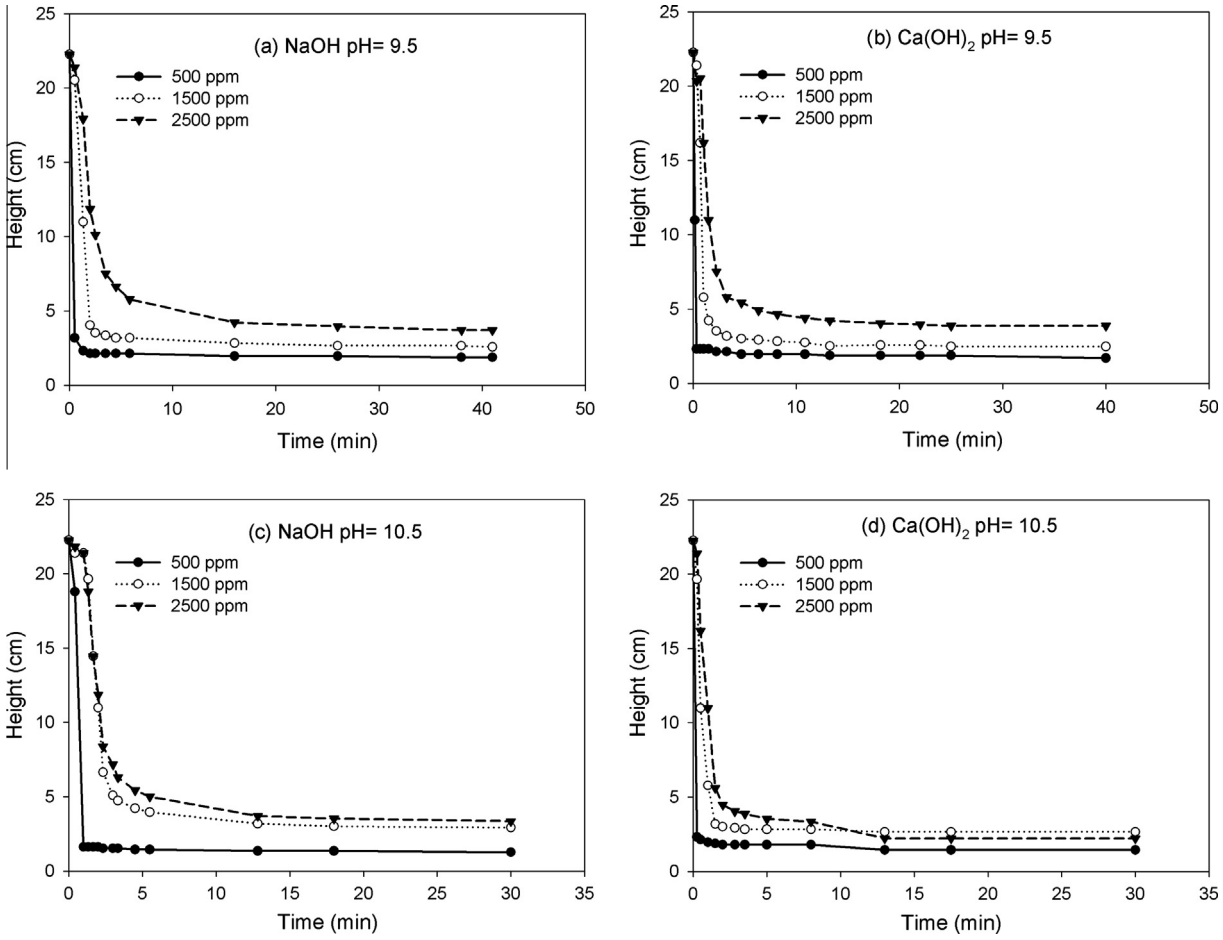

Fig. 4. Sedimentation rates at pH 9.5 and 10.5, with NaOH and $Ca(OH)_2$ and different dosages of PANS-PA2. (a) NaOH, pH = 9.5; (b) $Ca(OH)_2$, pH = 9.5; (c) NaOH, pH = 10.5; and (d) $Ca(OH)_2$, pH = 10.5.

were necessary, while to achieve pH 10.5, 460 ppm NaOH or 800 ppm $Ca(OH)_2$ were required.

First, it was tested if silica removal was affected by the pH regulator used. It was concluded that silica removal was not significantly affected and the differences between them were always within the experimental error of SiO_2 measurements. However, conductivity of the treated waters was higher when caustic soda was used instead of lime. At pH 9.5, the conductivities of treated waters were 2.5–2.8 mS/cm and 2.1–2.7 mS/cm for caustic soda and lime, respectively. These conductivities vary depending on the dosage of coagulant. At pH 10.5, when the dosage of pH regulator is higher, the differences are even higher: final conductivity of 3.0–3.2 mS/cm with caustic soda compared to 2.0–2.1 mS/cm with lime.

Although the use of lime can increase the turbidity of the waters, this effect was not relevant in these tests, presenting very similar turbidities with both pH regulators. This is probably due to the flocculant addition after pH adjustment and coagulation. Regarding COD removal, there were minor differences at pH 9.5; however, these differences became larger at pH 10.5: 23% COD removal with lime compared to 13% removal when caustic soda was used.

Another important factor to consider is the effect of the pH regulator on sedimentation rates. At initial pH 9.5, sedimentation rates (Fig. 4a and b) with lime were higher than in the case of caustic soda, especially in the first minutes. After that, sedimentation rate decreased and remained practically constant. The final height of the flocs was very similar for both pH regulators. The higher the coagulant dosage used, the lower sedimentation rate, as the production of flocs is higher and the settling is impeded. For 500 and 1500 ppm dosages, most of the sedimentation occurred during the first 5 min for both pH regulators. At 2500 ppm dosage, most of the sedimentation process took place in the first 10 min in the case of lime, whereas it took another 5 min in the cause of causticsoda.

At pH 10.5 (Fig. 4c and d), the differences in sedimentation rates became more evident. Sedimentation with lime was faster than with caustic soda: the sedimentation is almost finished in 5 min with lime but around 10 min in the case of caustic soda. Compared to the sedimentation rates obtained at pH 9.5, the sedimentation rates at pH 10.5 were faster as the lime flocs are heavier.

3.3. Flocculation monitoring by FBRM

The sequential additions of coagulant showed that at initial pH all products but alum decreased the total number of counts (TNC) at increasing coagulant dosages (Fig. 5) which is in agreement with a regular flocculation process where a number of particles are aggregated in larger flocs. PANS-PA2 was the product with the highest decrease in the TNC. On the other hand, alum showed an important increase (220%) in the TNC with around 2700 ppm of coagulant that coincides with a decrease in the mean chord size (MCS) as explained below. After that, TNC decreased to approximately initial counts range. Although all products but alum showed a decrease in the TNC, the extent of this decrease and the coagulant dosage at which the minimum was reached was different, depending on the tested coagulant and the pH. Regarding MCS coagulants showed also three different behaviors. PACl-MB, PACl-HB and PANS-PA1 showed an increase in the MCS smaller than 20%. These products also showed intermediate silica removal rates. PANS-PA2 was the product with the highest increase of 70% in the MCS and it was also the product with the highest silica removal rate. This maximum MCS was achieved with around 2500 ppm of coagulant that was in accordance with the maximum removal of silica obtained. On the other hand, alum was the only product that caused a decrease of 20% in the MCS.

At pH 9.5 all products showed the same tendency as at initial pH (Fig. 6). At this pH PANS-PA2 caused again the highest decrease in the TNC and consequently the highest increase in the MCS. For these four products, the decrease in the TNC appeared at higher coagulant dosages, around 2000 ppm, than at pH 8.3, because there was more alkalinity of the water at this pH. For that reason higher coagulant dosages could be added to the water without reaching charge reversal. The behavior of alum was the same than at pH 8.3. First, TNC decreased, then it increased with the coagulant dosage, but in this case, the maximum increment TCS achieved was 180%. That value was smaller than at initial pH and it was achieved with a higher dosage of coagulant (3800 ppm) (Fig. 8). Regarding MCS evolution, PANS-PA2 is again the one with the maximum increase in the particle size, but the differences with PACl-HB, PACl-MB and PANS-PA1 were smaller than at pH 8.3. At pH 9.5 these three products showed high silica removal rates and the differences with PANS-PA2, the most efficient product, became smaller. Again alum was the only product that caused a decrease in the MCS (around 25%). In this case, the decrease in MCS occurred at higher dosages higher (2400 ppm) than at initial pH 8.3 (around 1000 ppm).

At pH 10.5, there were differences in TNC compared with initial pH and 9.5 (Fig. 7). With all products TNC decreased up to a minimum value and then increased. PANS-PA2 showed the minimum value in the TNC with a dosage of 2300 ppm. With PACl-MB, PACl-HB and PANS-PA1 there was also a minimum in the TNC that appeared around 2000–2500 ppm. In the case of alum, TNC showed almost the same tendency as at the other pHs, TNC decreased 30% with 1700 ppm of alum and remained constants for a longer period of time than with the other two pHs. Then the TNC increased up to 30%. Regarding MCS evolution all products

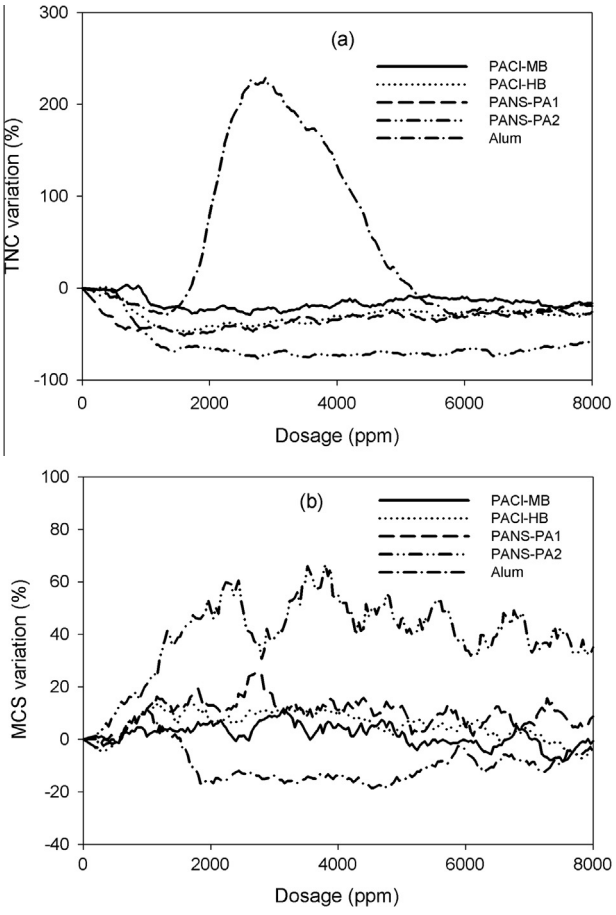

Fig. 5. TNC (a) and MCS (b) variation at pH = 8.3.

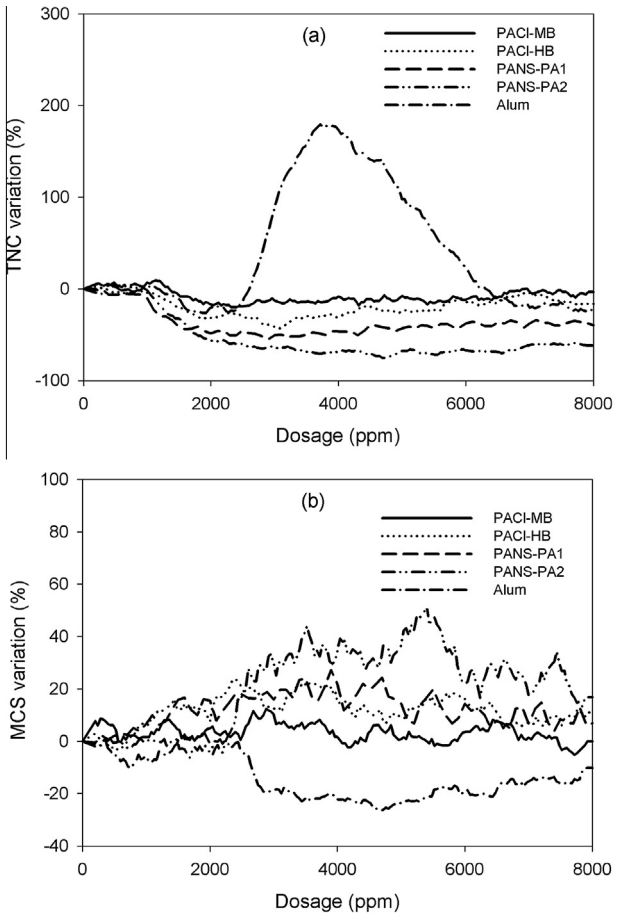

Fig. 6. TNC (a) and MCS (b) variation at pH = 9.5.

but alum showed similar tendencies. At this pH the increase in the MCS obtained with PANS-PA2 was smaller than the one obtained at pH 8.3 and 9.5 and was closer to the ones obtained with the rest of the products but alum. This fact is also in agreement with the differences on silica removal rates which became also smaller compared with pH 8.3 and 9.5. With alum, MCS started to decrease at a dosage of 4800 ppm.

As alum showed a totally different trend, its behavior will be explained in more detail. At the three pHs tested there was a maximum in TNC curve (Fig. 8). This maximum appeared when the pH of the water was around 4. As commented before, alum is the coagulant with both the highest aluminum content and lowest basicity and, consequently, the product with the highest alkalinity consumption. Even at the tested dosages in jar-tests (up to 2500 ppm) at initial pH = 8.3 final alkalinity was zero and almost zero at pH = 9.5. At high dosages of alum sweep flocculation occurred increasing the TNC as $Al(OH)_3$ precipitates. After that, when pH decreased to around 4.5 and there was not hydroxyl groups to form more $Al(OH)_3$, a dissolution of the fresh $Al(OH)_3$ precipitated occurred as at pH < 6 aluminum solubilizes in a high extent, causing a decrease in the TNC and MCS. The maximum in the TNC curves appeared at higher dosages at higher initial pHs, because with a higher initial pH there is a higher alkalinity which allow the formation of more $Al(OH)_3$ precipitates.

3.4. Optimum treatment option

To work at regular recovery rates in RO membranes (60–80%), it is necessary to decrease silica level down to 20–60 ppm. For an initial silica content of 140 ppm SiO_2 it was necessary, therefore, to achieve 60–85% silica removal. All the coagulants tested could reduce silica levels to at least 50 ppm. However, they did it at the highest initial pH tested (pH 10.5) and with high dosages, which implies high conductivity of the treated waters, slightly high final pH and high treatment costs. Final conductivity of the water has to be, at least, lower than 3.0 mS/cm. This conductivity is enough to work at 60% recovery in RO membranes, avoiding the need of a further treatment of the RO rejects before discharge (<7.5 mS/cm) which would affect significantly the economic feasibility of the process. All the coagulants achieved the required silica removal at pH 10.5,PACl-HB also achieved the required silica removal at pH 9.5 and the highest dosage (2000–2500 ppm). Without any doubt, PANS-PA2 is the product recommended for this application. It has a great versatility as it achieved the highest silica removal efficiencies (up to 97%) but, even more important in this application, it could achieve high silica removal rates even without pH adjustment of the water. Final silica concentrations were 45.4 and 37.5 ppm with dosages of 2000 and 2500 ppm, respectively. In these treatments the conductivity increased only from 2.2 mS/cm up to 2.4–2.5 mS/cm, and the COD removal rates are at the same time, the highest (26.5% and 27.7%, respectively). PANS-PA2 could be also used at pH 9.5 and dosages >1000 ppm to achieve the required silica removal, which would reduce the cost of the coagulation in the treatment, but slightly decreasing the other additionalbenefits. If the same dosage is used higher pH would improve the silica removal. For example, at 2500 ppm dosage, the pH adjustment to 9.5 increased the silica removal from 73.2% to 78.5% (compared to no pH adjustment), however, the conductivity

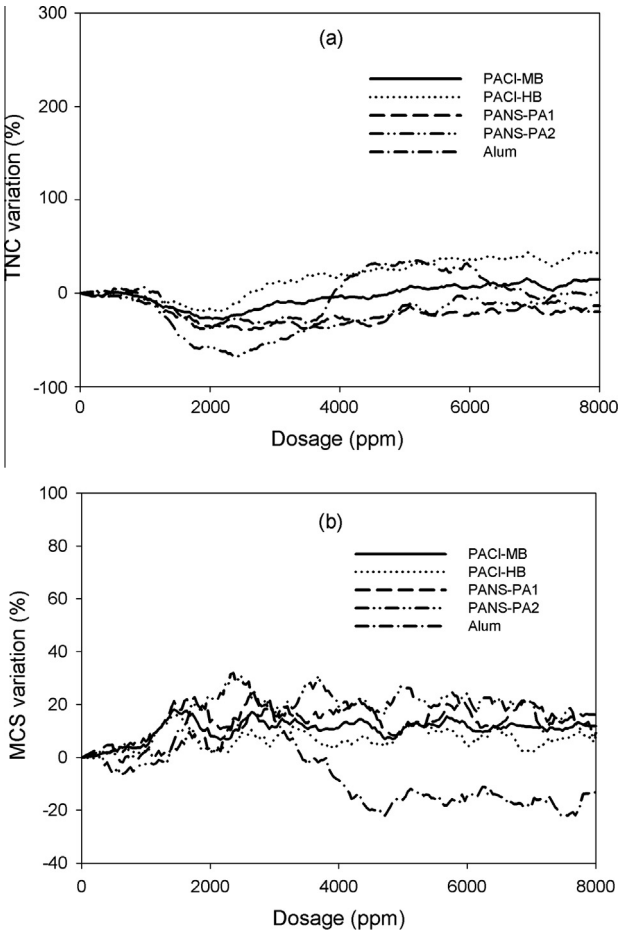

Fig. 7. TNC (a) and MCS (b) variation at pH = 10.5.

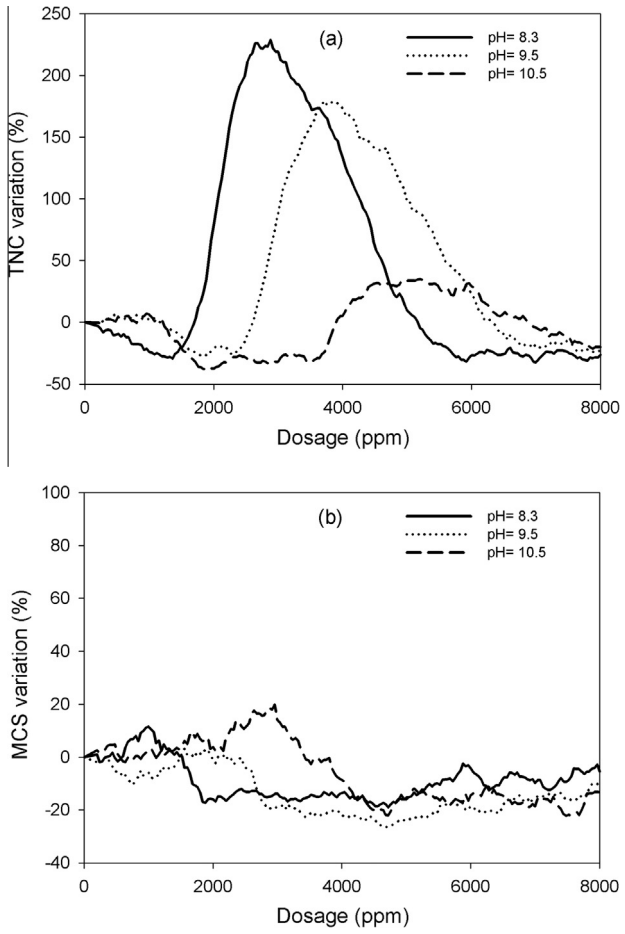

Fig. 8. TNC (a) and MCS (b) variation of alum at pH 8.3, 9.5 and 10.5.

increased from 2.5 mS/cm to 2.7 mS/cm and COD removal decreased from 28% to 22.3%. At initial pH 10.5 and 1500 ppm of coagulant, final silica concentration in water was 19.2 ppm, which was around half that at pH 9.5, and would be enough to work at 80% recovery in the RO process. However, conductivity was higher and COD removal was lower. In other different applications, the highest initial pHs and high dosages could be of interest, to achieve silica removals as high as 97% but in this application, a slightly lower silica removal is preferred if the quality of the waters is less affected.

Other possible solution, although with some drawbacks, could be the treatment with 500–1000 ppm of alum at pH 10.5. At these conditions, the silica concentration was reduced to 36.9-27.7 ppm (74-80% removal). The drawbacks of using alum, previously mentioned, are partially minimized because it was used at very low dosages. In these conditions, the final conductivity was moderate, around 3.0 mS/cm, as well as the sulfates increase, from 200 ppm to 430–560 ppm. However, it is important to notice that a fine control of alum dosage is required, as overdose can occur, reducing significantly silica removal rates and in, some cases, increasing the turbidity of the treated waters. For example, at pH 10.5, silica removal could decrease from 80% to 44% when using 2000 ppm instead of 1000 ppm. Other drawback is the limited COD removal achieved, around 3%.

PACl-HB could achieve final 66–67% removal of silica (47–48 ppm residual silica) with an intermediate pH adjustment (pH 9.5). In this case, the final conductivity would be 2.8–3.0 mS/cm and the COD removal could be the 15–20% range. Higher removals could be obtained at pH 10.5 (72–76%) but the conductivity would increase to 3.3 mS/cm and the COD removal decrease to 6–8%. On the other hand, PANS-PA1 could achieve final 75–92% removals at initial pH 10.5 and dosages ranging 1500–2500 ppm. Conductivity of the treated waters would be around 3.0 mS/cm and the COD removal would be in the 15–20% range.

Finally, lime is preferred to caustic soda as pH regulator. The silica removal efficiency with both pH regulators was the same but using lime, the conductivity of the treated waters was lower, the COD removal was higher and the sedimentation rates were faster. In addition, lime is considerably cheaper than caustic soda.

4. Conclusions

The bottleneck of deinking paper mills for reusing their effluent after advanced membrane technologies is high silica content of the water. It can be removed by coagulation; however, this treatment has to be optimized in terms of pH, nature and dosage of coagulant and chemical used for pH adjustment. This research proves that at higher pHs and dosages, the coagulation of silica is more efficient, reaching 97% silica removal with the best treatment. However, these high dosages and pHs, apart from the high costs, can produce an increase in the conductivity of the waters treated which could not be assumed for RO performance and probably, a final pH adjustment after the treatment would be necessary before water reuse.

The results demonstrate that PANS-PA2 was the most efficient and versatile coagulant. This product enables high enough silica removal efficiencies to operate at regular recoveries in RO processes (60–80%) with the advantage of an additional COD removal and a very limited conductivity increase. FBRM results showed that this product also generates the largest flocs. For the present application, a dosage of 2000 ppm without pH adjustment could be the optimum solution. Silica removal was around 70%, conductivity 2.4 mS/cm, final pH 8.1 and COD removal was 26%. For applications in which silica removal requirements are higher, higher pHs should be used.

The use of low dosages of alum (500–1000 ppm) at pH 10.5 could be another feasible alternative, as alum has a lower cost compared with the other products tested. In these conditions, a 75% silica removal could be achieved, however, the conductivity increase was higher than in the case of using PANS-PA2 (3.0 mS/cm) and there was a significant increase of sulfates in the treated waters (from 200 to 430–560 ppm). Final pH was higher than the required (8.6–9.7, depending on the dosage) and only a very low COD removal was achieved (3%). In addition, overdosing problems could occur, as the alkalinity consumption was very high and it could produce a pH decrease which could solubilize the previously formed $Al(OH)_3$ precipitates as it was demonstrated by FBRM studies.

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PUBLICATION II

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"Enhanced silica removal by polyamine- and polyacrylamide- polyaluminum hybrid coagulants"

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Chemical Engineering & Technology Research Article 1

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Enhanced Silica Removal by Polyamine- and Polyacrylamide-Polyaluminum Hybrid Coagulants

Silica removal is the main bottleneck for a high reuse of deinking paper mill effluents due to silica scaling on the reverse-osmosis units generally used. The efficiency of inorganic-organic hybrid coagulants formed by the combination of polyaluminum nitrate sulfate (PANS) with different dosages of cationic polyacrylamide (PAM) or polyamines (PA) on silica removal is analyzed. These hybrids significantly increased the silica and chemical oxygen demand (COD) removal at all pH values studied, with PA modification being the most efficient. While conventional aluminum coagulants allow high silica removal, only at both high pH and dosages the PA derivatives achieve high silica and soluble COD removal without pH adjustment. PAM hybrids only slightly improved the efficiency of PANS at the highest active contents. ■shortened, pls check■

Keywords: Aluminum salts, Deinking, Hybrid coagulants, Polyacrylamide, Polyamine, Silica removal

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1 Introduction

Water management in graphic paper industry has been traditionally based on reusing process water after internal treatments; however, the water reuse degree is limited by the accumulation of dissolved and colloidal material (DCM) [1]. A further reduction of fresh water consumption can only be based on effluent reuse after advanced membrane treatments and/or by the use of alternative water sources as municipal reclaimed water [2, 3].

In deinking paper mills, high silica levels are found in the process waters as sodium silicate is used as process additive. This high silica content is an issue, first, due to the stringent environmental legislation for effluent discharge, i.e., 50 mg L^{-1} SiO_2 in countries such as United States, Finland or Canada [4]; second, silica scaling limits the technical and economic feasibility of reusing the effluent after a membrane treatment scheme, as maximum allowable recoveries in reverse-osmosis (RO) units without silica pretreatment are as low as 20 % [2].

Sodium silicate is one of the most important additives in the deinking process as it improves the optical properties of the pulp. In the pulping stage, it enhances ink dispersion and facilitates its removal by flotation; in the bleaching stage, it acts as peroxide stabilizer by chelation of transition metals and pH buffer, controls corrosion, and is a surface-active agent [5]. Some attempts have been made to reduce the use of sodium silicate in the process [6, 7], but its variety of functions and low price makes sodium silicate the preferred option for papermakers.

Silica removal is usually performed during softening processes or by coagulation at high pH [4, 8–13]. These techniques are supposed to treat large volumes of water with high removal rates at low costs, which is a prerequisite for their use in papermaking. The most efficient removal technology depends mainly on the hardness content of the waters. For an efficient silica removal during a softening process, enough hardness in the waters must be ensured, especially magnesium hardness. If it is not high enough, as usually occurs in the effluent of deinking paper mills, it is necessary to add hardness to the waters, which increases the costs and the levels of dissolved solids in treated waters. In such cases, coagulation can be the preferred option.

One of the most used coagulants are polyaluminum chlorides. Compared to alum, they are effective in a wider range of pHs and at lower temperature, generate more compact and easily sedimentable flocs, are less likely to cause overdosage phenomena, and are less sensitive to varying water properties [14, 15]. As chlorides can cause corrosion problems, they are sometimes partially substituted by other species such as sulfates or nitrates, providing a new range of products: polyaluminum nitrates, polyaluminum sulfates or a combination of them, such as polyaluminum nitrate sulfate (PANS). The main differences between these products are their aluminum content, basicity, and the content of other species such as silica or calcium [16–18]. However, in some applications the efficiency of these products is still limited.

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There is a growing interest in developing hybrid products for improving coagulation/flocculation processes. From these hybrid materials, inorganic-organic hybrids are probably the most developed combinations [19]. Although they are more expensive than its inorganic counterpart, organic coagulants typically offer the advantage of lower dosages, broader pH operating range, and smaller sludge production [20]. Different inorganic coagulants such as aluminum salts and polyaluminum coagulants are combined with cationic organic polymers, the two most common being polyacrylamide (PAM) and polydimethyldiallylammonium chloride (PDADMAC) [20]. Other water-soluble polymers that can be adopted to prepare hybrid materials are polyamines (PA), polyimines, polyvinylpyridines, polyacrylic acid, polyvinyl sulfonic acid, polystyrene sulfonic acid, polyethylene oxide etc. [21].

Although the mechanism of polyaluminum coagulants is not perfectly understood, there is a consensus in that they can act by two primary flocculation mechanisms [16]: charge neutralization of the negative particles by adsorption of positively charged dissolved aluminum species, and enmeshment of particles in freshly precipitated $Al(OH)_3$, also known as sweep flocculation. However, in the area of hybrid coagulants, the number of possible combinations is large and there is a need to improve the knowledge on their efficiency and their flocculation mechanism. References on silica removal with hybrid coagulants, to the best of our knowledge, are practically non-existent.

Previous studies have demonstrated that coagulation with aluminum salts is effective for the treatment of deinking paper mill effluents; however, the operating pH, the required dosages, and thus the conductivity of the treated waters were very high [22]. Therefore, the process was neither economically nor chemically feasible. To avoid these drawbacks, here the efficiency of hybrid inorganic-organic coagulants based on the combination of PANS with a cationic PAM and quaternary polyamines at different proportions is evaluated. The final aim is to reduce the silica content in the effluent of a paper mill to increase the RO recovery from 20 % to 60–80 % without silica scaling and the main novelty lies in the use of hybrid coagulants for this application.

2 Materials and Methods

2.1 Water Samples

Water samples were taken from the effluent of a paper mill producing newsprint from 100 % recovered paper with highly closed water circuits and an average fresh water consumption of 7.5 $m^3 t^{-1}$. This effluent is treated by dissolved-air flotation followed by a biological treatment in a moving-bed bioreactor and a secondary dissolved-air flotation prior to its discharge to an urban wastewater treatment plant. The characterization of the effluent is given in Tab. 1, including the standard deviation from three replicates. The samples were taken during a period of high degree of closure of water circuits before a programmed stop of the production lines to determine the silica removal achievable under these conditions. The particle chord size distribution, determined by the focused-beam reflectance measurement (FBRM) technique, indicates that the mean and the median chord sizes of the particles are 43.7 and 34.3 µm, respectively. Most of the particles are in the 10–100 µm range (69.4 %), especially in the range of 30–100 µm (46.9 %), although there is also a significant proportion of particles < 10 µm (21.7 %).

2.2 Chemicals

Six coagulants were tested, all supplied by Sachtleben Wasserchemie GmbH. Their main characteristics are summarized in Tab. 2. PANS has an intermediate aluminum content and basicity (5.5 % Al, 46 % basicity), with 16.0 % NO_3^- and 3.0 % SO_4^{2-} contents. This product served as the base product to prepare five hybrid inorganic-organic materials with active contents of PAM and PAs (from 1× to 4×). PANS-PAM1, PANS-PAM2, and

Table 1. Characteristics of the effluent (raw water and dissolved fraction).

Raw water		Dissolved fraction (0.45 µm)	
Parameter	Value	Parameter	Value
pH	8.3 ± 0.1	Total solids [mg L^{-1}]	2950 ± 80
Conductivity (25 °C) [mS cm^{-1}]	3.4 ± 0.1	Turbidity (NTU)	5.6 ± 0.4
Total solids [mg L^{-1}]	3150 ± 100	COD [mg L^{-1}]	860 ± 25
Total suspended solids [mg L^{-1}]	180 ± 10	Silica [mg L^{-1} SiO_2]	180 ± 6
Turbidity (NTU)	155 ± 5	Sulfates [mg L^{-1}]	744 ± 26
Total alkalinity [mg L^{-1} $CaCO_3$]	1010 ± 40	Chlorides [mg L^{-1}]	176 ± 6
COD [mg L^{-1}]	1020 ± 30	Calcium [mg L^{-1}]	52.0 ± 1.8
BOD ([mg L^{-1}]	175 ± 10	Magnesium [mg L^{-1}]	6.4 ± 0.2
Cationic demand [meq L^{-1}]	1.95 ± 0.05		

Table 2. Characteristics of the coagulants tested.

Coagulant	Al [%]	NO_3^- [%]	SO_4^{2-} [%]	Active content [%]	Charge density [a] [meq g^{-1}]
PANS	5.5	17	3.6	–	0.60
PANS-PAM1	4.8	16	3.6	1×	1.13
PANS-PAM2	4.4	16	3.3	2×	1.18
PANS-PAM3	3.9	14	3.2	4×	1.20
PANS-PA1	4.7	16	3.2	1×	1.68
PANS-PA2	3.4	11.8	2.5	3×	2.57

a) Measured by colloidal titration.

PANS-PAM3 were obtained adding to PANS a high charge density and low-molecular-weight cationic PAM at different dosages. PANS-PA1 and PANS-PA2 were obtained by adding different dosages of a mixture of cationic quaternary polyamines of high charge density and different molecular weights. The coagulants were tested in combination with the same flocculant: an anionic PAM of high molecular weight and medium charge supplied by SERTEC-20 S.L. (Spain).

2.3 Jar Tests

Coagulants were tested at four dosages (500, 1000, 2500, 5000 mg L^{-1}), in combination with 10 mg L^{-1} of the flocculant, at three initial pHs: pH 8.3, which is the present pH at which the effluent is discharged (no pH regulation), pH 9.5, and pH 10.5. Initial pHs and coagulant dosages tested were selected according to previous tests [22].

First, the pH of the sample was adjusted to the selected initial pH by the addition of 10 wt % NaOH. After 1 min of high speed mixing at 200 rpm, the coagulant was added to the sample from a 10 wt % solution and mixed at 200 rpm during 2.5 min. Next, the flocculant was added from a 0.20 wt % solution and mixed for 10 min at slow speed (40 rpm). Finally, the sample was allowed to settle during 30 min and the supernatant was characterized by pH, conductivity, and cationic demand. Silica and chemical oxygen demand (COD) were measured in the dissolved fraction of the supernatant, obtained after filtration through a 0.45-μm PTFE syringe filter. Jar tests were carried out in a multiposition magnetic stirrer OVAN MultiMix Heat D at room temperature (20–25 °C) by duplicate, with an average error between replicates < 5 %. To avoid the possible degradation of the waters, all trials and analyses were carried out within seven days after sampling and the waters were always kept stored at 4 °C.

Conductivity and pH of the samples were analyzed with a GLP-32 conductivity meter and a GLP-22 pH-meter (Crison Instruments, S.A.). Cationic demand was measured by colloidal titration using a PCD 03 particle charge detector from Mütek GmbH and an automatic titrator (Compact I, Crison Instruments, S.A) with 0.001 N PDADMAC as titrant. Silica was photometrically determined as silico-molybdenum blue at 820 nm, using Nanocolor® silica standard tests, and COD by the Nanocolor® COD 1500 Method from Macherey-Nagel GmbH, according to ISO 15705:2003. Photometric measurements were carried out in duplicate on an Aquamate UV-Vis spectrophotometer (Thermo Scientific Inc.).

2.4 Flocculation Monitoring

FBRM is a covenient technique to monitor flocculation processes as it allows assessing flocculation behavior and flocculation mechanisms without the limitations of traditional methods such as charge titration [23–25]. The device generates a laser beam that is focused on a focal point describing a circular path at high speed (2000 rpm). ■shortened■

The FBRM probe used in the tests is a D500L model (Mettler-Toledo) with a measurement range of 1 to 1000 μm. In a typical trial, the probe was submerged into 200 mL sample and the stirring speed was fixed to 300 rpm. After 30 s of stabilization, the coagulants were continuously added to the sample: 100 mg L^{-1} of coagulant was added each 10 s up to a final dosage of 5000 mg L^{-1}, and the evolution of the mean chord size (MCS) and the total number of counts (TNC) were analyzed. When necessary (pH 9.5 and 10.5), pH adjustments were carried out previously.

3 Results and Discussion

3.1 Silica Removal

Fig. 1 clearly shows that high pHs and dosages are necessary to achieve high silica removal. At initial pH 8.3, the silica content continuously decreased up to a minimum of 35–85 mg L^{-1} (50–80% removal) at 5000 mg L^{-1}, depending on the product tested. PA derivatives were the most efficient coagulants since they achieved 75–80 % silica removal, compared to 55 % silica removal obtained by the base product PANS. The higher the PA content of the coagulant, the higher the silica removal, however, the differences were not large (20 % more for PANS-PA1 and 25 % for PANS-PA2). PAM hybrids also improved silica removal compared to PANS, although to a lower extent. Again, silica removal was enhanced by higher PAM contents. With 5000 mg L^{-1} dosage, PANS-PAM1 efficiency was very similar to

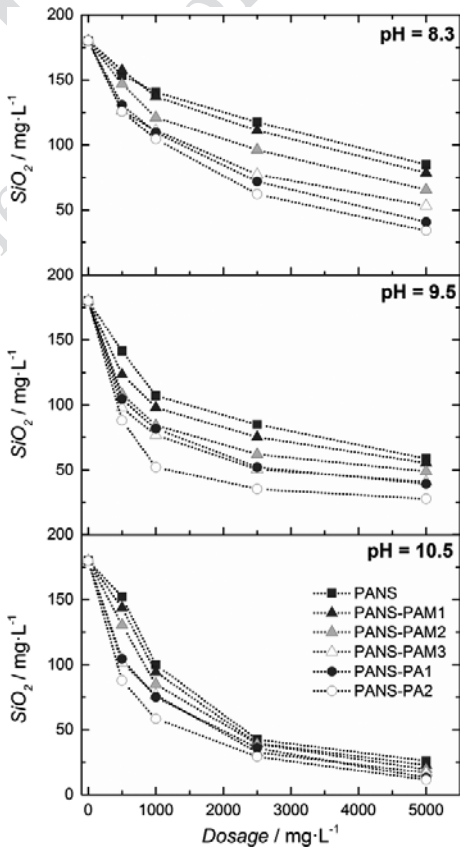

Figure 1. Silica vs. coagulant dosage at different initial pHs.

PANS (~ 55 % silica removal), however, PANS-PAM2 and PANS-PAM3 achieved 62.5 % and 70 % silica removal, respectively, i.e., 7.5 and 15 percentage higher silica removal than PANS.

Trends observed at initial pH 9.5 were almost the same like those at initial pH 8.3, achieving silica contents of 28–60 mg L^{-1} (70–85 % removal) at 5000 mg L^{-1}. Even more important, similar silica removal rates could be obtained with 2500 mg L^{-1} at initial pH 9.5 than those gained with 5000 mg L^{-1} at initial pH 8.3. In this case, silica removal differences between 2500 and 5000 mg L^{-1} dosages were not very high, thus indicating the optimal dosage was slightly higher than 2500 mg L^{-1}. The differences in efficiency among the coagulants were smaller at this pH than at initial pH 8.3.

The same trends were observed at initial pH 10.5. Higher silica removal rates were obtained, i.e., the silica content was reduced to 11–26 mg L^{-1} (85–94 % removal). Low silica contents can be also achieved at lower dosages: 26–42 mg L^{-1} (76–84 %) at 2500 mg L^{-1} and to 38–100 mg L^{-1} (44–67 %) at 1000 mg L^{-1}. Again the differences between 2500 and 5000 mg L^{-1} are very small and those in efficiency among the coagulants became smaller at this pH. Therefore, the benefits of using hybrid materials were more evident at the lowest pH (no pH adjustment) than at high pHs.

Literature indicates that silica removal by coagulation is enhanced at alkaline pHs. At such pHs, both $H_3SiO_4^-$ and $H_2SiO_4^{2-}$ are the predominant forms of dissolved silica, while at neutral pH ranges, silica is present as neutral form (H_4SiO_4). This negative charge at the surface of silica facilitates coagulation, independently of the coagulant used [4, 9, 12]. Besides, the coagulants can be more efficient at high pHs, i.e., aluminum salts require the consumption of alkalinity to form the active species. Therefore, high pHs and a parallel high alkalinity can lead to better efficiency. PAM and PA polyelectrolytes, however, do not consume alkalinity and can work efficiently in a wider pH range than aluminum products. Therefore, although higher silica removals are expected at higher pHs due to ionization of silica for all the coagulants, these removal increases would be higher in the case of PANS than in the case of PAM and PA derivatives. This is the reason why the main differences among the coagulants occur at the lowest initial pH, as observed experimentally [12].

On the other hand, it is well-known that the dosages required to achieve the same degree of destabilization with organic polyelectrolytes are usually lower than those of polyaluminum coagulants, which is one of the main advantages of using inorganic-organic hybrids [19, 20]. Therefore, higher active contents resulted in a higher silica removal for the same total coagulant dosage. PA derivatives were found to be much more efficient than PAM derivatives. Even with a four times higher active content used in PANS-PAM3 compared to PANS-PA1, the efficiency attained with both products was similar.

PAM usually enhances the interparticle bridging mechanism, especially if there is a high solids concentration [26]. On the other hand, high charge and low-molecular-weight PA generally enhance the patches formation flocculation mechanism [18, 27]. Therefore, the higher silica removal for PA hybrids indicates that patches formation could be more efficient than bridges formation for silica removal.

Taking into account silica solubility, it would be necessary to decrease silica to around 20–60 mg L^{-1} (67–89 % removal for an initial silica content of 180 mg L^{-1}) to work at regular recoveries of 60–80 % in RO membranes without silica scaling. To achieve this objective, the following combinations are possible, depending on the initial pH. At initial pH 8.3, only 5000 mg L^{-1} of PANS-PA2, PANS-PA1, and PANS-PAM3 could reach this aim. At initial pH 9.5, all the coagulants were successful at 5000 mg L^{-1}. In addition, PANS-PA2, PANS-PA1, and PANS-PAM3 at 2500 mg L^{-1} could achieve this objective, and even 1000 mg L^{-1} of PANS-PA2. Finally, at initial pH 10.5, all the coagulants meet this silica removal at 2500 and 5000 mg L^{-1}, and again only PANS-PA2 even at 1000 mg L^{-1}.

It is clear that high pHs promote better silica removal efficiencies at lower dosages, even avoiding the need of using hybrid materials to achieve the required silica removals. However, pH adjustment is detrimental for the process, especially due to the increase in conductivity of the treated waters but also related to treatment costs. Although hybrid coagulants can be used in applications where very high silica removals are required is at initial pH 8.3 ■sentence not clear■ (no pH adjustment) where the hybrids, especially PA hybrids, represented an important advantage compared to other coagulants.

3.2 COD Removal

Although the most critical parameter in this application is silica removal, any further COD removal is of interest to prevent organic fouling of the membranes. Usually, there is an inverse relationship between silica and COD removals [12, 22], meaning a kind of competition for the coagulant dosage added.

Fig. 2 shows the evolution of soluble COD content as a function of coagulant dosage at different initial pHs. As expected, COD removal decreased at high pHs, especially at initial pH 10.5, opposite to silica. At initial pH 8.3 and the highest dosage (5000 mg L^{-1}), COD could be reduced to 450–550 mg L^{-1} (35–50 % removal), to 465–565 mg L^{-1} (35–45 % removal) at initial pH 9.5, and to 550–635 mg L^{-1} (25–35 % removal) at initial pH 10.5.

PANS-PA2, PANS-PA1, and PANS were the most efficient products, independently of pH and dosage with very similar removal efficiencies: 45–48 % at initial pH 8.3, 45–46 % at initial pH 9.5, and 30–34 % at initial pH 10.5. PAM derivatives obtained also similar removal efficiencies, i.e., 36–42 % at initial pH 8.3, 34–42 % at initial pH 9.5, and 26–29 % at initial pH 10.5, with PANS-PAM3 being slightly more efficient than the other PAM derivatives with lower active contents. As a result, PA derivatives were those producing the highest COD removals.

The base product, PANS, had a similar removal efficiency like PA derivatives but the lowest silica removal efficiency. Finally, PAM derivatives, with an intermediate silica removal were the least efficient coagulants in COD removal. As commented before, there is a competition between the usage of the coagulant for destabilizing silica or organic material, which could explain why PANS was more efficient than PAM derivatives in COD removal. However, in the case of PA derivatives, their COD removal efficiencies were higher compared to the

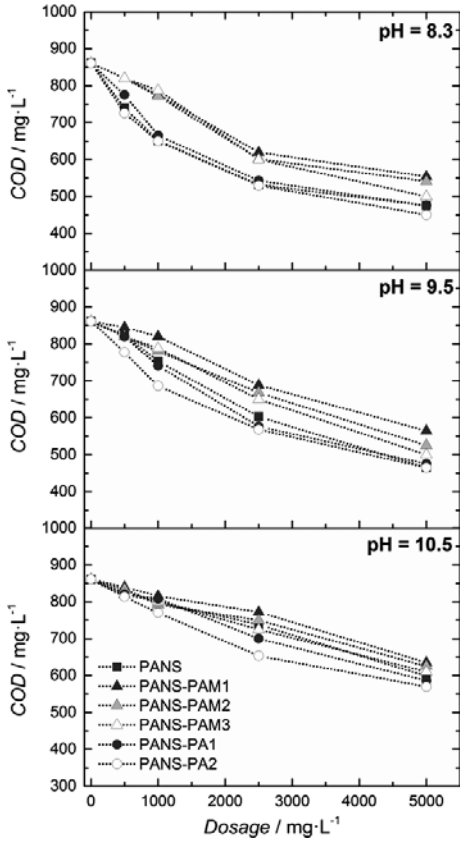

Figure 2. Soluble COD vs. coagulant dosage at different initial pHs.

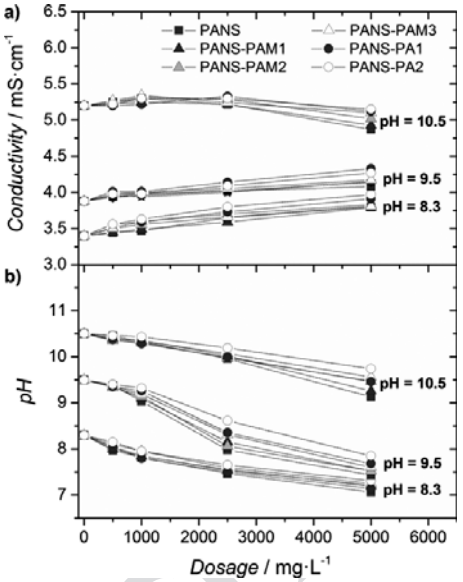

Figure 3. (a) Conductivity and (b) pH of clarified waters vs. coagulant dosage at different initial pHs.

other coagulants which achieved lower silica removal rates, very similar to the least efficient product in silica removal (PANS).

For these types of waters, the maximum soluble COD removal usually varies in the 20–25 % range [1, 17, 18, 30]. In this case, the maximum soluble COD ranged between 30 % and 50 %, depending on the initial pH, which is a great performance even using such high coagulant dosage (5000 mg L^{-1}). The high coagulant dosages tested in this study could be significantly reduced when applied under industrial regular operational conditions as these tests were carried out at a time when the contamination of the effluent was especially high. Under regular conditions, the soluble COD is < 500 ppm, the conductivity varies in the 2–3 mS cm^{-1} range and the cationic demand between 0.5 and 1.0 meq L^{-1}, compared to 860 ppm soluble COD, 3.4 mS cm^{-1} conductivity, and 1.95 meq L^{-1} cationic demand of the present study.

3.3 Conductivity and pH

The conductivity of the treated waters at different initial pHs and dosages is displayed in Fig. 3 a. A slight increase of the conductivity with coagulant dosage was observed, being almost linear with the dosage but at pH 10.5 and 5000 mg L^{-1}, where a decrease in conductivity was detected probably due to a softening process. There were only slight differences among the different coagulants, especially among the hybrid coagulants. According to Fig. 3b, the addition of the pH regulator (NaOH) was the main factor increasing the conductivity of waters. Only by pH adjustment, the conductivity of the waters increased from 3.4 mS cm^{-1} (initial pH 8.3, no pH adjustment) to 3.9 mS cm^{-1} (initial pH 9.5) and 5.20 mS cm^{-1} (initial pH 10.5). The high conductivity at initial pH 10.5 compared to pH 9.5 is due to the highest dosage of NaOH necessary to adjust the pH (800 vs. 200 mg L^{-1} NaOH).

The conductivity increase after the treatment must be kept at minimum to avoid both scaling of other inorganics on RO membranes and the need of a post-treatment of RO rejects before discharge, which would increase the treatment costs and the economic feasibility of the whole effluent reuse treatment. If RO membranes work at 60–80 % recoveries, the conductivity of RO feed should be between 1.5 and 3.0 mS cm^{-1} for direct discharge of RO rejects; the discharge limit is 7.5 mS cm^{-1} in this particular paper mill. Here, the effluent had already very high conductivity, i.e., 3.4 mS cm^{-1}, and direct discharge would not be possible without a post-treatment; however, at regular conductivities such as 2.0 mS cm^{-1}, it could be verified. Whatever the case, the lowest increase in the conductivity of the treated waters, the easiest and cheapest post-treatment rejects ■sentence not clear■ if not possible to avoid it completely.

Fig. 3 b presents the pH of the treated waters after the different treatments. Metal salts such as aluminum salts or ferric salts consume alkalinity to form their active flocculation species, i.e., $Al(OH)_3$ or $Fe(OH)_3$ which causes a pH decrease in the treated waters, the extent being dependent on the coagulant dosage, aluminum content, and basicity. Although total alkalinity of the raw water is high, around 1000 mg L^{-1} $CaCO_3$, the coagulant dosages used were high and thus significant reduction of the pH in the treated waters was observed. The pH of treated waters decreased to 7.0–7.2 at initial pH 8.3, to 7.4–7.8

at initial pH 9.5, and to 9.1–9.7 at initial pH 10.5. At initial pHs 8.3 and 9.5, both the RO accept and reject could be reused and discharged, respectively, without any pH adjustment (pH 6–9). However, at initial pH 10.5, pH adjustments would be necessary (final pH > 9).

The differences in final pH due to the type of coagulant were small, i.e., ~0.2–0.6 pH units depending on the initial pH tested, related to their aluminum content. The products with the highest aluminum content are those producing a higher pH decrease, i.e., PANS, while those with the lowest aluminum content (PANS-PAM3 and PANS-PA2), caused the lowest pH decrease.

3.4 Cationic Demand

Fig. 4 shows the cationic demand of the treated waters. As expected, the initial cationic demand was higher at higher initial pHs (1.95 meq L^{-1} at pH 8.3, 2.15 meq L^{-1} at pH 9.5, 2.65 meq L^{-1} at pH 10.5) due to the pH adjustment and the higher ionization of silica and other species such as fatty acids present in the papermaking effluent. As the cationic charge of the coagulants is relatively constant at the pH range tested, especially for the hybrid coagulants, the percentage removal of cationic demand was lower at higher initial pHs where the initial cationic demand is higher.

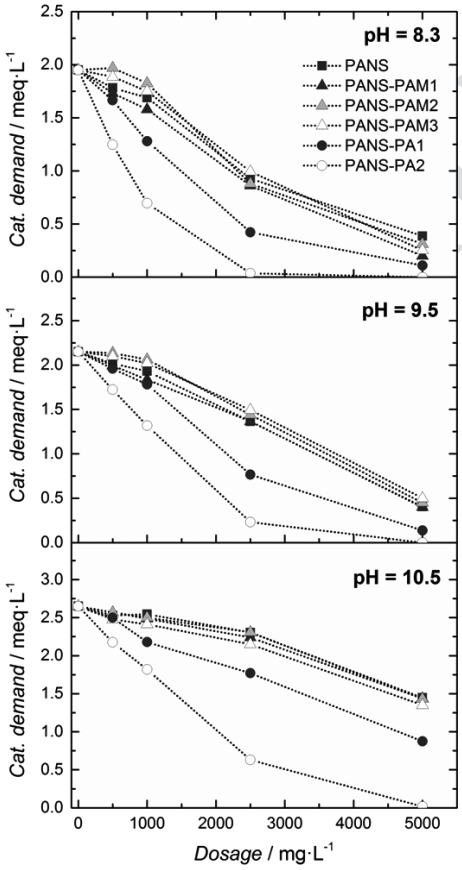

Figure 4. Cationic demand vs. coagulant dosage at different initial pHs.

PANS-PA2 and PANS-PA1 were the most efficient products reducing the cationic demand of waters due to their higher cationic charge caused by the addition of PA (Tab. 2). PANS-PA2 is the only coagulant that achieved complete neutralization of the cationic demand under certain conditions, i.e., at 2500–5000 mg L^{-1} at initial pH 8.3 and at 5000 mg L^{-1} at initial pHs 9.5 and 10.5. PANS-PA1 showed an intermediate efficiency between PANS-PA2 and the other products (PANS and PAMs hybrids). It reduced the cationic demand to a maximum of 0.11 meq L^{-1} at initial pH 8.3, 0.14 meq L^{-1} at initial pH 9.5, and 0.88 meq L^{-1} at initial pH 10.5. The rest of the coagulants, PANS, and their PAM derivatives exhibited similar efficiencies reducing the cationic demand of waters as expected by their similar cationic charge with PANS (Tab. 2). Slightly higher cationic demand removals would be expected with PAM hybrids compared to PANS, however, charge neutralization seems to be a secondary flocculation mechanism for PAM hybrids which is in agreement with a predominant interparticle bridging flocculation mechanism.

Although charge reversal occurred in some cases (PANS-PA2), silica removal still increased under these conditions, i.e., no restabilization of the formed flocs, thus charge neutralization was not the predominant flocculation mechanism for PANS and PA. These results confirmed that the predominant flocculation mechanism for PANS was sweep flocculation instead, in agreement with the high aluminum dosages and pHs used in the tests [15, 16].

3.5 Flocculation Monitoring

To explain the results obtained in jar tests, the flocculation process was monitored with the FBRM technique under the same conditions with the only difference of not using a flocculant. In regular flocculation, the agglomeration of small particles to form bigger ones produces a decrease in the number of particles and a parallel increase in the mean size of the particles. However, with the hybrid coagulants this behavior was not observed, independently of the tested conditions. The number of particles grew in all size ranges from 1 to 1000 μm due to two simultaneous processes: first, increase of the number of big particles caused by the aggregation of smaller ones into larger flocs; second, continuous increase in the number of the smallest particles, despite some of them are agglomerated to form larger flocs, due to a significant destabilization of DCM (< 1 μm). This DCM, previously not detected by FBRM (measurement range 1–1000 μm), grows after destabilization to produce small flocs, i.e., microflocs, bigger than 1 μm, thus they can be detected. If the number of particles coming from DCM destabilization is higher than that of particles being agglomerated to produce larger flocs, a net increase of the total number of counts is observed [30]. In these tests, most of the total increase in the number of particles was caused by small particles, mainly in the ranges of 1–10 and 10–29.3 μm.

The mean chord size decreased with all the coagulants tested except the base product PANS. If a strong destabilization of DCM takes place, there is a significant increase in the number of particles in the lowest size range. As these particles have a lower size than the particles initially present in the water and

the microflocs agglomeration takes place to a lower extent than the DCM destabilization, the mean chord size decreases. This is especially true if the main flocculation mechanisms are sweep flocculation or patches formation where flocs are smaller compared to other flocculation mechanisms such as interparticle bridging [29]. The strongest destabilization of DCM leads to the highest reduction of the mean chord size [18].

Fig. 5 illustrates the increase of the mean chord size (ΔMCS) and total number of counts (ΔTNC) for the different treatments at initial pH 8.3. The base product PANS was the only product increasing the MCS of the flocs at higher dosages, achieving 2 μm increase at the highest dosage. All PANS hybrids produced a continuous decrease in the MCS of the particles at higher dosages, ranging from 1.5 to 4.5 μm (1.7 μm for PANS-PAM1, 2.6 μm for PANS-PAM2, 3.6 μm for PANS-PAM3, 4.3 μm for PANS-PA1) but PANS-PA2 generated a significantly higher and faster reduction of the MCS by ~10–12 μm. All hybrids increased TNC to a greater extent than PANS (100 # s^{-1}). Again, the PANS-PA2 showed a totally different behavior, increasing more and faster the TNC: a maximum increase of 3800 # s^{-1} was observed at ~3250 mg L^{-1}. The other hybrids only increased the TNC from 350 to 700 # s^{-1}.

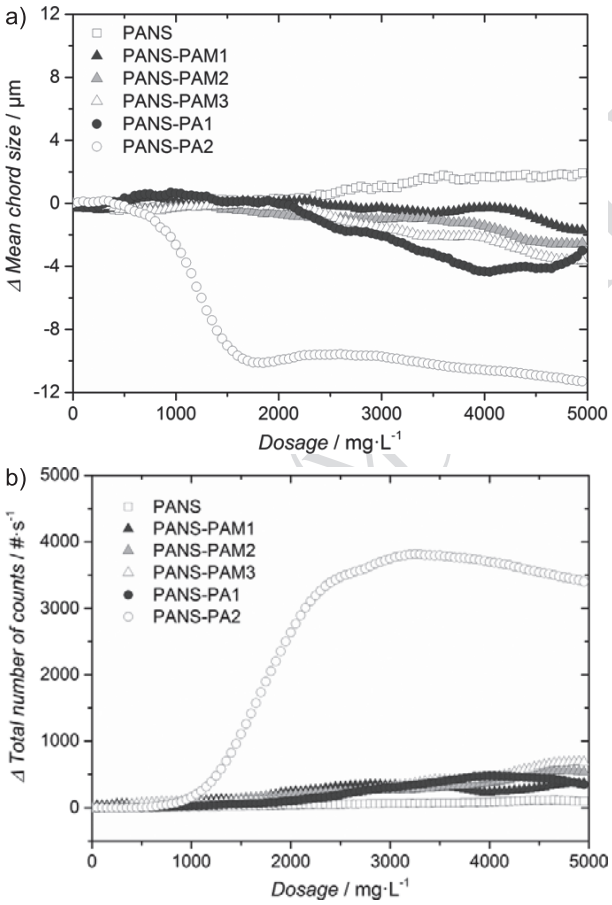

Figure 5. Evolution of (a) Δ mean chord size and (b) Δ total number of counts vs. coagulants dosage at initial pH 8.3.

These data confirmed that PANS is the least efficient product as it leads to the lower increase in the TNC, indicating a slight destabilization of DCM, together with the fact that the MCS did not decrease but increase. All hybrids were more efficient than PANS as they significantly destabilized the DCM, demonstrated by a pronounced growth in the TNC and a parallel reduction in the MCS. A marked destabilization of DCM is necessary for a high silica and COD removal, as most of these contaminants are in the dissolved and colloidal fraction of the water. According to these data, the most efficient product would be PANS-PA2, as was assessed experimentally. The second most efficient product was PANS-PA1, which obtained similar results to PANS-PAM3, but at a lower dosage and with a lower active content in its formulation. PANS-PAM1 and PANS-PAM2 were the least efficient products. For the same type of modification (PAM or PA), it was also proved that higher active contents always produce higher increases in the TNC and higher decreases in the MCS of the particles, i.e., more DCM destabilization.

In addition, the MCS decrease obtained for similar DCM destabilization degrees is an indication of the relative size of the flocs obtained after DCM destabilization. For example, for a similar DCM destabilization (TNC increase: 500–550 # s^{-1}), the MCS reduction was considerably lower for PANS-PAM2 (2.6 μm) than for PANS-PA1 (4.3 μm). Even for a higher degree of DCM destabilization as that obtained by PANS-PAM3 (750 # s^{-1}), the MCS decrease was still lower than for PANS-PA1 (3.6 vs. 4.3 μm). This indicates that the flocs formed by PA modifications are smaller than those generated by PAM modifications, which agrees with the suggested flocculation mechanism of patches formation in PA modifications and interparticle bridges formation in PAM modifications.

The same trends were also observed at initial pH 9.5 and 10.5 (data not shown). Again, PANS increased the MCS of the flocs up to a maximum of 2 μm at initial pH 9.5 and 5.6 μm at initial pH 10.5, while the TNC only grew slightly (15–20 # s^{-1} at initial pH 9.5 and 70–75 # s^{-1} at initial pH 10.5). As the MCS increased significantly for a very similar TNC increase at all pHs tested, the efficiency of PANS is slightly better at higher pHs, especially at initial pH 10.5. This justified that the larger differences between the hybrids and PANS occurred at lower pHs.

At initial pH 9.5 and 10.5, PANS-PA2 was again the most efficient in DCM destabilization, reducing the MCS by 10 μm at initial pH 9.5 (dosages > 2500–3000 mg L^{-1}) and 3.2 μm at initial pH 10.5 (dosages > 3500–4000 mg L^{-1}). Although the decrease in the MCS was much lower than at initial pH 8.3, especially at initial pH 10.5, the increase in the TNC was the highest: 4350 # s^{-1} compared to 3250–3750 # s^{-1}. This indicates that the flocs formed by PANS-PA2 increased in size at higher initial pHs which could be explained by two facts: first, a higher conductivity is detrimental to patches formation, while it can be helpful for bridging formation [29]; second, although the polyamines are effective in a wide pH range, its charge decreases at high pHs, e.g., the charge density of the pure PA used in the hybrids is around 25 % lower at pH 10.5 than at pH 7, and then decreases to zero at around pH 12. Therefore, at higher initial pHs, patches formation become less predominant and a partial interparticle bridging becomes possible, increasing the size of the flocs compared to lower initial pHs.

At initial pHs 9.5 and 10.5, PANS-PA1 reached an intermediate efficiency between PANS-PA2 and PAM hybrids. The maximum MCS reduction with PANS-PA1 was lower at initial pH 9.5 (0.9 μm) and pH 10.5 (1.5 μm) than at initial pH 8.3 (4.3 μm). TNC increased both at initial pH 9.5 (130 # s^{-1}) and pH 10.5 (75 # s^{-1}) but to a lower extent to the increase the decrease ■check sentence■ observed at initial pH 8.3 (480 # s^{-1}). This means that the efficiencies of PANS-PA1 and PANS-PA2 are slightly lower at initial pHs 9.5 and 10.5 than at initial pH 8.3, probably because patches formations became less predominant, and partial interparticle bridging starts playing a significant role. This agrees with the fact that silica removal was only slightly improved at pH 9.5 and 10.5 but COD removal was significantly lower. At initial pH 8.3, PANS-PA1 is more efficient than all PAM hybrids; however, at initial pH 9.5 and 10.5, its efficiency became similar to the most efficient PAM hybrid (PANS-PAM3).

Finally, PAM hybrids showed intermediate efficiencies between PANS and PA hybrids. At initial pH 8.3, TNC increased in the 365–700 # s^{-1} range, and this value was reduced to 50–300 # s^{-1} at initial pH 9.5 and even TNC decreased at pH 10.5 (40–120 # s^{-1}). While at initial pH 8.3 MCS decreased to 1.7–3.6 μm, this decrease was lower at initial pH 9.5 (1.5 to 2.3 μm) and even lower at initial pH 10.5 (0.3 μm maximum decrease, some products increasing MCS up to 0.5 μm). Again, according to FBRM data, PAM hybrids were also less efficient at initial pH 9.5 and 10.5 than at initial pH 8.3. This signifies that although more silica removal was obtained at higher pHs, the reduction in COD removal was more important and affects to a larger extent FBRM statistics. As commented before, PANS-PAM3 was the most efficient PAM hybrid, i.e., the higher the PAM active contents, the higher efficiency was obtained.

FBRM monitoring effectively detected the DCM destabilization but it was not possible to discern if this DCM is mainly organic or inorganic. Preliminary conclusions indicate that FBRM statistics could be more sensible to COD, probably due to the larger flocs of organics.

4 Conclusions

The high efficiency of hybrid coagulants in silica removal is demonstrated compared to traditional polyaluminum coagulants such as PANS, especially at low pHs, which would avoid pH regulation before coagulation. From the hybrids tested, PA derivatives are more efficient than PAM derivatives, even at lower active contents at all the pHs tested. Between the examined PA hybrids, PANS-PA2 is only slightly more efficient than PANS-PA1, despite its active content is higher (3× vs. 1×), indicating that the use of high active contents could not be necessary for this application, which would lead to lower treatment costs.

Several options are possible to reduce the silica content in the effluent to around 20–60 mg L^{-1}, avoiding silica scaling in RO membranes at 60–80 % recoveries. Although at all the initial pHs tested this objective can be achieved, it is at the lowest initial pHs where the COD removal is higher and the increase in conductivity and the decrease of pH are lower. However, under these conditions, higher coagulant dosages are necessary. As commented before, the main advantage of hybrid coagulants is their enhanced efficiency without a previous pH adjustment (initial pH of waters: 8.3). At initial pH 8.3, simultaneous high silica removal (75–80 %) and COD removal (45–50 %) can be obtained with PA hybrids, compared to 50 % silica removal and 45 % COD removal with PANS. The inverse relationship between silica and COD removal can be overcome with PA hybrids.

Flocculation monitoring by FBRM explains and justifies the results found by the jar tests although the differences observed by FBRM between PANS-PA1 and PANS-PA2 are larger than those in the jar tests. Hybrid coagulants reduced the MCS of the particles and increased the TNC, indicating different degrees of DCM destabilization. However, the base product PANS increased the MCS and only slightly the number of particles, which points to a limited DCM destabilization. The predominant flocculation mechanism of PA hybrids, i.e., patches formation, turned out to be more efficient than sweep flocculation and interparticle bridging for the destabilization of anionic contaminants of high surface charge like silica and organic colloids. The MCS decrease observed with the hybrids was lower at higher pHs while the increase in the TNC was generally higher at high pHs, thus indicating a stronger destabilization of DCM at the highest pHs, as observed in jar tests. Although FBRM monitoring detects the destabilization of DCM, it is not possible to determine if this DCM is mainly organic (COD removal) or inorganic (silica removal), however, FBRM seems to be more sensible to organic DCM removal.

During the last years, the authors have analyzed different alternatives to find the most suitable technique for the removal of silica prior to wastewater reuse in deinking applications. Coagulation with conventional and hybrid coagulants and softening at high pHs with the addition of soluble and sparingly soluble magnesium salts provided promising results with industrial waters. However, there is still room for improvement, especially regarding the high treatment costs. At present, adsorption as a new alternative for silica removal is studied.

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The authors have declared no conflict of interest.

Abbreviations

COD	chemical oxygen demand
DCM	dissolved and colloidal material
FBRM	focused beam reflectance measurement
MCS	mean chord size

PA	polyamine
PAM	polyacrylamide
PANS	polyaluminum nitrate sulfate
PANS-PA	polyaluminum nitrate sulfate-polyamine hybrids
PANS-PAM	polyaluminum nitrate sulfate-polyacrylamide hybrids
PDADMAC	polydimethyldiallylammonium chloride
RO	reverse osmosis
TNC	total number of counts

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Research Article: A high reuse of deinking paper mill effluents depends on successful silica removal. Formulations of hybrid coagulants based on the combination of an aluminum salt with polyacrylamide and polaymines are significantly more efficient than the base aluminum salts. They allow higher silica and chemical oxygen demand removals at considerably lower dosages without the need of pH regulation.

Enhanced Silica Removal by Polyamine- and Polyacrylamide-Polyaluminum Hybrid Coagulants

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Chem. Eng. Technol. **2015**, *38 (XX)*, XXX … XXX

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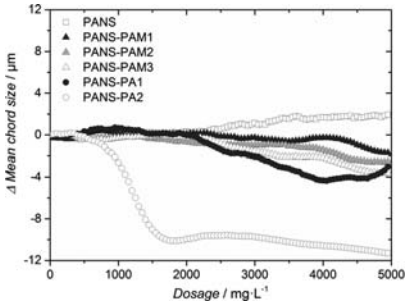

PUBLICATION III

I. Latour, R. Miranda, R. Carceller, A. Blanco

"Efficiency of polyaluminum nitrate sulphate-polyamine hybrid coagulants for silica removal"

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Efficiency of polyaluminum nitrate sulfate–polyamine hybrid coagulants for silica removal

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ABSTRACT

Previous studies have demonstrated the efficiency of commercial polyaluminum–polyamine coagulants for high silica removal from industrial effluents without pH adjustment. This paper studies the efficiency of newly developed tailor-made hybrid coagulants for silica removal, based on the combination of a commercial polyaluminum nitrate sulfate (PANS) and three polyamines (PAs) of different molecular weights. Four hybrids for each polymer, with different proportions of PANS and polyamine (5, 10, 15, and 20%) were tested at two initial pHs (8.4 and 10.5) and five dosages (in the range 500–2,500 mg/L). Results showed that without pH regulation (pH 8.4), all the hybrids were more efficient than PANS on silica removal, 5% of polyamine being the optimum content (>50 vs. 30% silica removal obtained by PANS). For the same level of efficiency (30% silica removal), the required dosages of hybrids are considerably lower than for PANS: 500 vs. 2,500 mg/L. At initial pH of 10.5, higher silica removal rates are obtained (90%) with all the products and the differences in efficiency between hybrid coagulants and PANS were minor. The hybrid coagulants were always more efficient in COD removal: 51 vs. 37% at initial pH 8.4, and especially at initial pH 10.5 (for similar silica removal): 31 vs. 4%. The effect of molecular weight of the PAs was significant for COD removal (higher molecular weight PAs are more efficient for COD removal), while it was not significant for silica removal efficiency. The main flocculation mechanisms and the visual aspect of the flocs for the different treatments have been analyzed. It is concluded that PANS induced a sweep flocculation, while PA hybrids produced flocculation by a combination of sweep flocculation and patch formation.

Keywords: Silica removal; Coagulation; Hybrid coagulant; Aluminum salt; Polyamine

1. Introduction

Coagulation is widely recognized as an efficient silica removal technique. In this sense, aluminum coagulants are effective for the treatment of high silica loaded waters such as deinking paper mill effluents [1–3]. Among aluminum coagulants, polyaluminum chlorides offer several advantages compared to traditional ones such as alum or sodium aluminate. They are effective in a wider range of pHs and at low temperature, generate more compact and easily sedimentable flocs, are less likely to cause overdosage phenomena and also less sensitive to water properties fluctuations [4,5].

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Although polyaluminum chlorides have been extensively used in the last decades for wastewater treatment, chlorides can cause corrosion problems, thus sometimes, chlorides are partially substituted by other species such as sulfates or nitrates, providing a new range of substituted coagulants. Polyaluminum nitrates, polyaluminum sulfates, or a combination of them, such as polyaluminum nitrate sulfates (PANS), have been developed and tested with success in different applications [6–8]. Besides, these products can also be modified with organic polymers to create inorganic–organic hybrids. The most extensively used organic polymers are cationic polyacrylamides (PAMs), polydimethyldiallylammonium chloride (p-DADMACs), and polyamines (PAs) [9–11]. Hybrid coagulants offer the advantages of allowing high removal rates at lower dosages, broader pH operating range, and smaller sludge production due to the synergy between the individual components [12].

Previous studies carried out by the authors proved that modifications of PANS coagulants with cationic polyelectrolytes improved the efficiency of PANS for silica removal [2,3]. In these studies, commercial hybrids based on a polyamine (PA) and two PAMs were tested. Results showed that PA hybrids were more effective for silica removal than PAM hybrids, allowing intermediate silica removal rates and significant COD removal even without pH adjustment. If pH adjustment was not needed, conductivity increase and pH decrease of the treated water would be lower and the effluent would be able to be treated by ultrafiltration (UF) and reverse osmosis (RO) with a normal recovery (the current limitation is 20% recovery) in order to reuse it in the paper mill [13].

Although commercial PA hybrids allow reducing the treatment cost as no pH regulation is required, these coagulants are expensive. This paper aims to generate new knowledge on the formulation and use of PANS–PA hybrids for industrial applications. Taking into account that PA prices are around double the price of the aluminum salts, one of the main factors to optimize is the percentage of polyamine combined with the aluminum salt. In this sense, the novelty of the paper is that different tailor-made coagulants are prepared combining a commercial PANS coagulant with three PAs of different molecular weights in different ratios (5–20 wt.% of PA) in order to optimize both, the PA type and the PA content. The objective is to obtain a new brand of highly effective products with low PA contents reducing the active content in the hybrids and the dosage needed in the process and thus the cost of the treatment. The effectiveness of the hybrids is studied at two initial pH levels (8.4 and 10.5) and at five dosages (500–2,500 mg/L). The requirements of the treatment are set in reducing silica concentration to around 20–60 mg/L to allow increasing RO recovery from 20% to 60–85%, without silica scaling problems in the RO membrane when reusing the effluent as fresh water in the process. Additionally, COD removal is also considered. Finally, the flocculation mechanism and floc aspect are studied in detail.

2. Materials and methods

2.1. Materials

2.1.1. Source of wastewater

This study was carried out with the effluent of a Spanish paper mill using 100% recovered paper to produce newsprint. This effluent is treated by a combination of a primary treatment by dissolved air flotation, followed by a secondary treatment in a moving bed bioreactor and a secondary dissolved air flotation. Water samples from the final effluent, before its discharge into an urban wastewater treatment plant, were taken. Table 1 summarizes its main characteristics. Dissolved fraction was obtained by filtration through 0.45-μm PTFE filters.

2.1.2. Chemicals

Different inorganic–organic hybrids have been prepared using PANS as the base product. PANS is a commercial PANS with an intermediate aluminum content and basicity (5.5% Al, 46% basicity), with 16.0% NO_3^- and 3.0% SO_4^{2-} contents. Hybrids were prepared by direct blending of PANS with three PAs of different molecular weights at ambient temperature, their molecular weight following the order:

Table 1
Characteristics of the effluent (raw water and dissolved fraction)

Raw water		
Parameter	Mean	Std. dev.
pH	8.4	0.1
Conductivity (25°C) (mS/cm)	1.8	0.1
Total solids (mg/L)	1,990	50
Turbidity (NTU)	11.4	0.7
Cationic demand (meq/L)	0.52	0.07
Dissolved fraction		
Total solids (mg/L)	1,890	40
COD (mg/L)	256	7
Silica (mg/L SiO_2)	145	11
Calcium (mg/L)	33.7	0.3
Magnesium (mg/L)	2.8	0.1

PA1 < PA2 < PA3. PANS and PA2 were supplied by Sachtleben Wasserchemie GmbH, while PA1 and PA3 were supplied by Kemira Oyj. Table 2 shows the main characteristics of these coagulants.

For each polyamine type, four different addition levels were tested. These levels were 5, 10, 15, and 20% wt% of commercial solutions (48–52% dry solids), the rest being PANS. Higher polyamine contents were also prepared, but the blends were unstable as evidenced by the appearance of turbidity within 24 h after its preparation. Additionally, PANS was also tested alone to evaluate its efficiency compared to the hybrid materials. Hybrids are noted as PANS–PAx-Z where PAx is PA1, PA2, and PA3 (depending on the polyamine used) and Z is the polyamine weight content in the hybrid. The aluminum content and the cationic charge of these hybrid coagulants, grouped by the commercial polyamine solution content, are shown in Table 3. Finally, all the hybrids and PANS were tested in combination with the same flocculant: an anionic polyacrylamide of high molecular weight and medium charge, supplied by Ciba (Switzerland).

2.2. Methods

For each coagulant, five dosages (500, 1,000, 1,500, 2,000, and 2,500 mg/L) were tested, those that were selected according to preliminary tests [2]. These dosages were tested at two pHs 8.4 (initial pH of the effluent) and 10.5, as silica removal increases at basic pHs and is almost removed completely at pH around 10.5 [2,3]. Higher pHs would increase significantly both the conductivity of the treated waters and the treatment costs, without further significant silica removals. Flocculant dosage was fixed at 10 mg/L in all the tests. A sample volume of 200 mL was used in all the experiments.

First, in the case of initial pH 10.5, the pH of the samples was adjusted by adding NaOH (10 wt./vol.%). After 30 s of high speed mixing at 200 rpm, the coagulant was added to the sample from a 10% wt./vol. solution and mixed at high speed (200 rpm) during 2.5 min. Next, the flocculant was added from a 0.10% wt./vol. solution and was mixed for 10 min at slow speed (40 rpm). Finally, the sample was allowed to settle during 60 min and the supernatant was characterized by pH, conductivity, cationic/anionic demand, and turbidity. Furthermore, reactive silica and chemical oxygen demand (COD) were measured in the dissolved fraction of the supernatant, obtained by centrifugation at 2,000*g* during 15 min in a Hettich Zentrifugen Universal 32. Jar tests were carried out in a multiposition magnetic stirrer OVAN MultiMix Heat D at room temperature (20 ± 2˚C) by duplicate, and the average error between replicates of the analytical measurements was always under 5%. Coagulants, the flocculant, and the pH regulator solutions were prepared on daily basis. To avoid the possible degradation of the wastewater, all trials were carried out within 5 d after the sampling and the waters were always kept stored at 4˚C until its used.

Table 2
Characteristics of the coagulants used for the hybrid formulations

Coagulant	Cationic charge (meq/g)[a]	Molecular weight
PANS	0.8	–
PA1	3.2	Low
PA2	3.4	Medium
PA3	3.8	High

[a]Expressed in g of commercial solution, measured through colloidal titration.

The pH was measured using a GLP 22 pH meter (Crison, S.A), according to Standard Method 4500 [14] and conductivity was determined with a GLP 31 conductivity meter (Crison, S.A.), according to the ISO 7888. Cationic and anionic demand was measured by colloidal titration using 0.001 N poly-diallyldimethylammonium chloride (p-DADMAC) and 0.001 N polyethylene sulfonic acid sodium salt (PES-Na) as titrants, respectively, in a CAS Charge Analyzing System supplied by AFG Analytic GmbH. Turbidity was measured with a LP 2000–11 nephelometer, supplied by Hanna Instruments, according to ISO 7027. Total solids were measured according to the Standard Method 2450 B [14]. Reactive silica was measured by flow analysis and photometric detection through silicomolybdate and reduction to molybdenum blue, using a FIA Compact (MLE GmbH), according to DIN EN ISO 16264 and expressed as mg/L of SiO_2. COD was photometrically measured by the Nanocolor® COD 1500 Method from Macherey-Nagel GmbH, according to ISO 15705:2003 in an Aquamate UV–vis spectrophotometer supplied by Thermo Scientific Inc. Finally, calcium and magnesium content was measured using a direct air-acetylene flame atomic absorption method, according to ISO-7980:1986 in a SpectraA 220 spectrophotometer supplied by Varian.

3. Results and discussion

3.1. Removal of contaminants

3.1.1. Silica

Fig. 1 shows silica removal rates obtained with different hybrid coagulants at initial pH 8.4 and 10.5.

Table 3
Characteristics of the hybrid coagulants

Coagulant	Polyamine content (wt.%)	Al (%)	Cationic charge (meq/g)
PANS	–	5.5	0.8
PANS–PAx-5	5	5.2	≈0.9–1.0
PANS–PAx-10	10	5.0	≈1.1
PANS–PAx-15	15	4.7	≈1.2
PANS–PAx-20	20	4.4	≈1.3–1.4

At initial pH 8.4, all coagulants were more effective than the base commercial polyaluminum salt (PANS). With PANS, silica removal obtained varied between 12 and 31% with 500 and 2,500 mg/L, respectively.

With PANS–PA1, maximum silica removal obtained was 47% with 2,500 mg/L of PANS–PA1–20. The other PA1 hybrids yielded very similar maximum efficiencies (around 40%) but at different dosages: 1,000 mg/L of PANS–PA1–5, 1,500 mg/L of PANS–PA1–10, and 2,000 mg/L with PANS–PA1–15.

At initial pH 8.4, PANS–PA2 hybrids showed slightly higher silica removal rates than PANS–PA1 hybrids (around 50%), with 2,500 mg/L of PANS–PA2–5 and PANS–PA2–10. With 500 mg/L, maximum silica removals of 39, 35, 26, and 23% were obtained with active contents of 5, 10, 15, and 20%, respectively. The addition of PA2 considerably improved silica removal especially at low dosages.

Silica removal efficiencies with PANS–PA3 hybrids were slightly lower than with PA2 but still higher than with PA1. In this case, maximum removal rates were achieved with 2,500 mg/L of the different hybrids and varied between 51% with PANS–PA3–5 and 40% with PANS–PA3–20. With 500 mg/L of PANS–PA3–5, 42% silica removal was obtained compared to 12% at the same dosage using PANS. On the other hand, silica removals obtained with 20% PA3 were lower than with the other three hybrids.

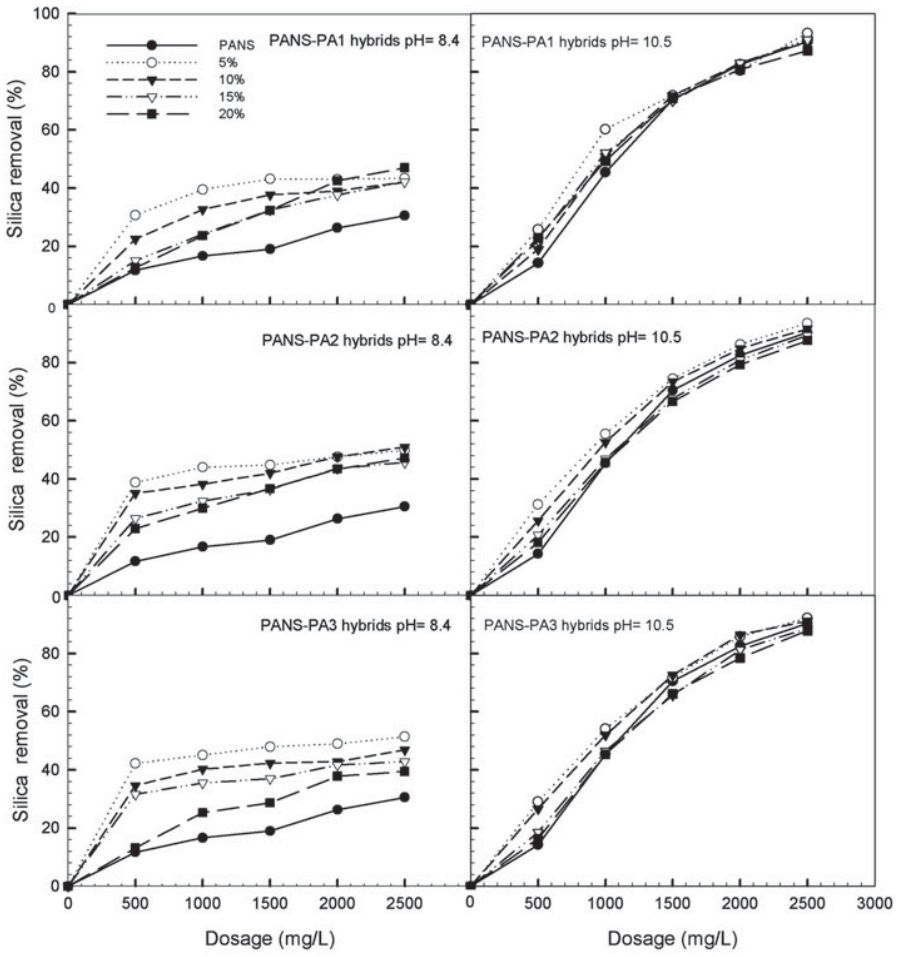

Fig. 1. Silica vs. hybrid coagulant dosage at different initial pHs.

As a general trend, it was observed that silica removal increased mainly at the lower dosages, while silica removal values remained almost constant at the highest dosages. This could be explained as at initial pH 8.4 only part of total silica is ionized, thus only a certain fraction of silica could be removed by coagulation. The higher alkaline pH, the higher ionization of silica, and hence higher removal rates could be achieved [15–17]. Very efficient products, such as the hybrids tested, removed most of silica ionized at low dosages. On the contrary, with a less efficient product such as PANS, silica removal continuously increased with the dosage and, even at the highest dosage tested; its efficiency was still far from those obtained with the hybrid coagulants. It was also observed that silica removal decreased with increasing polyamine content at the lower dosages. One of the factors affecting this behavior could be the lower aluminum content in the hybrid coagulant. In this sense, with the highest dosage of the hybrid coagulant (2,500 mg/L), where the aluminum content is high enough, the removal rates obtained with the hybrids were very close and the addition of the increased dosages of PAs did not have a detrimental effect on silica removal. It was also observed that, at lower dosages, high molecular weight polyamine was better for silica removal.

The synergy between the PAs and the aluminum salt allows achieving similar silica removal rates with 500 mg/L than with 2,500 mg/L of PANS, with only 5% of polyamine in the hybrids. Another advantage of using hybrid coagulants is that maximum 50% silica removal could be achieved compared to 31% with PANS, at 2,500 mg/L dosages.

Trends observed at initial pH 10.5 were very different to those obtained without pH regulation. At initial pH 10.5, silica removal continuously increased with the coagulant dosage. This could be explained by two simultaneous factors. The first one is that at this pH, silica was ionized in a larger extent than at pH 8.4, therefore more silica could be removed by coagulation. The second one is that at pH 10.5, there was more alkalinity available for aluminum coagulants to form the different aluminum hydroxides which are the active species in coagulation. At pH 10.5, the differences on silica removal rates between the hybrids and PANS were lower than at pH 8.4. On the other hand, the molecular weight of the polyamine or the percentage of polyamine in the hybrids had no significant effect. PANS was able to obtain 90% removal with 2,500 mg/L dosage. Moreover, still high removal rates of 71 and 83% were also obtained with lower PANS dosages: 1,500 and 2,000 mg/L, respectively. In the case of hybrid materials, silica removal rates were around 50, 70, 80, and 90% with 1,000, 1,500, 2,000, and 2,500 mg/L, respectively, for all the hybrids tested. At 500 mg/L, differences between the different hybrids were higher. In this sense, silica removal varied between 16% obtained with PANS–PA3–20 and 31% obtained with PANS–PA2–5, while with PANS was 14%.

As observed in previous studies, conventional and hybrid coagulants have large differences at lower pHs, while have similar efficiencies if the pH is high enough [2]. This is because aluminum coagulants are usually more efficient at high pHs as they require high alkalinity to form the aluminum hydroxides which are the active species on coagulations. Therefore, high pHs (and high alkalinities) can render better efficiency. On the other hand, PA polyelectrolytes do not require alkalinity consumption, allowing working efficiently in a wider pH range than aluminum products such as PANS. Therefore, although higher silica removals were expected at higher pHs due to ionization of silica, these increases would be higher in the case of PANS (as its efficiency is also increased) than in the case of PA hybrids (which has a similar efficiency in a wider pH range).

The use of the hybrid coagulants would not be justified at initial pH 10.5, since the marginal increase in silica removal would not compensate the increase in treatment costs due to the use of the organic polymers. This is completely different to what occurs at initial pH 8.4, where the use of hybrid coagulants would be clearly recommended. At initial pH 8.4, silica removal did not increase by increase in the polyamine content in the hybrid, showing the best results with 5% active content, which is also very beneficial for the treatment costs.

Taking into account the solubility of silica, to work at regular recoveries of 60–80% in RO membranes it would be necessary to decrease silica from 145 mg/L initial content to around 20–60 mg/L (60–85% removal). This objective could be achieved at pH 10.5 with all the hybrids and PANS, with dosages of 1,500 mg/L or higher. If higher removals were necessary it would be possible even to achieve a 94% silica removal with 2,500 mg/L of PANS–PA2–5 at initial pH 10.5. With no pH regulation, it was not possible to meet these stringent criteria as a maximum 50% removal rate was obtained. However, it could be an interesting option to reduce silica content in the effluent to achieve the necessary removal rates to meet SiO_2 limit for discharge (50 mg/L in Finland, Canada, or United States) [16] or to work at recoveries of 60–80% in RO membranes in paper mill effluents with around 100 mg/L initial SiO_2 content.

3.1.2. Chemical oxygen demand

Although the most critical parameter for effluent reuse in this paper mill is silica content, COD is also of interest to minimize the possible organic fouling on the membranes. Previous studies have demonstrated that there is a certain competition between COD and silica removal for a fixed dosage of coagulant, therefore silica and COD removals usually show opposite trends [1,2].

Fig. 2 shows the COD removal vs. dosage at initial pH 8.4 and 10.5. Opposite to silica, COD removal was lower at higher initial pH. At initial pH 8.4, the maximum COD removal was obtained at the highest dosage tested (2,500 mg/L) for all the hybrids. With the reference product (PANS), COD removals of 0, 12, 23, 31, and 37% were obtained with 500, 1,000, 1,500, 2,000, and 2,500 mg/L. At initial pH 8.4, PANS–PA1–10, among PA1 hybrids, was the best product at all the dosages. COD could be reduced from 270 to 160 mg/L (43% removal) either with 2,500 mg/L of PANS–PA1–5 or PANS–PA1–10. At initial pH 8.4, a maximum 44% COD removal was achieved with PANS–PA2–5. With PA2, maximum COD and silica removal were achieved under the same conditions of 2,500 mg/L of PANS–PA2–5. With PANS–PA3 hybrids, maximum COD removal of 51% was achieved with 2,500 mg/L PANS–PA3–15.

According to these results, COD removal increased with the active content of polyamine, but there was a maximum active content over which COD removal decreased. It was also observed that the higher the molecular weight of the polyamine the higher the removal rates. Additionally, the higher molecular weight of the polyamine the higher PA active content could be used in the hybrid before the efficiency decreased. In this sense, with 2,500 mg/L and 20% of active content, COD removals obtained were 8, 28, and 43% obtained with PA1, PA2, and PA3, respectively.

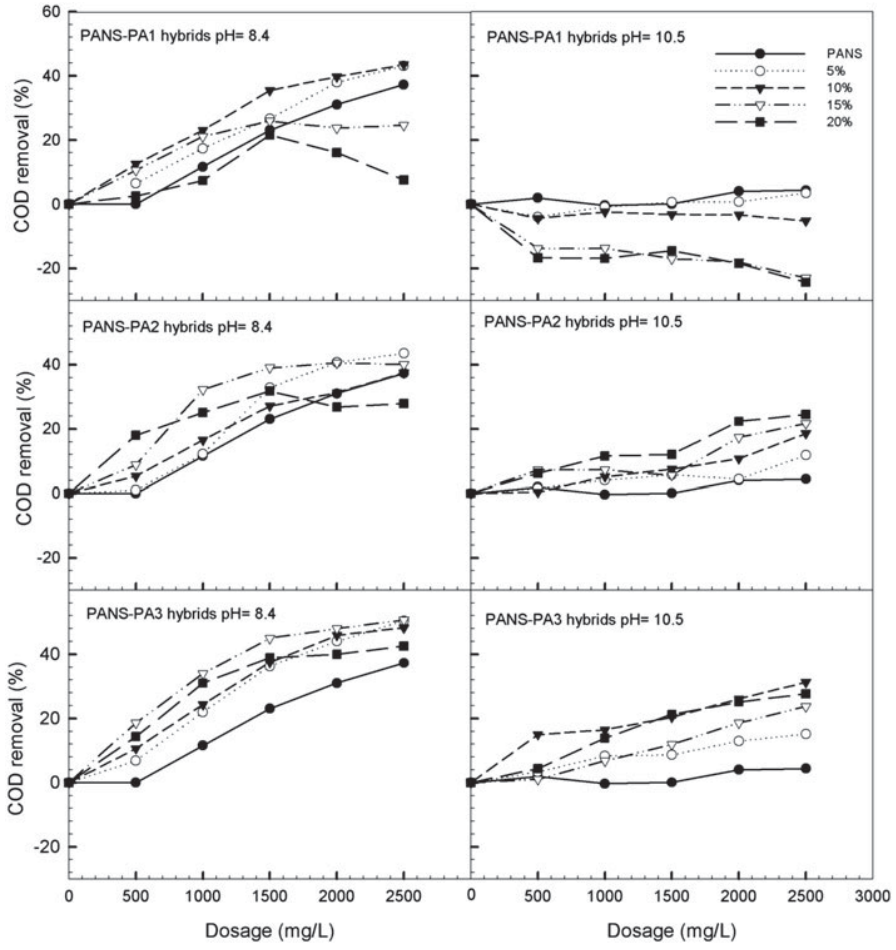

Fig. 2. COD vs. hybrid coagulant dosage at different initial pHs.

Moreover, COD removal rates obtained with PANS–PA3 hybrids were higher than with the reference product even with high silica removal rates which is of great interest. At pH 8.4, the optimum condition for silica and COD removal was obtained with 2,500 mg/L of PANS–PA3–5. Under these conditions, 50% silica removal and 50% of COD removal were achieved. As commented before, at initial pH 8.4, only part of the silica was ionized thus silica removal achieved a maximum at low dosages and then, remained constant. This did not occur with COD. In this case, the higher the dosage the higher the COD removal.

At pH 10.5, COD eliminations were lower than at initial pH 8.4. PANS obtained COD removal rates lower than 4% at the five dosages tested. This means that PANS had clearly more affinity for silica than for organic matter. PANS–PA1 hybrids did not remove COD, moreover, final COD values increased with the increase in the active content. The reason could be that the organic part of the hybrid coagulant could be measured as COD. COD removals with PA2 hybrids increased compared to PA1 hybrids. With PANS–PA2 hybrids, COD removal increased with the dosage and the active content, maximum removal of 24% was obtained with 2,500 mg/L of PANS–PA2–20. This maximum COD removal was not achieved under the same conditions of maximum silica removal. The decline in silica removal at the highest PA2 content was accompanied by an improvement in COD removal. Under the conditions of maximum silica removal (92%) at 2,500 mg/L of PANS–PA2–10, 19% COD removal was obtained. PANS–PA3 hybrids showed higher removal rates than other polymers and achieved a maximum COD removal of 31% with 2,500 mg/L of PANS–PA3–10, where the maximum silica removal of 91% was achieved. With 5% of active content, COD removal rates were slightly lower than with the rest of the PA3 hybrids tested. It seems that higher molecular weights of the polyamine (for a similar charge density) improve COD removal.

Based on the results obtained, it can be concluded that COD removal increased with the dosage of the hybrid and, opposite to silica removal, it decreased at higher initial pH. In general, it seems that high active contents impaired COD removal at pH 8.4, while enhanced COD removal at pH 10.5, probably due to the highest cationic demand at this pH which is still far from neutralization even at the highest active contents and dosages used. Finally, higher molecular weight PAs seem to be more efficient for COD removal.

3.1.3. Cationic demand

Another important parameter in coagulation processes is the cationic demand, which measures the surface charge of anionic particles in a suspension. A high reduction in the cationic demand is usually necessary to destabilize the contaminants of the waters.

The neutralization capacity of the different treatments is mainly governed by the charge density of the products, which can vary depending on the characteristics of the water such as pH or conductivity. As shown in Fig. 3, the three PAs had a considerable higher charge density than PANS (3.2–3.8 vs. 0.8 meq/g, Table 1). Additionally, it is important to notice that charge density of the aluminum salt was 0 meq/g at pHs over 9. Taking into account that high pHs are necessary for the ionization of silica, there is a need to find other type of products that do not lose their charge at alkaline pHs. In this sense, as it is observed in Fig. 3, the addition of the PAs to PANS made the charge of the products more independent of the pH. It is also important to consider that the initial cationic demand is higher at higher initial pHs because there is a higher content of hydroxide ions and, in a lower extent, some ionization of species such as carboxylic or fatty acids, which are present in the waters. Thus, to achieve charge neutralization at higher pHs, higher dosages of the coagulants are necessary.

As shown in Fig. 3, the charge density of the different hybrids was always higher than PANS and their charge was higher at increased polyamine active contents. On the other hand, there were no important differences on the charge density of the

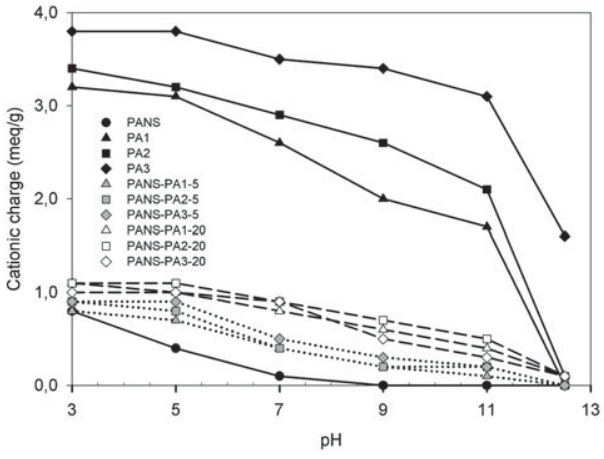

Fig. 3. Cationic charge vs. pH for the different coagulants.

different hybrids with the same percentage of polyamine. With the 20% hybrids, charge density was around 0.5–0.7 meq/g at pH 9 and around 0.3–0.5 meq/g at pH 11. Besides, for the 5% polyamine hybrids, charge density was around 0.1–0.2 meq/g at pH 9 and 11.

Fig. 4 shows final cationic demand with the different treatments. At initial pH 8.4 and 10.5, no charge reversal was achieved with the reference product (PANS), final cationic demand varied between 0.54 and 0.16 meq/L at pH 8.4 and 0.73–0.64 meq/L at pH 10.5. The decrease in cationic demand was higher at pH 8.4 than at pH 10.5 probably due to the lowest charge density of PANS at higher pHs. PA1 was the product with the lower charge density and its hybrids neither at pH 8.4 nor 10.5 achieved charge neutralization. Cationic demand of the treated water ranged 0.47–0.09 meq/L at pH 8.4 and 0.89–0.35 meq/L at pH 10.5.

With PA2 hybrids and at initial pH 8.4, charge neutralization occurred with PANS–PA2–15 and PANS–PA2–20 with dosages over 2,000 mg/L and over 1,500 mg/L, respectively. However, at pH 10.5, charge reversal did not occur. The cationic demand of the treated water varied between 0.8 meq/L with 500 mg/L of PANS–PA2–5 and 0.1 meq/L with 2,500 mg/L of PANS–PA2–20. PANS–PA3 also achieved charge reversal with the 15 and 20% hybrids but in this case at dosages higher than 2,000 mg/L. At pH 10.5, cationic demand varied between 0.72 meq/L with 500 mg/L of PANS–PA3–5 and 0.11 meq/L with 2,500 mg/L of PANS–PA3–20.

Although the reduction in cationic demand means the destabilization of anionic matter, it can be either inorganic (i.e. silica) or organic (i.e. COD). Therefore, a direct relationship between silica removal and cationic demand did not occur in all the cases, but it is clear that reduction in cationic demand is one of the main

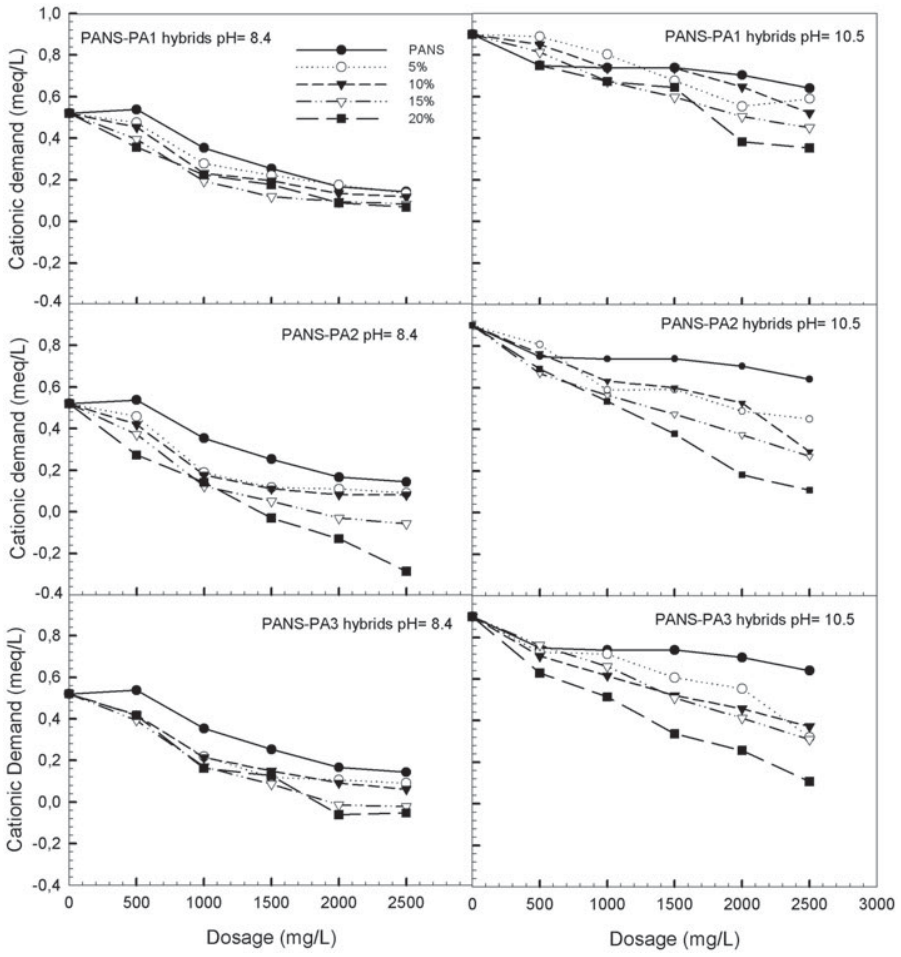

Fig. 4. Cationic demand vs. hybrid coagulant dosage at different initial pHs.

parameters affecting silica removal. It is very important to notice that charge reversal occurred for some hybrids (Fig. 4), however, this fact did not impair silica removal. This fact may be caused by the contribution of other coagulation–flocculation mechanisms apart from charge neutralization as explained in Section 3.2. It is also of interest that the higher the initial pH the higher the cationic demand. Consequently, when using coagulants with constant and even decreasing charge, the decrease in cationic demand would be lower. Moreover, higher initial pHs favor silica ionization, thus silica is removed by coagulation and/or precipitation [15–17].

3.1.4. Conductivity

Conductivity of the treated waters is also an important issue on this application for two reasons: (a) an important increase in the conductivity of the treated waters could increase scaling problems on RO membranes, which is exactly what is tried to be avoided and (b) a high conductivity of the treated waters could not make possible the direct discharge of RO rejects (discharge limit for this specific mill is 7.5 mS/cm), increasing the treatment cost and thus the economic feasibility of the whole effluent reuse treatment.

Final conductivity of the water is determined mainly by the pH adjustment and the nature and dosage of the coagulants used. At initial pH 10.5, the increase in conductivity caused by the pH regulation with NaOH was around 1 mS/cm compared to initial pH 8.4, i.e. conductivity of the water was 1.8 mS/cm at pH 8.4 vs. 2.8 mS/cm at initial pH 10.5. The coagulation treatment also affects the final conductivity but in a lower extent. Conductivity increases with the coagulant dosage, but this increase was in all the cases lower than 0.2–0.3 mS/cm at pH 8.4, and lower than 0.1 mS/cm at pH 10.5. The final conductivity with the reference product PANS was in the same range as the hybrid materials, as polyamine proportions are relatively low to observe significant changes.

3.1.5. pH

Metal salts such as aluminum salts consume alkalinity to form their active flocculation species, i.e. Al $(OH)_3$. This alkalinity consumption causes a pH decrease in the treated waters and its extent depends on the dosage of the product, their aluminum content, and basicity. In this study, the same dosages of the products were used, thus the differences were related to the aluminum content of the products and their basicity, which depends on the proportion of PANS in the hybrid materials. Theoretically, the higher the aluminum content and the lower basicity of the chemical, the higher the alkalinity consumption and hence, the higher pH decrease observed.

The pH after the treatment is also an important parameter to take into account when the water is going to be reused. To avoid any pH "shock" when mixing the treated effluent with process waters, which could cause several scaling phenomena, the pH should be around 7.5 ± 1.0. Besides, according to the discharge limits of the newsprint mill, the RO rejects should have a pH between 6.5 and 9.5 to avoid the need of a final pH adjustment.

Final pH was determined by: the pH adjustment before coagulation and the pH decrease caused by the alkalinity consumption of the coagulants. With the reference product (PANS), the highest pH decreases were obtained: 1.5 at initial pH 8.4 (final pH 6.9) and 0.9 at initial pH 10.5 (final pH 9.6). With the different hybrids, although the higher pH decrease was observed at the highest dosages, variations among the different hybrids were low, as the polymer content used was similar. With all the hybrids, pH decreased 1.2–1.5 units (final pH 6.9–7.2) at initial pH 8.4 and between 0.5 and 0.9 (final pH 9.6–10.0) at initial pH 10.5.

3.1.6. Turbidity

Turbidity varied depending on the treatment used. At initial pH 8.4, turbidity of the treated water decreased with the coagulant dosage. At this pH, with all the products tested including PANS, final turbidity lower than 3 NTU could be achieved. On the other hand, at pH 10.5, turbidity increased with the pH regulation from 10.4 NTU up to 30.0 NTU. At this pH, final turbidity also decreased with the coagulant dosage. PANS was able to reduce turbidity to 2.2 NTU. With the hybrids turbidity varied between 2.0 and 30.0 NTU.

3.2. Flocculation mechanism and flocs aspect

As commented before, high reduction in cationic demand is necessary to achieve high removal rates, however, other flocculation mechanisms, different to charge neutralization, are also possible. If the removal of the contaminants took place by charge neutralization, the maximum removal rate would be close to the isoelectric point and overdose would be possible (restabilization occurs at charge reversal). Charge neutralization is the main flocculation mechanism at

low dosages of aluminum. However, at high dosages of aluminum salts, where the solubility of $Al(OH)_3$ is exceeded, the main flocculation mechanism is usually "sweep flocculation". In this flocculation mechanism, the contaminants are removed by enmeshment in fresh precipitated flocs of $Al(OH)_3$. In this case, the optimum dosage of coagulant does not occur at the isoelectric point and no overdose phenomena are observed, even reaching charge reversal [5]. Generally, both mechanisms are also present. Due to the high dosages used in the present study, sweep flocculation seemed the predominant which is corroborated by the increased removal of contaminants at dosages exceeding the isoelectric point.

In the case of the PAs, other coagulation–flocculation mechanisms such as patch or bridging formation are common [18]. For polyelectrolytes of low to medium molecular weight and high charge density, as the PAs used in this study, patch model is usually the main flocculation mechanism. In this case, the maximum in the flocculation efficiency does not take place in the isoelectric point. This maximum is dependent on the charge of the local patches but occurs at ~50% coverage of surface particles. In the case of the hybrid coagulants, the flocculation mechanism would be the result of a combination of the flocculation mechanism of the aluminum salt (mainly sweep flocculation) and the polyamine (patch formation).

In this study, polyacrylamide was also added in a low dosage (10 mg/L) after coagulation. In this case, bridging formation is the typical flocculation mechanism for this high molecular weight and intermediate charge density polymer. However, depending on the initial pH and the nature of the coagulants, different aspect of the flocs were observed, especially when PANS and hybrid materials are compared. Figs. 5 and 6 show the aspect of the flocs obtained with PANS and the hybrids at initial pH 8.4 (Fig. 5) and initial pH 10.5 (Fig. 6). Pictures were taken just after flocculation and after 1 h settling.

At initial pH 8.4, flocs obtained with the PANS and the hybrids presented similar aspect. At this pH, the highest COD removal rates and the lowest silica removal rates were obtained, thus these flocs are mainly composed by organic matter. These flocs were very large and considerably light, presenting a higher tendency to float. On the other hand, at initial pH 10.5, silica removal increased, while COD removal decreased. As observed in Fig. 6, the flocs were clearly heavier than at pH 8.4 and settled very easily due to the higher density of flocs removing silica than those removing organic matter. Moreover, at pH 10.5, significant differences in the flocs obtained with PANS and with the hybrids were observed. Flocs obtained with PANS were small and homogeneously dispersed, which is in agreement with a predominant sweep

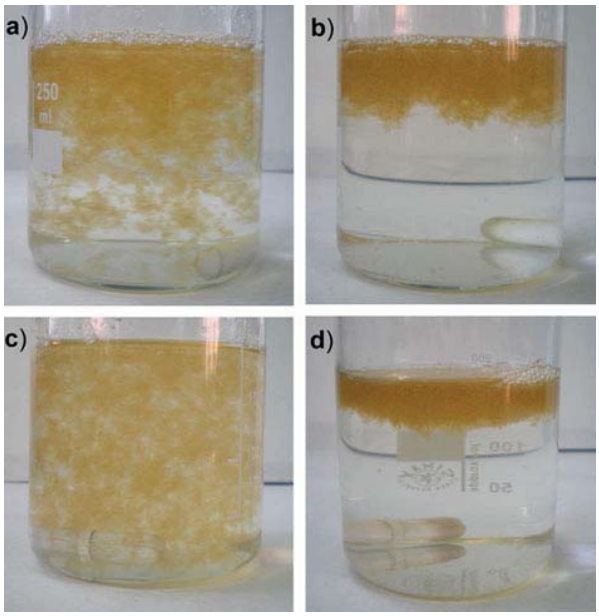

Fig. 5. Flocs formed at initial pH 8.4: (a) PANS after flocculation, (b) PANS after settling, (c) Example of hybrid material after flocculation, and (d) Example of hybrid material after settling.

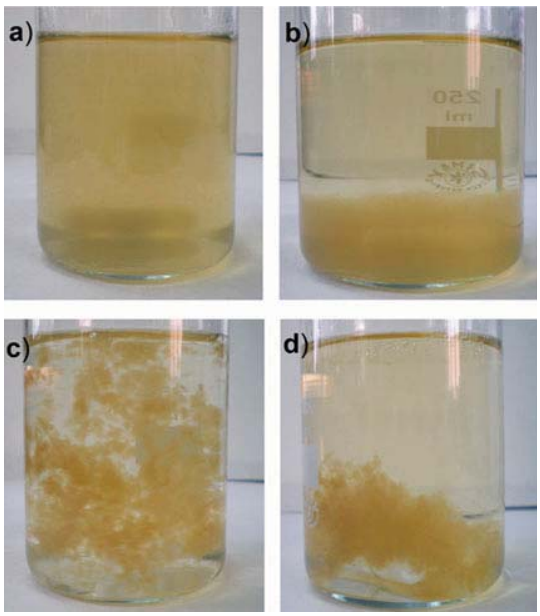

Fig. 6. Flocs formed at initial pH 10.5: (a) PANS after flocculation, (b) PANS after settling, (c) Example of hybrid material after flocculation, and (d) Example of hybrid material after settling.

flocculation mechanism. In the case of hybrids, the aspect of the flocs was similar to the one obtained at initial pH 8.4 but heavier and denser due to the higher presence of inorganic matter in the flocs. These flocs were larger than those obtained by PANS, therefore a partial patch flocculation mechanism enhanced the formation of larger flocs than those of sweep flocculation.

There were two factors affecting the behavior and aspect of the flocs, both conditioned by the initial pH. The first factor affecting the floc aspect is silica ionization. When silica is ionized, it is preferably removed compared to organic matter. In this case heavy flocs which settle easily are formed. Second, the flocculation mechanism is dependent on pH and the nature of the coagulants. As observed in Figs. 5 and 6, the aspect of the flocs obtained with the hybrid coagulants was similar at both operational pH indicating that the flocculation mechanism was the same. However, flocs formed by PANS were very different due to the higher extent of sweep flocculation at initial pH 10.5 than at pH 8.4.

4. Conclusions

(1) Hybrid coagulants are always more efficient than PANS, especially at lower pHs, being 5% the optimum polyamine content. This active content allows simultaneous high silica and COD removal rates and lower treatment cost.
(2) At initial pH 8.4, all the hybrid coagulants are more efficient than PANS in silica removal (50% maximum removal vs. 32% at 2,500 mg/L). Furthermore, the same silica removal (around 30%) is obtained with considerably lower dosages of the hybrids compared to PANS (500 vs. 2,500 mg/L).
(3) At initial pH 10.5, higher silica removal can be obtained (90%), however, differences between hybrids and PANS are lower than at initial pH 8.4. Therefore, in this case, hybrid coagulants would not be recommended.
(4) Hybrid coagulants are also more efficient for COD removal than PANS, 51 vs. 37% at initial pH 8.4 and 31 vs. 4% at initial pH 10.5. PAs of higher molecular weight are more efficient for COD removal.
(5) At initial pH 8.4, flocs are mainly composed by organic matter which form large and loose flocs with a higher tendency to float. At initial pH 10.5, flocs are mainly composed by inorganic matter (silica). These flocs are still large (especially those of the hybrid coagulants), but they are heavier and with a tendency to settle.
(6) The main flocculation mechanism for PANS is sweep flocculation, while for PANS–polyamine hybrids it is a combination of sweep flocculation and patch formation.

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PUBLICATION IV

R. Miranda, **I. Latour**, A. Blanco

"Influence of suspended solids on silica removal by coagulation with aluminum salts"

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INFLUENCE OF SUSPENDED SOLIDS ON SILICA REMOVAL BY COAGULATION WITH ALUMINUM SALTS

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Effluents with high silica content can exceed the discharge limits and/or limit the application of reuse treatments based on reverse osmosis membranes. In these cases, silica removal is usually carried out in the effluent by coagulation. In this work, silica is removed from process waters in dissolved air flotation (DAF) units used as internal treatments. It is hypothesized that the presence of a high content of small suspended solids and colloids in DAF units should favour the rate of precipitation of $Al(OH)_3$ and the orthokinetic flocculation, thus the removal efficiency of contaminants. Results confirmed that the coagulant required for silica removal in the process water is 20-50% lower than in the effluent, especially in DAF2, where the amount of suspended solids is higher and their size is smaller. If the main aim is silica removal, the most efficient coagulants are PAC-HB in DAF1 and PAC-MB in DAF2. If a simultaneous high removal of turbidity and soluble COD is required, the recommended treatment is PANS-PA2.

Keywords: dissolved air flotation, silica, papermaking, coagulation, aluminium

INTRODUCTION

The paper industry is a large consumer of fresh water, being the reduction of water use an issue of growing importance due to the stringent environmental legislation, the increase in water prices, the treatment costs, or simply due to the lack of water resources.[1-4]

The internal reuse of process water after the treatment with dissolved air flotation (DAF) units is the most common alternative used to reduce the fresh water consumption. In recycled newsprint mills, there are up to three or four DAF units in each production line (one in each water loop). In these units, suspended solids are easily removed, but dissolved and colloidal material (DCM) is almost completely recirculated into the process, accumulating in the water circuits, and thus limiting the degree of closure treatment.[5] However, with an adequate coagulation and flocculation, DAF units can also remove finely dispersed and colloidal particles (>0.1-0.2 μm).[6] Dual systems allow the removal of 80-99% suspended solids and, in the best cases, 10-30% of soluble COD.[7-10] Inorganic contaminants are usually not removed in DAF units, in fact, the conductivity of the treated waters is normally higher than before the treatment, especially when metal coagulants are used.

A variety of coagulants can be used in DAF systems, including alum, ferric chloride, polyaluminum chloride (PAC), polyamine (PA), polydiallyldimethylammonium chloride (PDADMAC), etc. Among them, aluminum based coagulants are probably some of the most versatile and widely used. In addition to alum, many types of polyaluminum coagulants are commercially available for water treatment, such as PAC, aluminum chlorohydrate and polyaluminum sulfates. These products differ in their basicity and strength, and can contain small amounts of other substances, such as sulphate, nitrate, silica and calcium.[11] Furthermore, polyaluminum based coagulants can be combined with cationic polyelectrolytes, such as PA or PDADMAC, in hybrid coagulants to improve their efficiencies.[9,12-13]

Silica is one of the most important salts accumulating in papermaking water circuits. The main origin of silica is the sodium silicate added as process additive for improving the deinking and bleaching processes, which are the most important stages to achieve the optical properties required for producing graphic papers.[14] Some attempts have been carried out to replace it,[15,16] however, its variety of functions

and low price make it very difficult. There are three main problems derived from high silica contents in the process waters. First, the deposit formation, especially in paper mills with highly closed water circuits, where typical levels are around 150-250 mg/L SiO_2.[17-19] Second, the discharge limit for the effluent set by environmental legislation for silica is more and more stringent, i.e. 50 mg/L in Finland, Canada or United States.[18] Finally, reclamation and reuse of the final effluent is an emerging technique to further reduce the fresh water consumption and even substitute it completely. In this case, reverse osmosis (RO) membranes are usually included as a final step to achieve the high quality water necessary to replace fresh water use at critical points of the process. In these cases, silica scaling limits RO recovery to a maximum of a 20%, thus limiting the economic and technical feasibility of the effluent reuse treatment.[3]

Although a great variety of techniques have been used for silica removal, the most common ones are the softening process or the coagulation at high pH.[18,20-26] These techniques obtain high removal efficiencies at low costs, which is a prerequisite to be used in the paper industry. A high initial hardness content, especially magnesium hardness, is usually required for silica removal by softening to avoid the addition of calcium and magnesium salts, which would significantly increase the dissolved solids of the treated waters and also the costs.[25,27] In these cases, but not restricted to them, coagulation is an attractive silica removal technique.

Previous studies have demonstrated that silica removal in the effluent requires high dosages of coagulants and high pHs to achieve the silica removal rates required to avoid silica scaling on RO membranes.[19,23] Without pH regulation (pH 8.3), the removal of silica in the effluent was always lower than 50%, even with the most efficient products at the highest dosage tested (2500 mg/L). This turns to an average of 25-40 mg coagulant per mg SiO_2 removed.[19] Since the effluent has a very low suspended solids content, the rate of precipitation of $Al(OH)_3$ could be improved at higher concentration of small suspended solids and colloids as they can act as nuclei for the formation of $Al(OH)_3$ precipitates.[28] Therefore, it is hypothesized that the coagulant demand, mg of coagulant per mg SiO_2 removed, would be lower in the inlet of DAF units (with higher suspended solids levels of small size and colloids) than in the effluent. In addition, silica removal in the inlet DAF streams would also contribute to obtaining cleaner water loops and would require less investment (existing DAF units are used).

Therefore, the approach presented in this study is different from previous studies as the objective is to remove silica using two existing DAF units by optimizing their coagulation chemistry with different aluminium based coagulants. In addition, it would be of major importance to determine if in these process streams, due to the high concentration of suspended solids and colloids, it is possible to achieve higher removal of silica per mg of coagulant used, as the dosages required for silica removal in the effluent have been previously determined to be very high, especially at neutral pHs.

EXPERIMENTAL

Materials

Waters

Water samples were taken from the inlet of two DAF units of a newsprint mill, named DAF1 and DAF2. The main characteristics of these waters are shown in Table 1. Additionally, Figure 1 shows the chord size distribution of the waters, measured by the focused beam reflectance measurement (FBRM) technique (1-1000 μm size range), and Table 2 summarizes the main statistics related to the number and size of suspended particles.

Although the level of total solids (TS) and total dissolved solids (TDS) is not very different in both DAF units, there are important differences in terms of total suspended solids (1620 mg/L in DAF1 and 3350 mg/L in DAF2) and their size (see Figure 1). In DAF2, the mean chord size and median chord size of suspended particles are 10.4 μm and 7.1 μm, respectively. Furthermore, 65.3% of the suspended particles are lower than 10 μm and 87.0% lower than 20 μm (Table 2). However, the suspended solids are larger in DAF1: 43.7 μm mean chord size and 34.4 μm median chord size. This higher amount of suspended solids and their lower size result in a considerably higher turbidity in DAF2 waters than in DAF1 waters.

Table 1
Characteristics of DAF1 and DAF2 inlet waters and DAF1 and DAF2 blanks

	DAF1 inlet	DAF2 inlet	DAF1 blank	DAF2 blank
pH	6.9	7.7	6.8	7.6
Conductivity (25 ºC) (mS/cm)	2.62	2.13	2.12	1.74
Total solids (mg/L)	5520	6590	3394	3520
COD (ppm)	3665	3310	2332	2420
Total suspended solids (mg/L)	1620	3350	183	930
Turbidity (NTU)	680	2400	268	1850
Cationic demand (meq/L)	1.16	1.28	0.99	1.00
Total alkalinity (ppm $CaCO_3$)	856	1425	645	1020
After centrifugation				
Total solids (mg/L)	3898	3240	3211	2590
Dissolved silica (mg/L SiO_2)	273	240	225	200
Dissolved COD (ppm)	2600	2285	2010	1876
Dissolved turbidity (NTU)	21.8	89	18.0	76

Table 2
Average chord sizes of the particles in the raw waters: DAF1 vs. DAF2

	DAF1		DAF2	
Mean chord size (1-1000 µm) (µm)	43.7		10.4	
Median chord size (1-1000 µm) (µm)	34.4		7.1	
		%		%
Number of particles (1-5 µm) (#/s)	234	10.7	633	33.2
Number of particles (5-10 µm) (#/s)	240	11.0	613	32.1
Number of particles (10-20 µm) (#/s)	282	12.9	413	21.7
Number of particles (20-29.3 µm) (#/s)	213	9.7	160	8.4
Number of particles (29.3-50.1 µm) (#/s)	451	20.6	71	3.7
Number of particles (50.1-100 µm) (#/s)	574	26.3	14	0.8
Number of particles (100-199.5 µm) (#/s)	183	8.4	2	0.1
Number of particles (199.5-1000 µm) (#/s)	11	0.5	0	0.0
Total number of particles (1-1000 µm) (#/s)	2188	100.0	1906	100.0

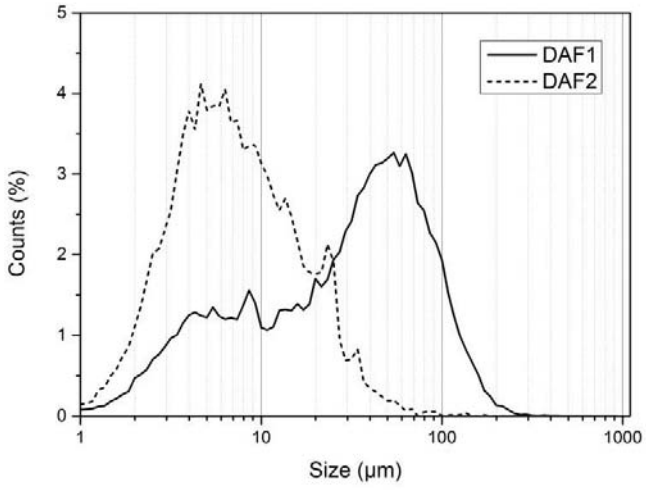

Figure 1: Chord size distribution of DAF1 and DAF2 waters

Table 3
Characteristics of the coagulants used in this study

Coagulant	Al_2O_3 (%)	Basicity (%)	Charge density (meq/g)	Density (g/cm^3)	pH	Dry content (%)
Alum	15.3	0	-	-	-	-
PAC-MB	16.8	37	1.77	1.37	< 1	34.1
PAC-HB	9.7	85	1.67	1.22	2.7	29.5
PANS	10.2	46	1.22	1.27	2.6	21.7
PANS-PA1	8.8	-	1.68	1.26	2.0	21.3
PANS-PA2	6.05	-	2.57	1.23	3.0	20.4

Coagulants

Table 3 summarizes the main properties of the six aluminium coagulants tested. Alum ($Al_2(SO_4)_3 \cdot 18H_2O$), reagent grade, was supplied by Panreac. PAC-MB is a conventional polyaluminum chloride with high aluminum content and intermediate basicity (16.8% Al_2O_3, 37% basicity), supplied by Sachtleben Wasserchemie GmbH, while PAC-HB is a high basicity polyaluminum chloride with intermediate aluminium content (9.7% Al_2O_3, 85% basicity) with a small amount of silica, supplied by Kemira Ibérica S.A. PANS is a polyaluminum nitrate sulphate with intermediate aluminum content and intermediate basicity (10.2% Al_2O_3, 46% basicity), having a 16.0% NO_3^- and 3.0% SO_4^{2-} contents, and PANS-PA1 and PANS-PA2 are two derivatives obtained by the addition of different dosages of a high charge density and low molecular weight quaternary polyamine to PANS; all these three coagulants were supplied by Sachtleben Wasserchemie GmbH. The active content in PANS-PA1 is around three times lower than in PANS-PA2. All the coagulants were tested in combination with an anionic polyacrylamide of high molecular weight and medium charge used as flocculant, supplied by SERTEC-20 S.L. (Spain).

PANS-PA1 was included in the tests with DAF2 waters after the good results obtained by PANS-PA2 with DAF1 waters, to determine if it was possible to reduce the cost of this hybrid coagulant by reducing the polyamine active content.

In DAF1, the dosages of the coagulants were selected according to preliminary tests, varying from 25 to 250 ppm Al_2O_3. As the dosages of the coagulants in terms of commercial products were very different, in the second study all the products were tested at the same dosages of commercial products (100-1250 mg/L), independently of their aluminium content. For a better comparison between the studies, the commercial product dosage has always been used for the discussion of the results.

Methodology

DAF tests

Experiments were carried out in a lab-scale DAF unit (Flottatest FTH3) supplied by Orchidis Laboratoires. A sample volume of 1 L was used in all the cases. In these tests, first the coagulant was added to the sample from a 10% wt/vol solution and mixed at high speed (180 rpm) during 2.5 min. Next, the flocculant was added from a 0.10% wt/vol and mixed at slow speed (40 rpm) for 10 min. Finally, a 20% tap water (200 mL) saturated in air at 7 bar was added, and after 10 min flotation time, samples were collected from the bottom of the jars.

A number of blanks for each DAF waters were carried out without adding any chemical, to consider the dilution of the samples due to the addition of air-saturated water during flotation (20%) and the physical efficiency of the DAF (without any chemicals). The average values for these blanks are referred to as 0 mg/L dosage and their characteristics are summarized in Table 1. All the experiments were carried out at room temperature (20-25 ºC) by duplicate, and the average error between replicates was around 5%. To avoid the possible degradation of the waters, all trials and analyses were carried out within five days after the sampling and the waters were always kept at 4ºC before use.

The different treatments were evaluated for turbidity, total solids, chemical oxygen demand (COD), cationic/anionic demand, alkalinity, pH and conductivity in the clarified waters, and turbidity, silica, total solids and sulphates in the dissolved fraction of clarified waters. The dissolved fraction was obtained after centrifugation of clarified waters at 2000 g during 15 min in a Universal 32 centrifuge (Hettich Zentrifugen GmbH). Total solids and turbidity were measured according to Standard Methods 2540B and 2130B, respectively,[29] using a Hanna LP-2100 turbidimeter for turbidity. COD was measured by the Nanocolor® COD 1500 method from Macherey-Nagel GmbH, using an Aquamate Vis spectrophotometer (Thermo Scientific Inc.), according to ISO 15705:2003. Cationic/anionic demand was measured by colloidal titration using a Charge Analyzing System (CAS) supplied by AFG Analytic GmbH and polydiallyldimethylammonium chloride (PDADMAC (0.001 N) and polyethylene sulfonic acid sodium

salt (PES-Na) (0.001 N) as titrants, depending on the sample charge. Silica was measured by ISO standard 16264:2002 "Water quality – Determination of soluble silicates by flow analysis (FIA and CFA)". In this method, silica reacts with molybdate under acidic conditions to form yellow beta-molybdosilic acid; this acid is subsequently reduced with stannous chloride to form a heteropoly blue complex that has an absorbance maximum at 810 nm. Total alkalinity was measured by titration of the sample to pH = 4.5 with H_2SO_4 0.1 N, using an automatic titrator (Compact I model, supplied by Crison) connected to a pH probe, according to EPA 310.1 method. Sulphates were measured by the Nanocolor® Sulphate 200 or Sulphate 1000 methods from Macherey-Nagel GmbH, using an Aquamate Vis spectrophotometer (Thermo Scientific Inc.). Finally, the pH and conductivity of the samples were analyzed using a GLP-22 pH-meter and a GLP-32 conductivity meter (both supplied by Crison Instruments, S.A.).

RESULTS AND DISCUSSION

Removal of contaminants

Turbidity and solids

DAF1 waters had a turbidity of 680 NTU. DAF1 blank, without chemicals, had a turbidity of 268 NTU (60.6% removal, including the 20% removal due to the dilution of the raw waters with water saturated in air). This indicates the size of suspended solids is large enough to be significantly removed without the addition of any chemical. The addition of 10 mg/L flocculant further reduced the turbidity to 196 NTU (71.2% removal referred to raw waters, 27% removal referred to blank). When coagulants were used, turbidity removal increased continuously with the dosage up to around 1500 mg/L, with only marginal increases at higher dosages (Figure 2a). While PANS-PA2, PAC-HB and PANS decreased turbidity to a maximum of 55-60 NTU (80-85% removal) at around 1500 mg/L, alum and PAC-MB decreased turbidity to a maximum of 80-90 NTU (65-70% removal), at around 1000 mg/L. Dissolved turbidity (data not shown) also decreased at higher dosages of coagulant, with no significant differences at dosages higher than around 1000 mg/L. In this case, PANS-PA2, PAC-HB and PANS decreased the dissolved turbidity from around 22 NTU to 9.5-10.5 NTU (50-60% removal), while in the case of alum and PAC-MB, the minimum dissolved turbidity obtained was around 10 NTU (alum) and 13.5 NTU (PAC-MB).

In the case of alum and PAC-MB, an increase in turbidity and dissolved turbidity was observed at dosages >1000 mg/L, indicating that restabilization by charge reversal could have taken place. Although alum and PAC-MB were the products with the highest aluminum content (15.3-16.8% Al_2O_3), the same aluminum dosages were tested for all the coagulants and this effect was not observed for any of them. The explanation of this behavior is related to the higher pH decrease after the treatment with these coagulants due to their low basicities (final pH around 5.4 for alum and 6.0 for PAC-MB). The pH of minimum solubility of $Al(OH)_3$, which produces the larger amount of $Al(OH)_3$ precipitates and the lower residual aluminum concentration, is around 6.0 for alum and 6.2-6.4 for PACs.[30] For these reasons, the lower pH at which aluminum salts can be used is limited to around 5.5-5.8, depending on the temperature and the presence of other species, i.e. sulphates, phosphates, etc.[31] In these industrial waters, this pH limit seems to be slightly lower: around 5.8 for alum and 6.0 for PAC-MB.

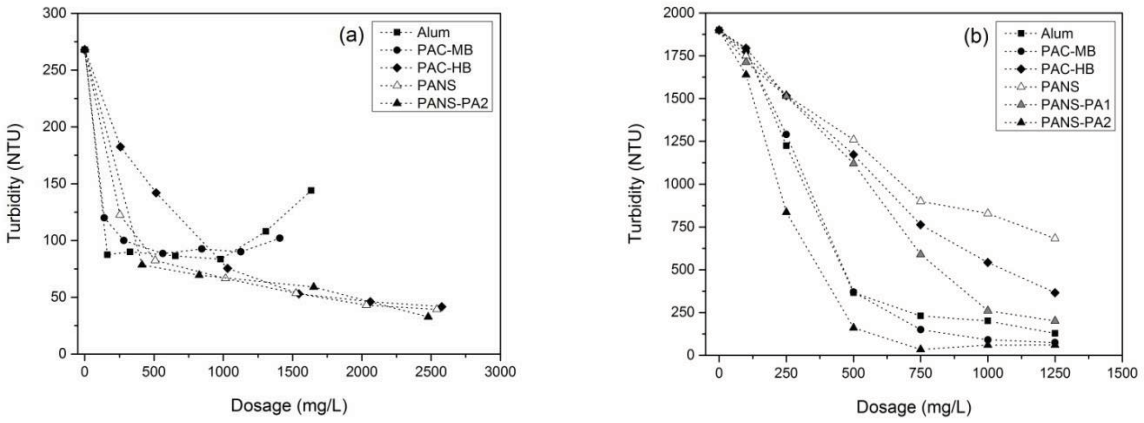

Figure 2: Turbidity of clarified waters from (a) DAF1 and (b) DAF2 vs. dosage of coagulants

Although around 50% of total solids were suspended solids in DAF2 waters, these suspended solids had a very small size to be efficiently removed without any previous coagulation, especially for a DAF laboratory cell with worse hydrodynamics than industrial DAF units. Without chemicals or using only flocculant, there was no significant removal of turbidity, the decrease in turbidity from 2400 NTU (inlet DAF2 waters) to 1850 NTU (DAF2 blank) or 1750 NTU (DAF2 with 10 mg/L flocculant), was mainly justified by the 20% saturated in air-tap water used for flotation. However, aluminium salts resulted to be very efficient in reducing turbidity (Figure 2b). The most efficient products were PANS-PA2, PAC-MB and alum. At the highest dosages of these products, the turbidity of the clarified waters could be reduced to 60-120 NTU (93-97% removal) and even at intermediate dosages, i.e. 500 mg/L, 90% removal could be achieved (150-350 NTU residual turbidity). On the other hand, PANS and PAC-HB were the lowest efficient products, with turbidity removals varying in the range 65-80% (350-700 NTU residual turbidity), even at 1250 mg/L dosage. The efficiency of PANS-PA1 was intermediate. The dissolved turbidity in DAF2 waters was not reduced by DAF without previous coagulation (data not shown). The dissolved turbidity of the blank and after adding 10 mg/L of flocculant (both 76 NTU) was practically the same as the dissolved turbidity of the raw waters (89 NTU) after considering the 20% dilution with tap water. When coagulants were used, the most efficient products were again PANS-PA2, PAC-MB and alum, reducing dissolved turbidity to 5-10 NTU (≈90% removal). The other products had similar efficiency, which was very low compared to the previous three coagulants; dissolved turbidity is 25-50 NTU (35-70% removal).

Comparing DAF1 and DAF2 treatments, the optimum ones for the removal of turbidity were opposite. In DAF1, the coagulants with the highest basicities (PAC-HB and PANS) plus PANS-PA2 were the most efficient, independently of their aluminium content. However, in DAF2, the most efficient products were those with the highest aluminium content (PAC-MB and alum), which were the least efficient coagulants in DAF1, and again PANS-PA2. In principle, at the same commercial dosage, PAC-MB and alum could produce a larger amount of $Al(OH)_3$, thus a higher removal of contaminants. Nevertheless, in DAF1, the pH was the most critical parameter, and due to the lower basicity of these products, a large pH decrease was observed, which impaired its efficiency due to the rapid increase of solubility of aluminium at pHs lower than 5.8-6.0. On the other hand, PANS-PA2 was the coagulant with the lowest aluminium content but including a polyamine in its composition, which also contributes to the destabilization of the contaminants. The combination of PANS with polyamine was very efficient in reducing turbidity independently of the water tested.

Similar conclusions could be obtained from the analysis of total and dissolved solids of the clarified waters from DAF1 and DAF2 waters (data not shown). In DAF1, PANS-PA2 and PAC-HB reduced total solids from 3.39 g/L of the DAF1 blank to 3100-3150 mg/L, which means around 10% TS removal and 3% TDS removal (TDS in DAF1 blank is 3210 mg/L). Although PANS-PA2 and PAC-HB increased the level of inorganics in waters due to their inorganic nature (a higher final conductivity in treated waters was observed), final TDS were lower than the DAF blank as they also removed an important amount of DCM. On the other hand, PAC-MB and PANS-PA increased slightly the total dissolved solids, indicating a lower removal of DCM. Finally, alum increased up to 8% the TDS due to the important amount of sulphates released to waters, however, some DCM was removed as the increase in TDS was lower than expected by the sulphates content in alum (540 mg/L sulphates at 1250 mg/L alum dosage).

In DAF2 waters, higher solid removals for similar levels of total and dissolved solids were achieved. Even the DAF blank achieved an important removal of suspended solids, from 3.35 g/L to 0.93 g/L (72.2% removal), although only a 22.9% removal of turbidity was achieved. This apparent controversy could be explained because in DAF blank the biggest size particles were removed predominantly, which contributes most to the total weight of suspended solids, while the smallest size particles, contributing less to the total weight of suspended solids, but being the main origin of turbidity, were not removed. In DAF2 waters, the most efficient products were PANS-PA2 and PAC-MB (2200-2300 mg/L). PANS-PA2 removed 38% TS and 15% TDS, while PAC-MB removed 35% TS and around 10% TDS. The next products in terms of efficiency were PANS-PA1, PAC-HB and alum, with TS ranging between 2.55-2.67 g/L (24-30% TS removal) and almost no removal of dissolved solids (TDS in DAF2 blank is around 2.59

g/L). As occurs in DAF1, if the sulphates theoretical release were subtracted to final TS, the TDS would be around 1.99 g/L, i.e. 23% dissolved solids removal, a value that is in agreement with the high turbidity and dissolved turbidity removals obtained.

Silica

Without coagulation treatment, silica was not removed at all by DAF. The 20% reduction of silica in DAF1 and DAF2 blanks (225 and 200 mg/L SiO_2, respectively), compared to the raw waters (273 and 240 mg/L SiO_2, respectively), was caused by the dilution of the sample after the addition of water saturated in air during the flotation process. Similar results were obtained when adding 10 mg/L flocculant (223 mg/L SiO_2 in DAF1 and 197 mg/L in DAF2). The use of aluminum salts increased significantly the removal of silica (Figure 3). As shown, there was a continuous improvement of silica removal with the coagulant dosage, independently of the coagulant tested, similar to what was observed for COD.

In the treatment of DAF1 waters, only small differences among the coagulants were observed, the main difference was observed between PAC-HB and PANS-PA2 (the most efficient coagulants) and PANS (the least efficient coagulant). PAC-HB and PANS-PA2 obtained 27-28% removal at around 1500 mg/L (residual 162-164 mg/L SiO_2) and 37-41% at around 2500 mg/L (residual 133-142 mg/L SiO_2). On the other side, PANS obtained an 18% removal at around 1500 mg/L (184 mg/L SiO_2) and 35% removal at around 2500 mg/L (residual 154 mg/L SiO_2). The other coagulants (alum and PAC-MB) achieved intermediate removal efficiencies, around 22% at 1500 mg/L (residual 175 mg/L SiO_2). According to silica removal rates, the following ratios (mg of coagulant required per mg of SiO_2 removed) were obtained (0-1500 mg/L): 25 for PAC-HB, 27 for PANS-PA2, 28 for PAC-MB, 29 for alum and PANS-PA2, and 37 for PANS.

For the treatment of DAF2 waters, PAC-MB, alum and PANS-PA2 were the most efficient products, achieving a maximum of 30-35% removal (residual 130-140 mg/L SiO_2) at 1250 mg/L. The other coagulants (PANS, PANS-PA1 and PAC-HB) obtained similar efficiencies, varying in the 20-25% range (residual 150-160 mg/L residual SiO_2) at the same dosage 1250 mg/L. In this case, the following ratios (mg of coagulant per mg of SiO_2 removed) were obtained (0-1250 mg/L): 19-20 for alum, PAC-MB and PANS-PA2 and 26-29 for PANS, PAC-MB and PANS-PA1.

In general, the higher the aluminum content, the higher the possibility of producing larger amounts of $Al(OH)_3$ precipitates, therefore, the higher the efficiency of the sweep flocculation mechanism. This was also observed by Chuang *et al*.[21] for the treatment of brackish water where the silica removed by mg of aluminum both for alum and a PAC was the same.

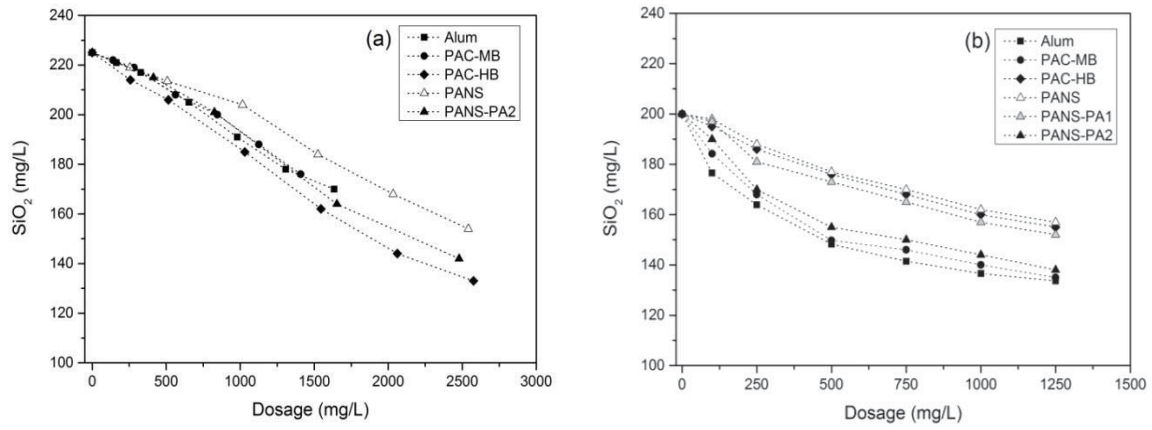

Figure 3: Soluble silica of clarified waters from (a) DAF1 and (b) DAF2 vs. dosage of coagulants

Although the consumption of alkalinity was high and similar pH decreases after coagulation were obtained in DAF2 compared to DAF1, the initial pH in DAF2 was higher, therefore, virtually all the coagulants work under the best conditions and there is a low amount of silica ionized. For this reason in DAF2, the most efficient products were alum and PAC-MB, the coagulants with the highest aluminum content (15.3-16.8% Al_2O_3), and PANS-PA2, the coagulant with the lowest aluminum content (6.0% Al_2O_3), but with the highest active content of polyamine in its formulation, which compensated for the lower aluminum content. The least efficient products, PANS and PAC-HB, were the coagulants with the lowest aluminum content (9.7-10.2% Al_2O_3) and finally, PANS-PA1 was slightly more efficient than PANS due to the PA addition, however, still far from PANS-PA2 due to their lower active content.

In DAF1 waters, however, differences in silica removal were not correlated with the aluminum content of the coagulants. For example, the most and the least efficient coagulants had similar aluminum contents (9.7% Al_2O_3 for PAC-HB and 10.2% Al_2O_3 for PANS), and these aluminum contents were intermediate among the coagulants tested. In this case, the most important factor in silica removal was the final pH of the treated waters and it was more affected by the basicity than by the aluminum content of the coagulant. It is important to notice that the most efficient product in the removal of silica for the treatment of DAF1 waters (PAC-HB) was the less efficient for the removal of silica in DAF2 waters. The reason is that a low pH decrease is not critical in DAF2 waters (higher initial pH and higher initial alkalinity), then the aluminum content became more important (9.7% Al_2O_3 of PAC-HB vs. 15.3-16.8% Al_2O_3 for alum and PAC-MB). As commented earlier, the products with lower basicities (alum and PAC-MB) obtained a lower efficiency in DAF1 due to the rapid increase of solubility of aluminum at pHs lower than 5.8-6.0.

Soluble COD

Soluble COD was not removed by DAF1 without coagulants or using only flocculant, the value of 2050 ppm (around 20% lower than DAF1 inlet waters) could be entirely explained by the dilution of the waters in flotation. For all the coagulation treatments, the higher the coagulant dosage, the higher the COD removal, up to around 1500 mg/L (Figure 4a). The most efficient products were PAC-MB, alum and PANS-PA2. They achieved a maximum reduction of soluble COD in the range 19-21% (final soluble COD 1580-1615 ppm). PANS and especially PAC-HB showed lower efficiency in the removal of soluble COD: 13% removal for PANS (1675 ppm) and 6% removal for PAC-HB (1890 ppm).

The same occurred when the inlet DAF2 waters were treated without chemicals or only 10 mg/L flocculant. No removal of soluble COD was achieved (1876 ppm soluble COD). PANS-PA2 and PAC-MB are the most efficient products, removing 28% and 24% of soluble COD, respectively, at 1250 mg/L (Figure 4b). Next, alum and PANS-PA1 had similar efficiency (20% removal soluble COD). Finally, the least efficient products (PAC-HB and PANS) achieved 9-12% soluble COD removal.

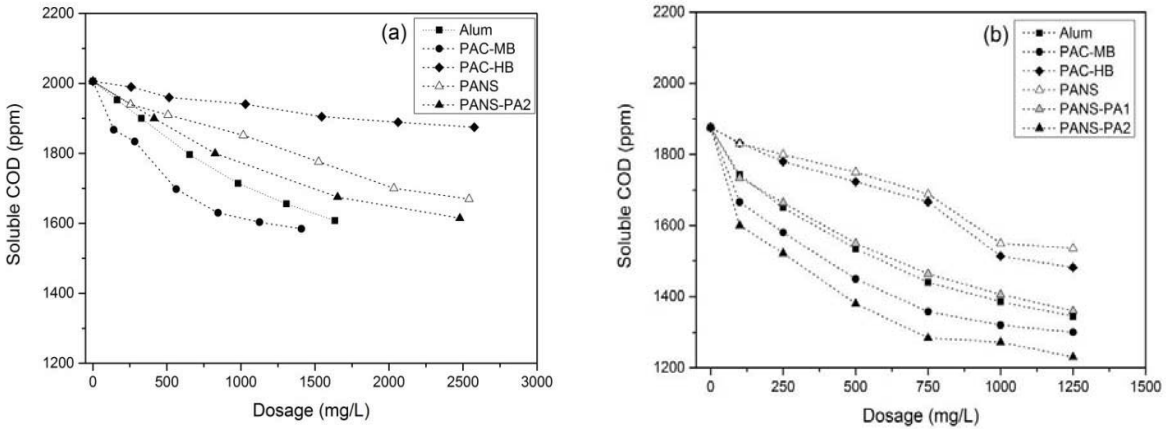

Figure 4: Soluble COD of clarified waters from (a) DAF1 and (b) DAF2 vs. dosage of coagulants

Comparing DAF1 and DAF2, the maximum removals of soluble COD in DAF2 were higher than in the case of DAF1 (24-28% vs. 20%). The most efficient products in silica removal in DAF1 waters were the least efficient in removing COD, i.e. PAC-HB (6% soluble COD removal). In DAF2 waters, however, alum and PAC-MB still had intermediate soluble COD removals. Finally, PANS-PA2 was the only coagulant that maintained a high removal of soluble COD even for high silica removals (20% in DAF1 waters and 28% in DAF2 waters).

Cationic demand

Both DAF1 and DAF2 blanks have similar cationic demand (around 1.0 meq/L) and neither DAF without chemicals nor the addition of 10 mg/L flocculant reduced the cationic demand more than the 20% expected due to the addition of tap water, as the main origin of cationic demand lies in the dissolved and colloidal fraction. When treating waters from DAF1, there are important reductions of cationic demand (Figure 5a). According to the reduction of cationic demand, three groups could be distinguished among the coagulants tested. The first group was PANS-PA2, which produced charge reversal at dosages higher than 2500 mg/L (data not shown), however, this charge reversal did not affect soluble COD or silica removal, indicating that other different flocculation mechanisms than charge neutralization were taking place. The second group was formed by PAC-MB and alum, with final cationic demand at the highest dosages tested of 0.07-0.10 meq/L (90-93% removal). The third group was formed by PAC-HB and PANS, achieving around 75% removal (0.24-0.25 meq/L final cationic demand).

The same three groups of products could be distinguished in DAF2 waters (Figure 5b). PANS-PA2, which was the most efficient product, achieved a final cationic demand of only 0.04 meq/L at 1250 mg/L (96% removal), very close to neutralization of the charge of the particles. The second group was formed by PANS-PA1, alum and PAC-MB. These products had an intermediate efficiency in removing the cationic demand (73-76% at 1250 mg/L) with final values of 0.26-0.27 meq/L. Finally, PANS and PAC-HB decreased cationic demand to 0.48-0.52 meq/L (48-52% removal) at 1250 mg/L.

The trends observed in cationic demand are related to the charge density of the coagulants although the correlation is not perfect as the flocculation active species for aluminum-based products are formed after the coagulant is added to waters. If we consider the aluminum content of the coagulants, as PAC-MB and alum have similar aluminum content (15.3-16.8% Al_2O_3), their neutralization capacity should be very similar, as observed.

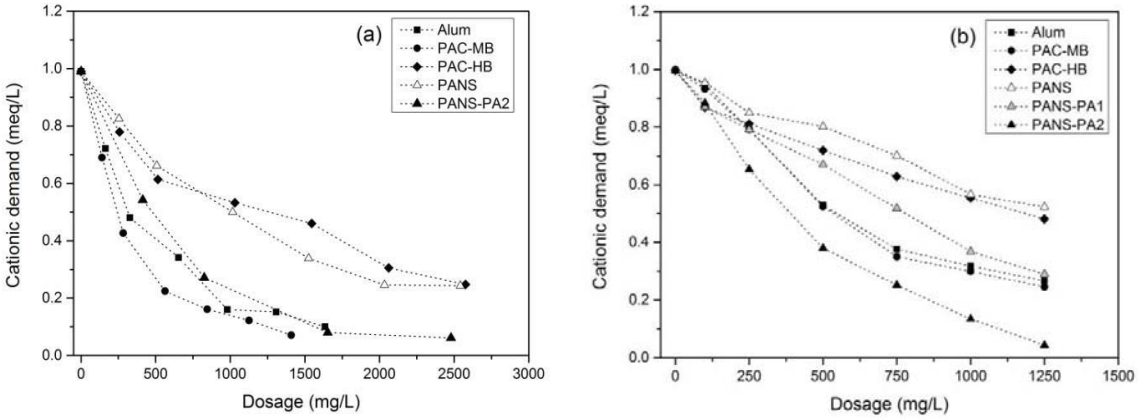

Figure 5: Cationic demand of clarified waters from (a) DAF1 and (b) DAF2 vs. dosage of coagulants

On the other hand, PANS and PAC-HB have an intermediate aluminum content of 9.7-10.2% Al_2O_3, therefore they are less efficient products in reducing the cationic demand, as was also observed. For hybrid coagulants, such as PANS-PA1 and PANS-PA2, there are also cationic polyelectrolytes (PA) contributing to the charge neutralization of the particles apart from aluminum. Therefore, although with lower aluminum contents, PANS-PA2 is the most efficient product in removing cationic demand and PANS-PA1 has a similar efficiency to those of PAC-MB and alum. Furthermore, it is necessary to consider the pH depression after coagulation treatment as the cationic demand decreases at lower pHs. Comparing the cationic demand removals in DAF1 and DAF2 waters, very similar removals were achieved, the slightly lower reduction with DAF2 waters justified by the lower dosages of coagulants tested. This indicates the neutralization capacity of the coagulants tested was similar, although there was a slightly different contamination load and pH in the waters.

pH

When alum or PAC is added to waters, aluminum hydrolyzes forming a variety of Al species or Al-hydroxide precipitants. In the present study, due to the high dosages used, $Al(OH)_3$ was the predominant formed species and sweep flocculation the main flocculation mechanism.[11] Due to the formation of $Al(OH)_3$, there was a consumption of alkalinity and a parallel pH decrease, which depends on the coagulant dosage, its aluminum content and basicity. The addition of 1 mg/L of alum, for example, resulted in the consumption of 0.5 mg/L $CaCO_3$ of alkalinity, while a PAC with 50% basicity would consume half, 0.25 mg/L $CaCO_3$. As the clarified waters would be reused directly within the process without any pH adjustment, the pH decrease should be as low as possible to avoid pH shocks, which could result in the formation of deposits and operational problems in the process. Although the initial alkalinity of the waters is high, the dosages of coagulant were also high, therefore a significant pH decrease was observed.

The initial pH of the DAF1 inlet and DAF1 blank was 6.8-6.9, while these values were 7.6-7.7 for DAF2. In the tests with DAF1 waters, again three groups could be distinguished in terms of pH decrease after the treatment (Figure 6a): PAC-HB and PANS-PA2 decreased less the pH (<0.3 pH units, final pH 6.5-6.6 at the highest dosage), PANS had an intermediate effect (0.5 pH units decrease, final pH 6.8), and alum and PAC-MB were those decreasing most the pH (pH decrease <0.8-1.0 units, final pH 5.8-6.0). In the tests with DAF2 waters, PAC-HB decreased pH only by 0.2 pH units, PANS-PA1 and PANS-PA2 decreased by around 0.3-0.4 pH units, PANS and PAC-MB decreased pH by around 0.5 units and finally, alum, by around 0.8 pH units, all at the highest dosage tested (Figure 6b).

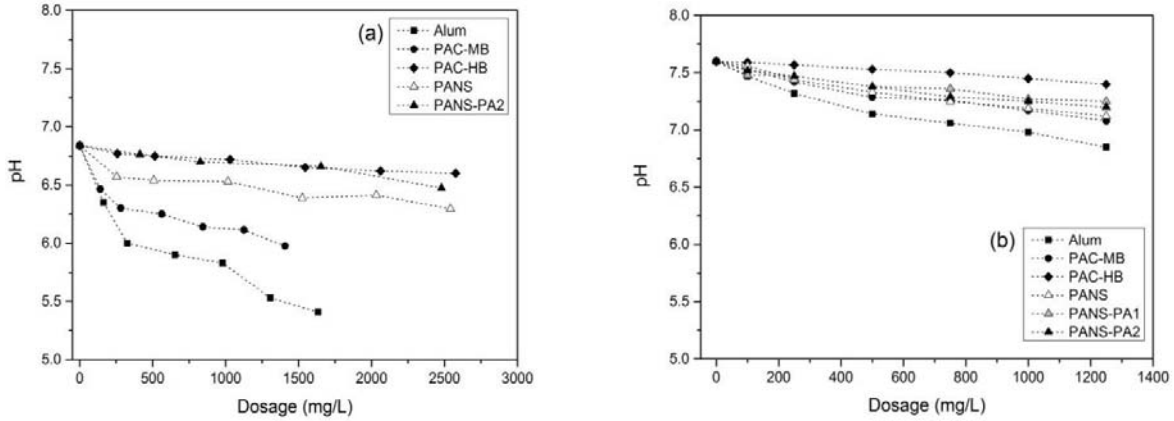

Figure 6: pH of clarified waters from (a) DAF1 and (b) DAF2 vs. dosage of coagulants

Alum and PAC-MB were the products causing higher pH decrease because they were the coagulants with the highest aluminum content and with the lowest basicities. This is especially important when treating DAF1 waters, where the initial pH of waters is lower than in DAF2, as commented earlier. The products that decreased less the pH of the waters were PAC-HB and PANS-PA2; PAC-HB due to the intermediate aluminum content (9.7% Al_2O_3) but the highest basicity (85%), and PANS-PA2 due to the lowest aluminum content (6.05% Al_2O_3) and intermediate basicity (46%). Finally, PANS and PANS-PA1 resulted in intermediate pH decrease as they have intermediate aluminum contents and basicities. Although the pH decrease was always lower than 1.0 pH unit, the coagulants decreasing the pH to a lower extent are those preferred. At similar dosages of commercial products, the pH decrease in DAF1 waters was higher due to the lowest alkalinity compared to DAF2 (1425 vs. 856 ppm $CaCO_3$), i.e. the pH decrease with 1250 mg/L of alum is around 1.3 pH units in DAF1, while it was around 0.8 pH units in DAF2.

Conductivity

The conductivity of raw waters from DAF1 was 2.6 mS/cm and the conductivity of blank was 2.1 mS/cm (19.1% removal). In the same sense, the conductivity of raw waters from DAF2 was 2.13 mS/cm and the conductivity of blank 1.74 mS/cm (18.3% difference). This means DAF is not able to remove inorganics, at least without chemicals. In fact, all the treatments produced an increase in the conductivity of the waters, this increase being higher at higher dosages, which is in agreement with the inorganic nature of all the coagulants tested (Figure 7).

In DAF1 tests, PAC-HB and PANS-PA2 were the products increasing less the conductivity of the waters. With these products, even at the highest dosage tested, the conductivity increased from 2.1 mS/cm up to 2.4-2.5 mS/cm. With the other coagulants, a final conductivity of 2.7-2.8 mS/cm was obtained at the highest dosages tested. One of the most important drawbacks of using alum, which is the cheapest coagulant, is the increase of the conductivity of treated waters due to sulphates release (2.9 mS/cm). With the other coagulants, although some of them have a small amount of sulphates in their composition (i.e. PANS or PANS-PA), the increase in sulphates was always lower than 10-15 mg/L. In DAF2 waters, similar trends were obtained. PAC-HB was the coagulant that increased the least the conductivity of the waters, from 1.74 to 1.80 mS/cm at the highest dosage. PANS, PANS-PA1 and PANS-PA2 showed a very similar behaviour, increasing the conductivity of the clarified waters to 1.90-1.95 mS/cm. Finally, PAC-MB increased the conductivity to 2.2-2.3 mS/cm, and alum, to 2.42 mS/cm.

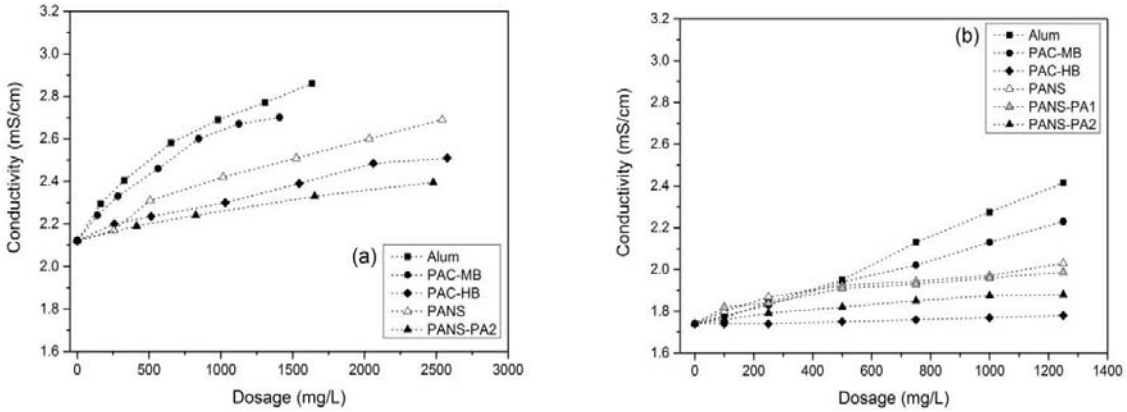

Figure 7: Conductivity of clarified waters from (a) DAF1 and (b) DAF2 vs. dosage of coagulants

Totally comparable results were obtained for the two DAF units. There was an important increase of conductivity in the treated waters, but in the case of PANS-PA2 and PAC-HB, which is a very important advantage compared to other products due to the high dosages necessary for efficient silica removal. A lower final conductivity of the treated water constitutes an additional advantage for the chemical treatments tested as, depending on the final conductivity, the RO rejects must be treated or not before discharge (conductivity limit is 7.5 mS/cm).

Comparison of silica removal efficiency in different process streams with different levels of suspended solids

As it was hypothesized before, the presence of a high concentration of suspended solids (especially those of smaller size) and colloids could be beneficial for the removal of contaminants, as they could act as precipitation nuclei for $Al(OH)_3$ and promote orthokinetic flocculation. In a previous study carried out by the authors, some of the coagulants tested in the present work (alum, PAC-HB, PANS-PA1 and PANS-PA2) were used to remove silica from the effluent of the same paper mill at three different initial pHs (8.3, 9.5 and 10.5) and dosages up to 2500 mg/L commercial product.[19] In this study, the following ratios (mg of coagulant required per mg of silica removed) were obtained: 35 for alum (although an optimum dosage was observed at dosages lower than 2500 mg/L), 39 for PAC-HB, 34 for PANS-PA1 and 24 for PANS-PA2 at initial pH 8.3. From another study with the same effluent (unpublished), a ratio of 45 was obtained for PANS. Table 4 shows the comparison of these results with those obtained in the present study with DAF1 and DAF2 waters.

The main differences in the contaminant load of the different process water streams (DAF1, DAF2 and effluent) are summarized in Table 5. Although the lowest pH tested (pH 8.3) is slightly higher than the pH of DAF1 and DAF2 waters (pH 6.8 and 7.6, respectively) and silica removal is enhanced at higher pHs, the results obtained clearly demonstrate that a higher efficiency for silica removal in terms of mg of coagulant required per mg SiO_2 removed are obtained if silica is removed from process water in the internal DAF treatments. These higher efficiencies were obtained even in waters that are more contaminated in terms of cationic demand, COD or conductivity than in the effluent, conditions which usually turn in higher coagulant requirements. Obviously, it is easier to remove a contaminant when the initial content is higher, however, the differences in silica content were not so large (140 mg/L SiO_2 in the effluent compared to 200-225 mg/L SiO_2 in DAF blanks).

As can be seen in Table 4, the coagulant demand in DAF units is around 20-50% lower than the same treatment applied on the effluent. The main differences in coagulant demand are for alum, PAC-HB and PANS, while the differences in efficiency of PANS-PA1 and PANS-PA2 are less important as their flocculation efficiency is not coming only from their aluminum content, but also from the polyamine included in their formulation. The removal of silica in DAF2 is clearly better than in DAF1 due to the higher concentration of suspended solids and their considerably lower size, even for a similar contamination load in DAF1 and DAF2 waters, including similar total dissolved solids and silica contents. It seems that a higher concentration of suspended solids is more important than total dissolved solids for promoting the flocculation of contaminants either by increasing the rate of precipitation of $Al(OH)_3$ or by improving orthokinetic flocculation. The slightly higher pH in DAF2 compared to DAF1 (around 1.0 pH unit) could also be relevant, however, the pH in DAF2 is still far from pK 9.5, where the orthosilicic acid (H_4SiO_4) is transformed to $H_3SiO_4^-$ and pK 12, when $H_3SiO_4^-$ is transformed in $H_2SiO_4^{2-}$, which would improve the removal of silica by coagulation due to higher silica ionization.[18,20,23]

Table 4
Ratio mg of coagulant required per mg of silica removed in DAF1 waters, DAF2 waters and the effluent

	Alum	PAC-MB	PAC-HB	PANS	PANS-PA1	PANS-PA2	Dosage range
DAF1	29	29	25	37	-	27	0-1500 mg/L
DAF2	19	19	28	29	26	20	0-1250 mg/L
Effluent	35	-	39	45	34	24	0-2500 mg/L

Table 5
Contamination load of DAF1 waters, DAF2 waters and the effluent

	pH	Cat. demand (meq/L)	SiO_2 (mg/L)	TSS (mg/L)	Conductivity (mS/cm)	Soluble COD (ppm)	TDS (mg/L)
DAF1 blank	6.8	0.99	225	1620*	2.12	2050	3211
DAF2 blank	7.6	0.99	200	3350*	1.74	1876	2590
Effluent	8.3	0.50	140	125	2.20	560	1705

* Values from the raw water.

Table 6
Ratio mg of coagulant required per mg of soluble COD removed in DAF1 waters, DAF2 waters and the effluent

	Alum	PAC-MB	PAC-HB	PANS	PANS-PA1	PANS-PA2	Dosage range
DAF1	4.1	3.3	15.3	6.6	-	5.0	0-1500 mg/L
DAF2	2.3	2.2	3.2	3.7	2.4	1.9	0-1250 mg/L
Effluent	10	-	12.4	-	8.8	19.8	0-2500 mg/L

If silica removal rates obtained in this study are compared to other studies from the literature, the removal efficiency is considerably higher. For example, S.H. Chuang *et al*.[21] obtained silica removal ratios (mg of coagulant per mg SiO_2 removed) around 25 with a polyaluminum chloride (30% Al_2O_3) and 48 with alum. In this study, they treated wastewater from a high-tech industrial park with initial 25-30 mg/L SiO_2, using coagulant dosages of 100-500 mg/L commercial PAC and 200-1000 mg/L alum, at initial pH 7.5. The level of TDS was around 1800 mg/L and the conductivity of 17-1.9 mS/cm, similarly to the values for the present study, but the levels of suspended solids and COD were considerably lower: 10-30 mg/L suspended solids (2-5 NTU of turbidity) and 20-25 ppm COD. The silica removal ratios obtained were very similar to those obtained when the effluent of the paper mill was tested,[19] where the suspended solids were also very low compared to DAF inlet waters (Table 2).

On the other hand, in the treatment of brackish water with 21 mg/L SiO_2, using up to 180 mg/L of a PAC, S. Chen *et al*.[20] obtained a ratio of 25 mg of coagulant per mg of silica removed at around pH 7. Although the suspended solids or turbidity of the waters were not given, it is expected that the suspended solids would be considerably lower than those of DAF1 and DAF2 waters, very similar to that of the effluent of the paper mill, as usually occurs with brackish waters. The ratio of 25 would mean a higher efficiency in silica removal than in the effluent of the paper mill, however, it is important to notice these brackish waters had a high level of initial hardness (90 mg/L Ca, 80 mg/L Mg), which also promotes silica removal either by the adsorption on $CaCO_3$ or $Mg(OH)_2$ or by co-precipitation as calcium and magnesium silicates. Other references have been analyzed, but it is difficult to make a direct comparison with the results obtained in the present study due to the different conditions tested and the lack of some analytical parameters of the waters tested (initial hardness, total suspended solids, etc.), which are of great importance for comparison purposes.

Although the most important parameter considered in this study is silica, it is necessary to comment that the same decrease in coagulant demand has been also observed for soluble COD removal (see Table 6). A direct comparison between the effluent and the results obtained with DAF waters can not be carried out as there is a large difference in soluble COD (1876-2050 ppm in DAF blanks compared to 560 ppm for the effluent), however, large differences have been also found. DAF1 and DAF2 results could be compared together as the values of soluble COD are similar. Again, there is a clear improvement in the soluble COD removal when treated waters from DAF2 are compared to DAF1 waters (around 50% lower mg of coagulant per mg soluble COD removed). This confirms that the presence of a high amount of suspended solids of small size promotes the removal of COD by sweep flocculation, as previously observed for silica.

CONCLUSION

Without chemicals or using only flocculant, the removal of contaminants is almost negligible in DAF units, especially in DAF2s, due to the small size of suspended solids. In DAF1, the pH decrease after coagulation is the most critical factor for silica removal, therefore, PAC-HB and PANS-PA2 (<0.3 pH units decrease) are the recommended treatment options. PAC-HB is selected when the most important contaminant is silica (40% silica removal, 6% soluble COD removal), while PANS-PA2 is recommended for high silica removals together with high turbidity and COD removals (35% silica removal, 20% soluble COD removal). In DAF2, the most efficient products in silica removal are those with the highest aluminum content, i.e. alum and PAC-MB, plus PANS-PA2. However, the use of alum is not recommended as it largely increases the conductivity of the waters and produces the largest pH decrease. Therefore, the use of PAC-MB and PANS-PA2 are the recommended treatment options. For DAF2 waters, PAC-MB should be used if the most important requirement is silica removal (35% silica removal, 24% soluble COD removal) and PANS-PA2 if high silica removals are necessary, but also high turbidity and COD removals (30% silica removal, 28% soluble COD removal).

The results obtained indicate that the coagulant demand for silica removal in the effluent can be reduced significantly by treating the inlet of DAF units, especially in DAF2. The coagulant demand can be reduced to 35-50% for the coagulants with the highest aluminum contents (alum and PAC-HB) and around 20% with PANS, PANS-PA1 and PANS-PA2, apart from contributing to having cleaner water circuits compared to silica removal on the effluent. The reason is the presence of a higher concentration of suspended solids of a small size and colloids, which improves the removal of contaminants by sweep flocculation as they can act as precipitation nuclei for $Al(OH)_3$ and also promotes orthokinetic flocculation.

Depending on the initial silica content and the objectives of the treatment (direct discharge or effluent reuse treatments with RO membranes), a post-treatment in the effluent for silica removal could be necessary or not. The most important finding of this study is that silica removal should be carried out preferentially in DAF units used as internal treatments for process waters, avoiding as much as possible the removal of silica from the effluent due to the considerably larger coagulant demands for similar silica and COD removals.

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PUBLICATION V

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"Flocculation mechanisms of different aluminum salts in the flotation of industrial waters"

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FLOCCULATION MECHANISMS OF DIFFERENT ALUMINUM SALTS IN THE FLOTATION OF INDUSTRIAL WATERS

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ABSTRACT

Flocculation behaviour and strength and reversibility of the flocs formed by five different aluminum coagulants used for the removal of contaminants by dissolved air flotation (DAF) have been studied. These aluminium coagulants include: alum, a polyaluminum coagulant of high aluminium content and intermediate basicity (PAC-MB), a polyaluminum salt of intermediate aluminium content and high basicity (PAC-HB), a polyaluminum nitrate sulphate of intermediate aluminium content and basicity (PANS) and one composite coagulant formed by the combination of PANS with a mixture of polyamines (PANS-PA). In this case, the pH suppression (and thus the basicity) of the aluminum coagulants was the main factor affecting the removal of contaminants by DAF. Results demonstrated that the main flocculation mechanism vary with the aluminum dosage, being predominant charge neutralization at low dosages and sweep flocculation at high dosages. While the strength factor is very similar for all the pure aluminum coagulants and almost constant with the dosage (85-90%), the recovery factor decreased from 50-70% to almost zero at the highest dosages. The behaviour of the hybrid coagulant (PANS-PA) is completely different: the strength factor decreases with the dosage, from 81% to 66%, and the recovery factor was always around zero, independently of the dosage. Due to the mixture of several PA of different molecular weight used in the formulation of PANS-PA, its flocculation mechanism participates both from partial patches formation (regarding flocculation and deflocculation) and partial bridges formation (regarding reflocculation).

Keywords: flocculation mechanisms, aluminium, polyamine, dissolved air flotation, FBRM, hybrid coagulants

1. INTRODUCTION

Paper industry is a large consumer of fresh water, the reduction of water use being an issue of growing importance due to the stringent environmental legislation, the increase in water prices, the treatment costs, or simply due to the lack of water resources [1,2]. Internal reuse of the water after the treatment with dissolved air flotation (DAF) units is the most common alternative used in paper mills to reduce fresh water consumption.

In recycled newsprint mills, there are up to three or four DAF units in each production line (one within each water loop). In these systems, suspended solids are easily removed but the dissolved and colloidal material (DCM) is almost completely recirculated into the process, accumulating in the water circuits, and thus limiting the degree of circuits closure [3]. However, with an adequate coagulation and flocculation, DAF units can also remove finely dispersed and colloidal particles (>0.1-0.2 μm). In these conditions, DAF units can remove 80-99% of suspended solids, and in the best cases, 10-30% soluble COD [4-7]. On the other hand, the removal of inorganic contaminants is almost negligible. In fact, the conductivity of the treated waters is usually higher than before the treatment, especially when metal coagulants are used.

A variety of coagulants can be used in DAF systems, including alum, ferric chloride, polyaluminum chloride (PAC), polyamine (PA), polydiallyldimethylammonium chloride (PDADMAC), chitosans, etc. Aluminum based coagulants are probably some of the most versatile and widely used. In addition to alum, many types of polyaluminum coagulant are commercially available for water treatment such as aluminum chlorohydrate, PAC and polyaluminum sulfates. These products differ in their basicity and strength, and can contain small amounts of other compounds such as sulphate, nitrate, silica and calcium [8]. Furthermore, polyaluminum based coagulants can be used with cationic polyelectrolytes such as PA or PDADMAC in hybrid coagulants for an improved performance [6,9-10].

The flocculation mechanism is of great importance in coagulation-flocculation processes as both the size and the structure of the formed aggregates affect the contaminants removal efficiency [11]. There are several possible flocculation mechanisms described in the literature including charge neutralization and flocculation by enmeshment ("sweep flocculation"), interparticles bridging and patches formation, among others. In general, the predominant flocculation mechanisms for alum and polyaluminum coagulants are charge neutralization and flocculation by enmeshment [12]. In the pH range of 6-7, coagulation conditions are considered favorable for aluminum-based coagulants due to the presence of positively charged Al species and the fact that most of the Al coagulant added is precipitated to form floc particles (conditions of minimum solubility of $Al(OH)_3$) [8]. At similar pHs, very roughly, it can be said that charge neutralization mechanism is predominant at low aluminum dosages, while the precipitation of $Al(OH)_3$ and the subsequent enmeshment of colloids in the precipitate is predominant at high aluminum dosages. However, it is important to notice that destabilization with metal coagulants cannot be exclusively attributed to any particular mechanism. In a particular instance, destabilization may be produced by one or several mechanisms [13].

Apart from the nature and dosage of the coagulant used, there are also other factors determining the flocculation mechanisms involved in a flocculation process such as the nature and the surface charge of the particles, the pH of the suspension, the amount of colloidal and suspended solids, the ionic strength, etc. For example, in systems where particle concentration is high enough for collisions to take place in a time scale similar to that required for the polymer to attain a flattened configuration, bridging formation is favoured to patches formation [14-16]. Furthermore, a high conductivity of the waters may sift patching aggregation towards bridging aggregation [15].

There are many studies regarding the flocculation of model suspensions with aluminum salts, some of them also analyzing also the strength and recovery after shear forces of the flocs formed (deflocculation and reflocculation studies). However, they usually focus on model suspensions of kaolin [17-18], humic acids [19] or a combination of both [20-22]. Furthermore, there are only limited references regarding the flocculation mechanisms of hybrid or composite coagulants, most of them using iron-based hybrids [23], however, to the best knowledge of the authors, not for aluminum-based hybrids.

Therefore, the main objective of this paper is to study the flocculation behaviour and flocculation mechanisms of different aluminum coagulants, including an aluminum-based hybrid coagulant with a mixture of polyamines of different molecular weight, and its influence on the removal of contaminants by dissolved air flotation in industrial waters from recycled paper manufacturing.

2. MATERIALS AND METHODS

2.1. Materials

Waters. Water samples were taken from the inlet of a DAF unit of a recycled newsprint mill. The main characteristics of these waters are shown in Table 1. The mean and median chord size of the particles (1-1000 μm size range) are 43.7 and 34.4 μm, respectively, both measured by a focused beam reflectance measurement (FBRM) probe [24-25]. The distribution of particles among the different size ranges is the following: 34.6% (1-20 μm), 30.3% (20-50 μm), 26.3% (50-100 μm) and 8.9% (>100 μm).

Table 1.- Characteristics of the DAF1 inlet waters and DAF1 blanks.

	DAF Inlet	**DAF blank**
pH	6.9	6.8
Conductivity (25 ºC) (mS/cm)	2.62	2.12
Total solids (mg/L)	5520	3394
COD (ppm)	3665	2332
Total suspended solids (mg/L)	1620	183
Turbidity (NTU)	680	268
Cationic demand (meq/L)	1.16	0.99
Total Alkalinity (ppm $CaCO_3$)	856	645
After centrifugation		
Total solids (mg/L)	3898	3211
Dissolved silica	273	225
Dissolved COD	2600	2050
Dissolved turbidity (NTU)	21.8	18.0

Chemicals tested. Five aluminum-based coagulants were tested. Table 2 summarizes their main properties. Alum ($Al_2(SO_4)_3{\cdot}18H_2O$), reagent grade, was supplied by Panreac. PAC-MB is a conventional polyaluminum chloride with high aluminum content and intermediate basicity (16.8% Al_2O_3, 37% basicity), supplied by Sachtleben Wasserchemie GmbH, and PAC-HB is a high-basicity polyaluminum chloride with intermediate aluminium content and a small amount of silica in its composition (9.7% Al_2O_3, 85% basicity), supplied by Kemira Ibérica S.A. On the other hand, PANS is a polyaluminum nitrate sulphate with an intermediate aluminum content and basicity (10.2% Al_2O_3, 46% basicity), having a 16.0% NO_3^- and 3.0% SO_4^{2-} contents. PANS-PA is a composite coagulant obtained by the addition of a small amount of quaternary polyamines of different molecular weight and high charge to PANS. PANS and PANS-PA were both supplied by Sachtleben Wasserchemie GmbH. Coagulants were tested in DAF tests in combination with an anionic polyacrylamide of high molecular weight and medium charge, supplied by SERTEC-20 S.L. (Spain).

Dosages of the coagulants were selected according to preliminary tests, varying from 25 to 250 ppm Al_2O_3, while the flocculant dosage was fixed in all the cases to 10 mg/L.

Table 2.- Characteristics of the coagulants used in this study.

Coagulant	**Al_2O_3 (%)**	**Basicity (%)**	**Charge density (meq/g)**	**Density (g/cm^3)**	**pH**	**Dry content (%)**
Alum	15.3	0	-	-	-	-
PAC-MB	16.8	37	1.77	1.37	< 1	34.1
PAC-HB	9.7	85	1.67	1.22	2.7	29.5
PANS	10.2	46	1.22	1.27	2.6	21.7
PANS-PA	6.05	-	2.57	1.23	3.0	20.4

2.2. Methodology

DAF tests. DAF tests were carried out in a lab-scale DAF unit (Flottatest FTH3) supplied by Orchidis Laboratoires. The combination of DAF tests with flocculation tests allowed studying together flocculation and flocculation mechanisms with the removal efficiency of contaminants such as turbidity or COD by different chemical treatments. Cationic demand and pH of the

134 treated waters were also measured to get a deeper understanding on the coagulation-flocculation
135 process. The only difference between flocculation and DAF tests was the addition of a dosage of
136 flocculant in DAF tests to improve solids separation. The details of the methodology and
137 analytical methods used for characterizing waters can be found in [26]. A number of blanks for
138 each DAF waters were carried out without adding any chemical, to consider the dilution of the
139 samples due to the addition of air-saturated water during flotation (20%) and the physical
140 efficiency of the DAF (without any chemicals). The average values for these blanks are referred
141 as 0 mg/L dosage and their characteristics were summarized together with those of DAF inlet
142 waters in Table 1. All the experiments were carried out at room temperature (20-25 ºC) by
143 duplicate, and the average error between replicates was around 5%. To avoid the possible
144 degradation of the waters, all trials and analyses were carried out within five days after the
145 sampling and the waters were always kept at 4ºC before use.
146
147 Flocculation monitoring and tests. Flocculation monitoring was carried out using Focused Beam
148 Reflectance Measurement (FBRM) technique. The principle of FBRM is that a laser beam is
149 directed down the probe and focussed at, or near the window at the tip. The optics is rotated
150 around an axis parallel to the probe, so that the beam traces a circular path. When particles
151 intercept its path, the light is reflected and propagated back through the probe window to the
152 detector. The particle will continue to reflect light until the focused beam has reached the
153 opposite edge of the particle. The time duration of the backscattered light pulse allows the
154 particle chord length to be calculated as the time taken for the beam to cross the particle, divided
155 by linear speed of the beam's rotation. This optical length corresponds to a random chord length
156 of the particle, that is, a straight line between any two points on the edge of a particle. The width
157 of the chords will be dependent on the particle's size, shape and orientation [27-29]. Thousands
158 of chord length measurements are collected per second, producing a histogram in which the
159 number of the observed counts is sorted in several chord length channels over the measurement
160 range. From these data, total number of counts (TNC), mean chord size (MCS), counts in
161 specific size intervals, and other statistical parameters can be easily calculated [24,25,30].
162
163 This system is able to study the flocculation behaviour without the limitations of traditional
164 methods such as charge titration, which are not valid when bridging or patching mechanisms

dominate the system [31]. In the last years, FBRM has been specifically used for the chemical optimization of DAF units treating thermomechanical pulp and deinking pulp waters [5,7,32,33]. In the present study, the FBRM device used is model D600S, supplied by Mettler Toledo, with a measurement range of 1-1000 µm.

Two different flocculation studies were carried out: the flocculation by successive coagulant additions and the flocculation-deflocculation-reflocculation tests. The flocculation by successive coagulant additions were carried out by the addition of increased dosages of the different coagulants to a sample of 250 mL while stirred at 200 rpm with the FBRM probe submerged on it. A total dosage of 1000 ppm Al_2O_3 of coagulant were added through successive steps of 25 ppm each 30 s, using a 10% wt./vol. coagulant solution.

In the flocculation-deflocculation-reflocculation tests, single dosages of coagulant were tested from 25 to 250 mg/L Al_2O_3. In these trials, the probe was also submerged into a 250 mL sample stirred at 200 rpm. After 30s of stabilization time, the dosage of the coagulant was added from a 10% wt./vol solution. Then, the system was allowed to evolve for 2.5 min. After this time, the mixing speed was increased to 500 rpm and maintained during 2 minutes to break the formed flocs. Finally, the mixing speed was reduced to 200 rpm again and the system was monitored for other 5 minutes to analyse the reversibility of the flocs after the shear forces ended. Mixing intensities used for flocculation and the breakage of the flocs stages were selected according to preliminary tests carried out with these waters.

From these tests, the strength or breakage factor (SF) and recovery or re-growth factor (RF) were calculated using Ec. 1 and 2, where: MCS_1 is the maximum MCS value before the flocs breakage, MCS_2 is the MCS value when the flocs were broken after intensive stirring and MCS_3 is the maximum MCS value for the flocs re-growth after the intensive stirring.

$$SF = \frac{MCS_2}{MCS_1} \quad \text{[Ec. 1]}$$

$$RF = \frac{MCS_3 - MCS_2}{MCS_1 - MCS_2} \quad \text{[Ec. 2]}$$

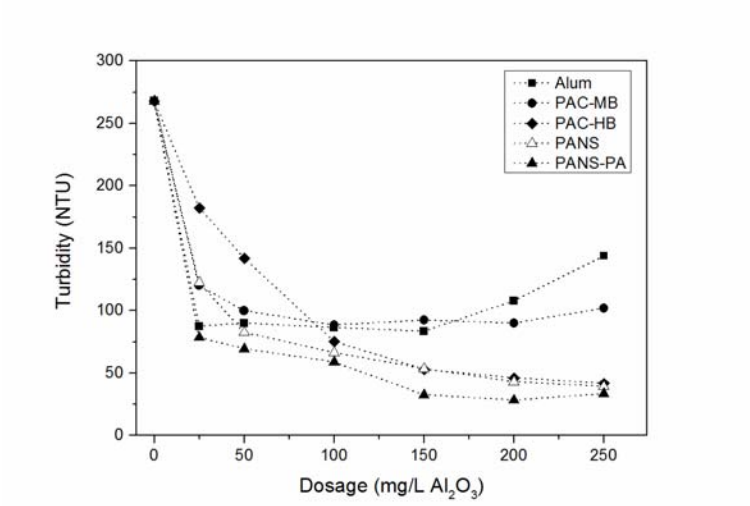
3. RESULTS AND DISCUSSION

193

194 **3.1. DAF tests**

195

196 **Turbidity.** Raw waters have a turbidity of 680 NTU. DAF blank, without chemicals, reduced
197 turbidity to 268 NTU (60.6% removal, including the 20% removal due to the dilution of the raw
198 waters with water saturated in air during flotation). Removal of turbidity in the clarified waters
199 increased greatly with coagulant addition but the turbidity values remained practically constant at
200 dosages higher than 150 mg/L (Figure 1). PANS, PANS-PA and PAC-HB decreased the
201 turbidity to 30-40 NTU (85-90% removal referred to blank), while alum and PAC-MB decreased
202 turbidity to 80-90 NTU (65-70% removal referred to blank).



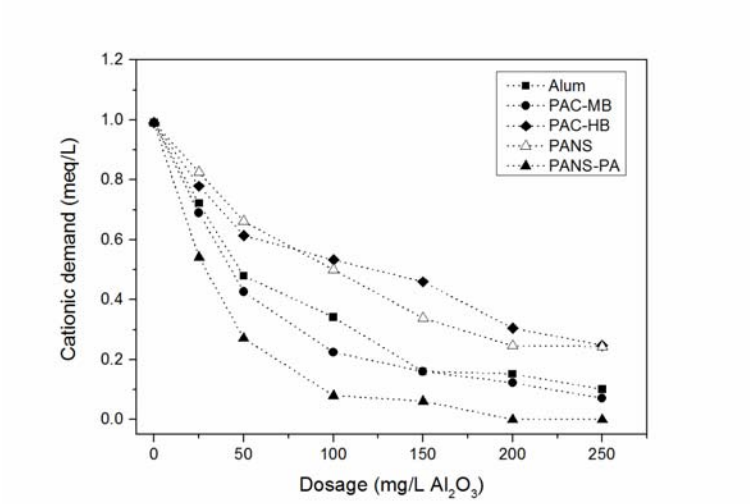
203

204 Figure 1.- Turbidity of clarified waters vs. dosage of coagulants.

205

206 In the case of alum and PAC-MB an increase of turbidity and dissolved turbidity (data not
207 shown) was observed at dosages higher than 100 mg/L in the case of alum and 200 mg/L for
208 PAC-MB, respectively. This could indicate that restabilization by charge reversal could be taking
209 place. However, the cationic demand of the clarified waters did not corroborate this. At the
210 dosages tested, there were important reductions of cationic demand but none of the coagulants
211 reached charge reversal, except PANS-PA (Figure 2). In fact, according to the reduction of
212 cationic demand, three groups can be distinguished among the coagulants tested. First group is
213 formed by PAC-MB and alum, with final cationic demand at 250 mg/L of 0.07-0.10 meq/L (90-
214 93% removal). Second group of coagulants is formed by PAC-HB and PANS, achieving around

215 a 75% removal (0.24-0.25 meq/L final cationic demand). Finally, PANS-PA produced charge
216 reversal at higher dosages than 150 mg/L, but the removal of contaminants was not affected at
217 all.



218

219 Figure 2.- Cationic demand of clarified waters vs dosage of coagulants.

220

221 The explanation of this efficiency decrease at high dosages for alum and PAC-MB can be
222 explained by the pH suppression after the treatment. When alum or PACs are added to waters,
223 aluminum hydrolyzes forming a variety of cations and precipitates such as $Al(OH)_3$, especially at
224 high aluminum dosages. Due to the formation of $Al(OH)_3$, there is a consumption of alkalinity
225 and a parallel pH decrease, depending on the aluminum dosage and the basicity of the coagulants
226 [8]. The same three groups can be distinguished now in terms of pH suppression (Figure 3):
227 PAC-HB and PANS-PA were the products which decreased less the pH (<0.3 pH units, final pH
228 6.5-6.6 at the highest dosage), PANS induced an intermediate decrease (0.5 pH units decrease,
229 final pH 6.8), and finally, alum and PAC-MB are those products decreasing most the pH of the
230 clarified waters: final pH around 5.4 for alum and 6.0 for PAC-HB. Although the same
231 aluminum dosages have been tested for all the coagulants, the highest pH suppression of alum
232 and PAC-MB are a consequence of their low basicities (0% in the case of alum and 37% in the
233 case of PAC-MB), compared to the basicity for PANS (46%) and PAC-HB (85%). The pH of
234 minimum solubility of $Al(OH)_3$, which produces the larger amount of $Al(OH)_3$ precipitates and
235 the lower residual aluminum concentration, is around 6.0 for alum and 6.2-6.4 for PACs [12].
236 For these reasons, the lower pH at which aluminum salts can be used is usually limited to around

5.5-5.8, depending on the temperature and the presence of other species in the waters, i.e. sulphates, phosphates, etc. [34]. In these industrial waters, this pH limit seems to be slightly higher: around 5.8 for alum and 6.0 for PAC-MB as at these pHs the efficiency in turbidity removal decreased despite no charge reversal occurred.

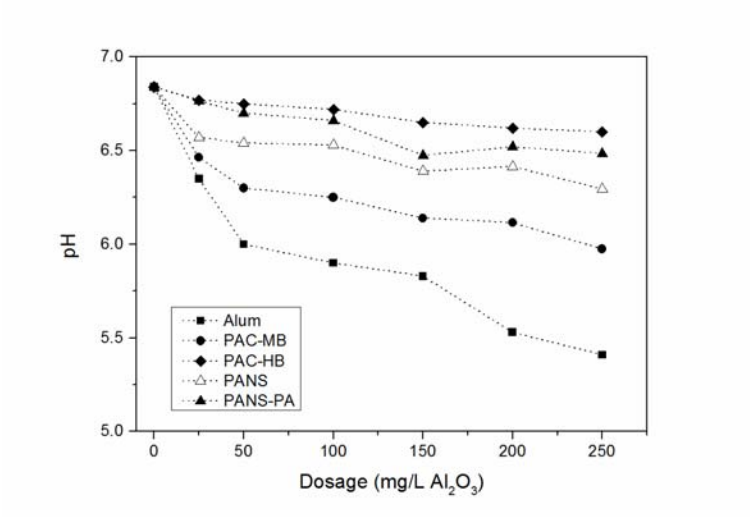


Figure 3.- pH of clarified waters vs dosage of coagulants.

Removal of COD and silica. For all the coagulation treatments, the higher dosage the higher COD is removed, however, at the highest dosages (200-250 mg/L Al_2O_3), there were only marginal removals in COD. The most efficient products are PAC-MB, alum and PANS. They achieved a maximum reduction of soluble COD in the range 17-21%. PANS-PA (13% removal), and especially PAC-HB (6% removal), had a very low efficiency in the removal of soluble COD. Other parameter of interest in these industrial waters is silica as there is a high concentration which can produce deposits in the process and limit the technical and economic feasibility of a possible effluent reuse treatment by membrane technologies, i.e. silica in DAF inlet is 275 mg/L and 225 mg/L in the DAF blank. Again silica removal increased with the coagulant dosage with all the coagulants tested. However, there are two clear groups of coagulants in terms of silica removal: PAC-HB and PANS-PA, which are the most efficient products, with silica removals between 45% and 50% (125-130 mg/L residual silica) and the other coagulants (PANS, PAC-MB and alum), with silica removals in the 30-35% range (155-175 mg/L residual silica).

It is clearly demonstrated that the coagulants with the highest efficiency in removing soluble COD are those with the lowest efficiency in silica removal, being the opposite true. This is a very important fact as the coagulant type and dosage used in the industrial DAFs are usually optimized in terms of suspended solids and COD removal and for this specific case, there is also an important interest in removing silica from these waters. In summary, comparing the whole results for turbidity, COD and silica removal, PANS-PA and PAC-HB are the most efficient treatments.

3.2.FLOCCULATION STUDIES

3.2.1. Flocculation by successive coagulant additions

First, small dosages of coagulants were added successively to waters to determine the main differences among them and a preliminary optimal dosage. In the beginning, the mean chord size (MCS) of the particles increased with the successive coagulant additions because the destabilization of the particles allows their aggregation. When the total added dosage was higher than the optimal, no more aggregation took place, therefore, the MCS stopped increasing and started decreasing due to the steric stabilization or electrostatic repulsion.

When consecutive additions of the coagulant were tested (Figure 4a), two products were clearly more efficient in the destabilization and aggregation of the particles: PANS-PA and PAC-HB. They both increased the MCS of the particles around 8 μm (from 36 μm to 44 μm) at their optimal dosages. PANS has an intermediate efficiency, with around 3 μm MCS increase, and PAC-MB and alum are those increasing less the MCS (around 1 μm). The flocculation indexes of the coagulants, which measures the ratio between the maximum MCS obtained after flocculation and the initial MCS, expressed as percentage, were the following: PANS-PA (20.5%), PAC-HB (19.9%), PANS (8.9%), PAC-MB (3.2%) and alum (2.5%).

If the TNC is analyzed (Figure 4b), again PANS-PA and PAC-HB are the most efficient products in reducing TNC, which means an important aggregation of particles took place, which is in agreement with the large MCS increase observed. Although both products are very efficient,

PANS-PA reduced the number of counts in a higher extent (2000 #/s, which means a 71% reduction from the 2800 #/s initial value) than PAC-HB (1250 #/s decrease, 45% reduction of the initial value). On the other hand, alum and PANS have similar efficiencies, the maximum reduction of TNC being around 1000 #/s (36% of the initial value), while with PAC-MB the maximum reduction was lower than 600 #/s (21% of the initial value).

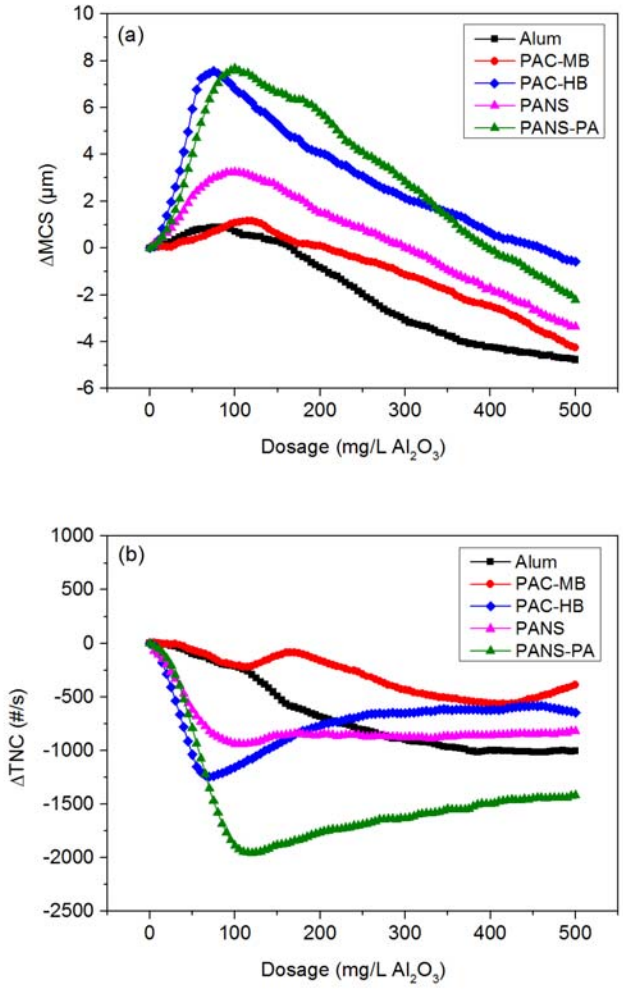


Figure 4.- (a) MCS and (b) TNC vs. dosage of coagulants.

Furthermore, the dosage at the maximum of the MCS evolution curve or at the minimum of the TNC evolution curve are preliminary optimal dosages of the products. In this case, the differences between the products are not very large, the optimal dosages ranging between 75 mg/L and 125 mg/L Al_2O_3 for all the coagulants tested.

Considering together the MCS increase and the TNC decrease obtained by the different coagulants, their flocculation efficiencies should follow this order: PANS-PA ≈ PAC-HB > PANS > alum ≈ PAC-MB. It seems that the higher basicity of the product, the higher efficiency, with the only exception of PANS-PA, which includes polyamines in its formulation and must be considered apart. The importance of the basicity is related to the large pH suppression observed after the treatment due to the high aluminum dosages required for treating the waters. This large pH suppression made alum and PAC-MB not working at the optimum conditions for the minimum solubility of $Al(OH)_3$ at the highest dosages used.

3.2.2. Flocculation-deflocculation-reflocculation studies

Next is studied the strength of the flocs and the effect of shear intensity of the flocs formed with the different treatments. As the behavior observed showed a continuous transition from the behavior at the lowest dosage (25 mg/L) to the highest dosage (250 mg/L), thus the flocculation-deflocculation-reflocculation curves for these two extreme dosages were chosen to be shown in Figures 5-6. For a detailed comparison among the different coagulants, the chord size distribution curve at the different stages of this study for each coagulant at 25 and 250 mg/L are also shown in Figures 7-8. The results obtained in these studies will be analyzed stage by stage. First flocculation, second deflocculation (and strength factor) and finally, reflocculation (and recovery factor).

Flocculation stage. At the flocculation stage, low dosages of the coagulants (25-50 mg/L) were not able to significantly increase the MCS or reduce the TNC, except PAC-HB (Figures 5 and 7). However, at higher dosages of coagulant (>100 mg/L), a significant increase in the MCS and a significant decrease in TNC were observed, which demonstrates a significant agglomeration of the particles took place (Figures 6 and 8). In all the cases, the extent of the agglomeration

increases at the highest coagulant dosages but for PAC-HB. At 25 mg/L, PAC-HB was the coagulant increasing in a largest extent the MCS (around 10 µm), while the rest of the coagulants achieved a MCS increase in the 1.0-1.5 µm range. At 250 mg/L, the composite flocculant (PANS-PA) was the product obtaining the highest increase in the MCS (around 12 µm) while for the other coagulants this increase was always < 4 µm. In addition, the TNC decrease induced by PANS-PA was as high as 1400 #/s, compared to 500-1000 #/s with the other coagulants.

As commented before, in the case of PAC-HB, high dosages do not favor the flocculation processes, as a lower decrease of the TNC and a lower increase in MCS was observed (see Fig. 7c and Fig. 8c for comparison). However, DAF tests demonstrated that this product is very efficient in removing turbidity, silica and COD, and its efficiency increases at higher dosages, with no apparent restabilization according to turbidity or cationic demand measurements. The reason for this apparent controversy could be the shape of the flocs formed by PAC-HB. A previous study with similar industrial waters showed that polyaluminum chlorides of high basicity can induce a linear aggregation of the particles which generates cylindrical coagula, much longer but with similar diameter of the original particles [35]. As the probability the laser beam to intercept the particle at the longer side is much lower than at the shorter side, this aggregation cannot be measured directly by FBRM technique and this could justify why the MCS increase and the TNC decrease is lower at the highest dosages tested.

If we study the different size ranges of the flocs formed, we can see that at low dosages of the coagulant, there is an important increase in the number of particles in the 10-100 µm range, while this increase is less important at the highest dosages. This means the particles with the lowest sizes are coagulated first, while at higher dosages, larger size particles are also coagulated.

Deflocculation stage and strength factor. Deflocculation process was characterized by a decrease of the MCS of the particles and an increase in the TNC at all the dosages tested. All the coagulants showed similar behavior, both in trends and values, but PANS-PA. The deflocculation process decreased the MCS of the particles, this decrease being lower at increased dosages for all the coagulants and always in the 4-8 μm range (see Figures 7-8). However, with PANS-PA, the MCS decrease increases at higher dosages and these MCS decreases are considerably larger than with the other coagulants (8-18 μm). This could be explained by the fact that PANS-PA was the product increasing in a larger extent the MCS during the flocculation stage, therefore, it is possible the deflocculation occurs to a larger extent than with other coagulants which produced a lower increase in the MCS formed during the flocculation stage (Figures 7-8).

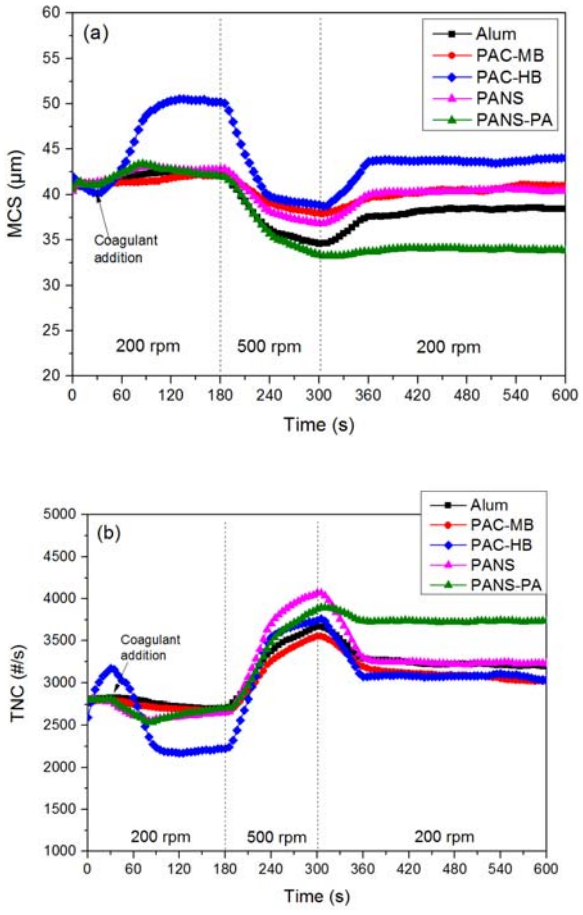


Figure 5.- (a) MCS and (b) TNC at 25 mg/L Al_2O_3 coagulant vs. time in flocculation-deflocculation-reflocculation studies.

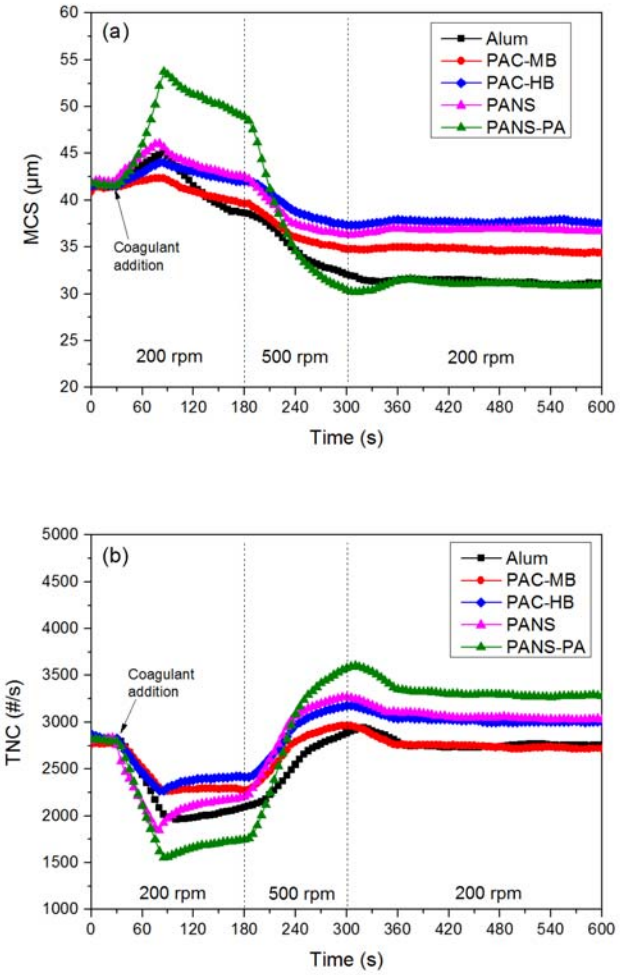
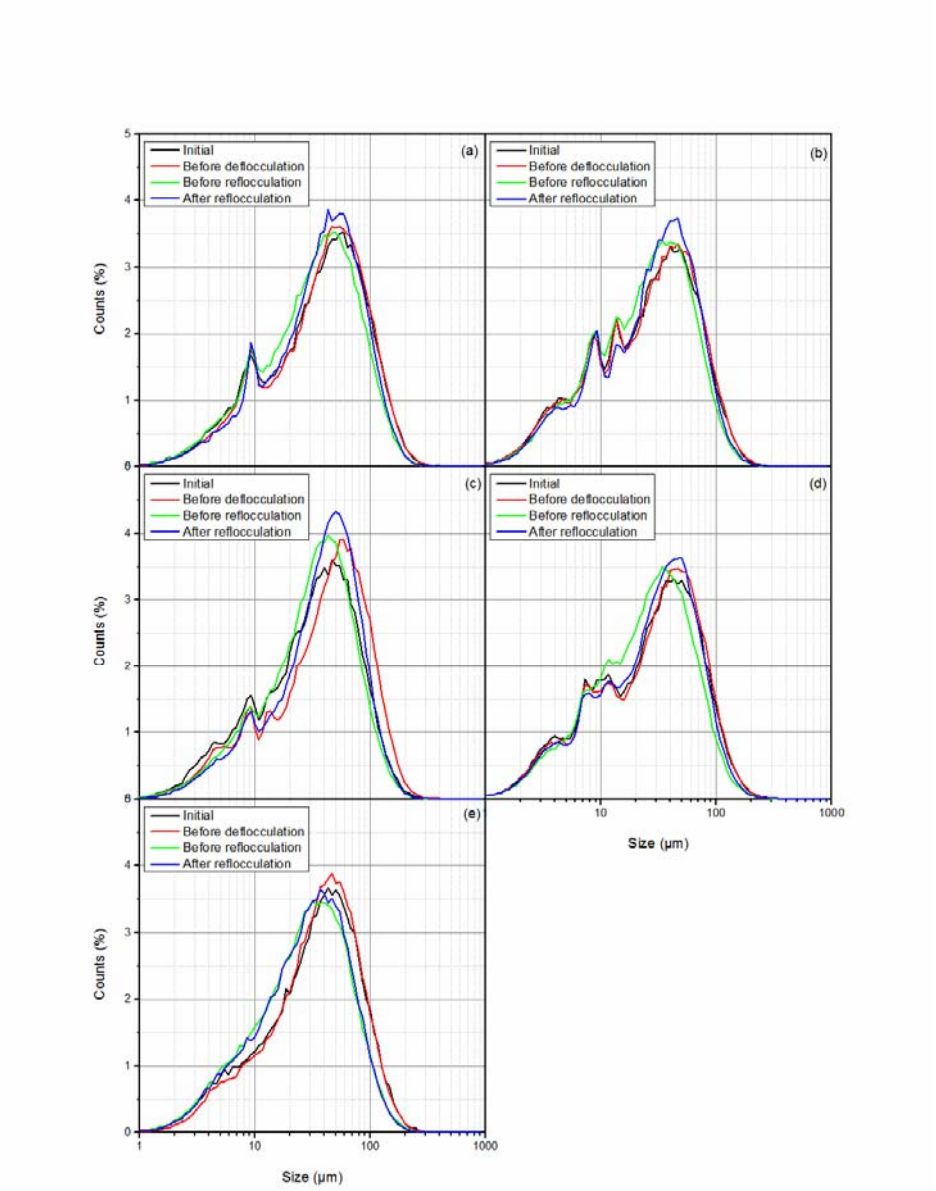
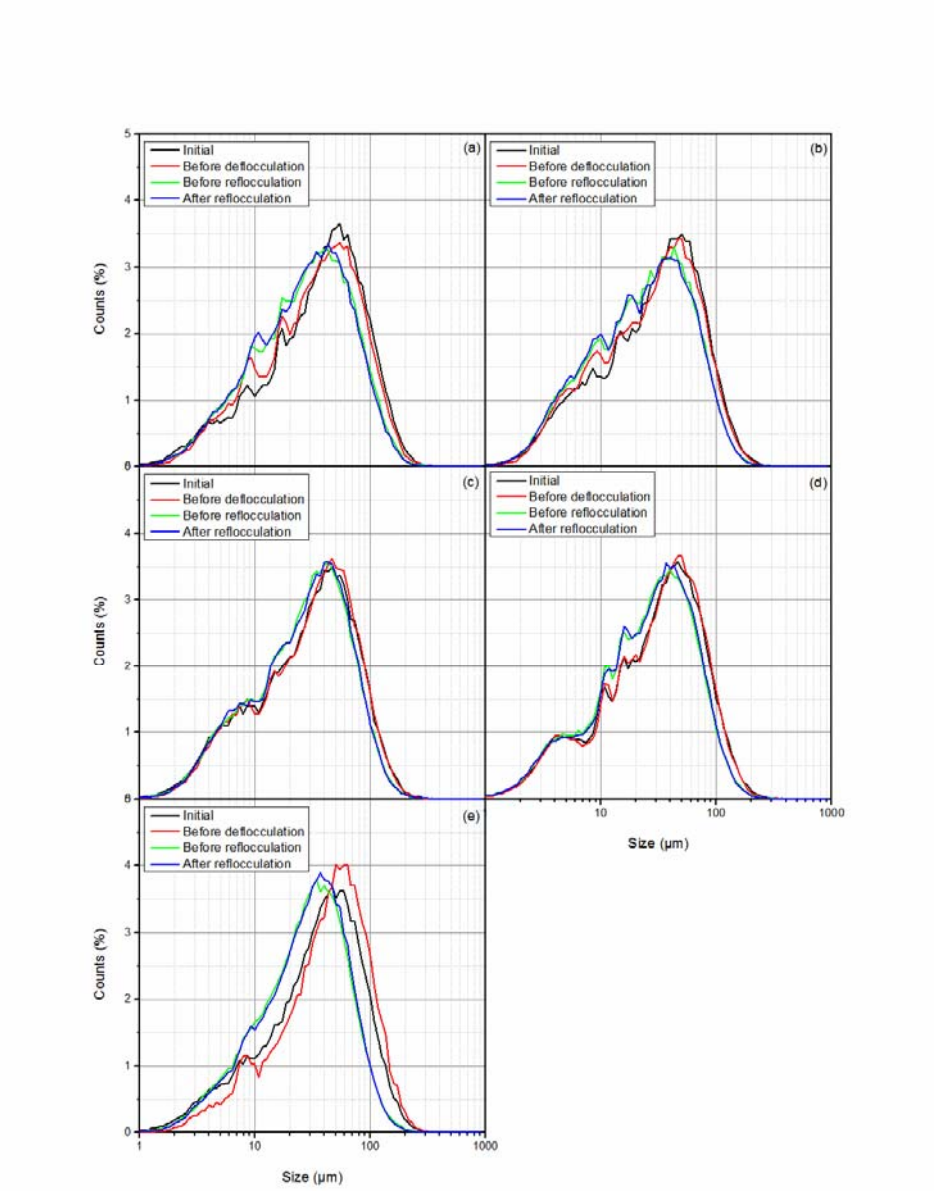


Figure 6.- (a) MCS and (b) TNC at 250 mg/L Al_2O_3 coagulant vs. time in flocculation-deflocculation-reflocculation studies.



379

380 Figure 7.- Chord size distribution curves at different stages of the flocculation-deflocculation-
381 reflocculation study, all the coagulants at 25 mg/L: (a) alum, (b) PAC-MB, (c) PAC-HB, (d)
382 PANS, (e) PANS-PA. Note: before deflocculation = after flocculation; before reflocculation =
383 after deflocculation.



384

385 Figure 8.- Chord size distribution curves at different stages of the flocculation-deflocculation-
386 reflocculation study, all the coagulants at 250 mg/L: (a) alum, (b) PAC-MB, (c) PAC-HB, (d)
387 PANS, (e) PANS-PA. Note: before deflocculation = after flocculation; before reflocculation =
388 after deflocculation.

389

390 In a similar way, the TNC increase decreases at the highest dosages for all the coagulants but
391 PANS-PA, i.e. from 1000-1500 #/s at 25 mg/L to 500-1000 #/s at 250 mg/L. In the case of
392 PANS-PA, the TNC increase increased from around 1800 #/s at 25 mg/L to 2500 #/s at 250
393 mg/L. This means PANS-PA flocs are very sensitive to high shear forces, probably due to the
394 larger flocs obtained by PANS-PA compared to the other aluminum coagulants. In this sense, at
395 dosages ≥100 mg/L, just before deflocculation, MCS is around 55 μm compared to an initial
396 value of 47 μm. Therefore, it is expected that more particles will be broken (and the MCS will
397 decrease in a higher extent) than with other coagulants. Although all the flocs were subjected to
398 the same hydrodynamic stress, it is well known that the largest flocs are also the weakest [36].
399
400 The differences in the strength of the formed flocs was also analyzed by the strength factor
401 (Figure 9). As expected, the strength factor is very similar for all the treatments but PANS-PA.
402 The strength factor for pure aluminum coagulants is high (around 85-90%), indicating the flocs
403 formed are high resistant to shear forces. These values are very similar for all the coagulants
404 tested and they are independent from the dosages used. As commented before, charge
405 neutralization and sweep flocculation are the two main flocculation mechanisms for alum and
406 PAC coagulants. The flocs obtained in charge neutralization are soft, with limited shear
407 resistance [24-25]. Similarly, the strength of flocs formed by sweep flocculation are also weak
408 and prone to breakage, however, there is a possibility to be at least higher shear resistance than
409 charge neutralization [37]. In fact, some authors have obtained a higher strength for flocs formed
410 by charge neutralization than those formed by sweep flocculation [19,38], while others have
411 obtained the opposite result [39]. This can be explained because the flocs produced by
412 precipitation are of widely varying shear strength and density, as recognized by J. Bratby (2006)
413 [13], and also because there is an inherent combination of charge neutralization and sweep
414 flocculation mechanisms, especially in complex systems such as the one studied. In principle, at
415 the lowest dosages tested it should be predominant charge neutralization while at the highest
416 dosages, sweep flocculation. Due to the low variation of strength factors observed for both
417 mechanisms, it can be said that the floc strength is very similar for both flocculation mechanisms
418 in the analyzed system.

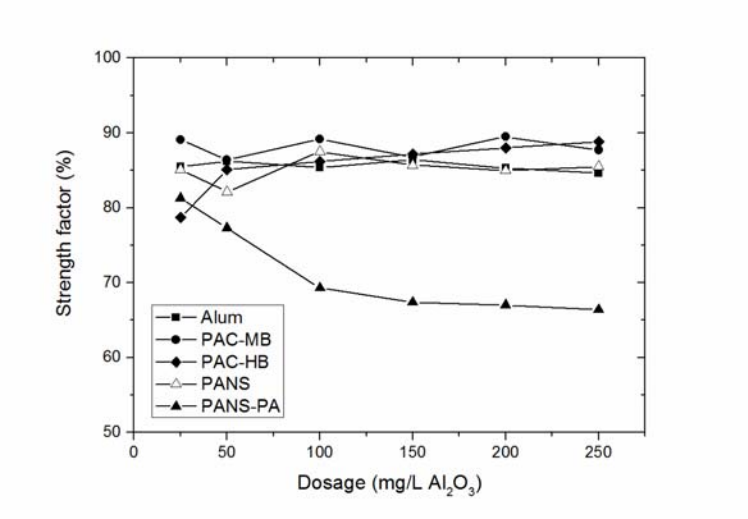


Figure 9.- Strength factor for the different coagulants and used dosages.

In general, PACl products give stronger flocs than alum at equivalent aluminum dosages [40], however the results obtained in this study are practically the same for alum and PACl products. Differences in the strength factor for the different pure aluminum salts are around the experimental error but in the case of PAC-HB. In this case, a ten points increase in the strength factor was observed from the lowest dosage (25 mg/L, 78.1%) to the highest dosage (250 mg/L, 88.8%), most of this increase occurring at the lowest dosages (85.1% strength factor at 50 mg/L). Although the strength factor is very similar to other aluminum salts at the highest dosages, a lower shear resistance of the flocs have been observed at the lowest dosages tested. This fact could be related to the pH of minimum solubility of aluminum salts and the Al concentration at these conditions. According to D.J. Pernitsky and J. Edzwald (2003) [12], the solubility of Al at the pH of minimum solubility is larger for high basicity non sulphated polyaluminum chlorides such as PAC-HB (36 µg/L Al, pH 6.4) than for other types of aluminum coagulants, i.e. alum (16 µg/L, pH 6.0) and medium basicity sulphated, such as PANS (29 µg/L Al, pH 6.3). This would justify that there is more dissolved aluminum at the conditions of minimum solubility and thus the amount of $Al(OH)_3$ precipitated is lower for PAC-HB than for other aluminum salts. This would mean that the importance of sweep flocculation at low dosages is slightly lower and that of charge neutralization slightly higher than for other aluminum salts at the same aluminum dosage. As the shear resistance of the flocs formed by charge neutralization are very low (in some cases lower than this of sweep flocculation), this explains would explain why the strength

441 factor of PAC-HB at low dosages is slightly lower than for the other aluminum coagulants, while
442 this difference became negligible at dosages higher than 50 mg/L.
443
444 On the other side, the strength factor of PANS-PA is much lower than those of the pure
445 aluminum salts, decreasing with the dosage from 81% (at 25 mg/L) to 66% (at 250 mg/L). The
446 most important decrease was observed at the lowest dosages (25-100 mg/L), while the strength
447 factor was almost constant (65-70%) at higher dosages. This in agreement with the results of
448 MCS obtained after flocculation at the different dosages tested. At 25 mg/L and 50 mg/L, the
449 initial MCS of the waters increased to 46.1 μm and 45.9 μm, respectively, while at dosages of
450 100 mg/L and higher, MCS before deflocculation was almost constant, varying in the 54-55 μm
451 range. PANS-PA flocculation mechanism is a combination of the flocculation mechanism of
452 PANS and PA. If PANS primarily acts by charge neutralization and sweep flocculation,
453 depending on the dosage, the flocculation mechanism of PA can be patches formation or
454 interparticles bridging formation. The flocs formed by patches are generally soft, small and rigid,
455 while the flocs formed by bridges are big, hard and flexible. If the main flocculation mechanism
456 would be bridges formation, the strength factor should be higher than for pure aluminum
457 coagulants, while if it would be patches formation, the values should be very similar to that of
458 pure aluminum coagulants. However, the strength factor is only similar to that of pure aluminum
459 coagulants at 25 mg/L and then decreased largely with the dosage. The explanation can be the
460 patches formation became impaired at dosages higher than 25 mg/L. As commented previously
461 in DAF tests, PANS-PA cationic demand was almost zero at dosages higher than 100 mg/L, and
462 charges close to zero would not be beneficial for patches formation.
463
464 In general, floc strength increases with decreasing flocs sizes [41]. In the tests carried out, the
465 MCS of the flocs have clearly increased from 25 to 250 mg/L, i.e. from 1.4 to 3.4 μm for alum,
466 from 1.1 to 3.0 μm for PAC-MB, from 2.0 to 4.0 μm for PANS, and from 2.3 μm to 12.0 μm for
467 PANS-PA. The only product which showed other behavior was PAC-HB, where the MCS
468 decreased from 9.7 μm (at 25 mg/L) to 2.4 μm (at 250 mg/L). Despite these increases in the
469 MCS after flocculation, however, the strength of the flocs is very similar for all the dosages
470 tested (the differences among the products but PANS-PA are not very large). With PANS-PA,
471 the coagulant which produced the largest MCS increases during coagulation, it was observed a

472 reduction in the strength factor, especially at dosages lower than 100 mg/L. At dosages higher
473 than 100 mg/L, the size of the flocs remained approximately constant with the dosage, which is
474 in agreement with the almost constant value of the strength factor.
475
476 **Reflocculation stage and recovery factor.** As occurred during the deflocculation processes, the
477 behaviour of the coagulants is very similar but PANS-PA. With PANS-PA, there is almost no
478 reflocculation independently of the dosage used, with a very constant MCS after reflocculation
479 and only small MCS increases from 0 to 0.5 μm are observed during reflocculation. With the rest
480 of the coagulants, the higher dosage used the lower increase in the MCS of the particles after the
481 shear forces stopped, thus indicate the decrease in the reversibility of the flocs at increased
482 dosages. At low dosages (25-50 mg/L), all the pure aluminum coagulants increased the MCS
483 during reflocculation in the 3-5 μm range and in the 0-1 μm range at the highest dosages.
484
485 After 5 minutes of reflocculation, the MCS of the particles was always lower and the TNC
486 always higher than those of the initial waters, being this difference more important in the case of
487 PANS-PA than in other coagulants. The explanation is related to two facts: (a) the reversibility
488 of the flocs and (b) the effect of shearing forces on the initially present particles. It has been
489 observed that without using any coagulant, and only increasing the shearing forces, the TNC
490 could increase largely while the MCS decreased largely (Figure 10). The higher value of TNC
491 and lower MCS observed after reflocculation indicate the particles of the suspension are not
492 stable with the shear forces. This is reasonable according to the fact these waters are partially
493 flocculated; these waters are the rejects from different process stages, some of them were
494 flocculants were used, after several cycles of use).

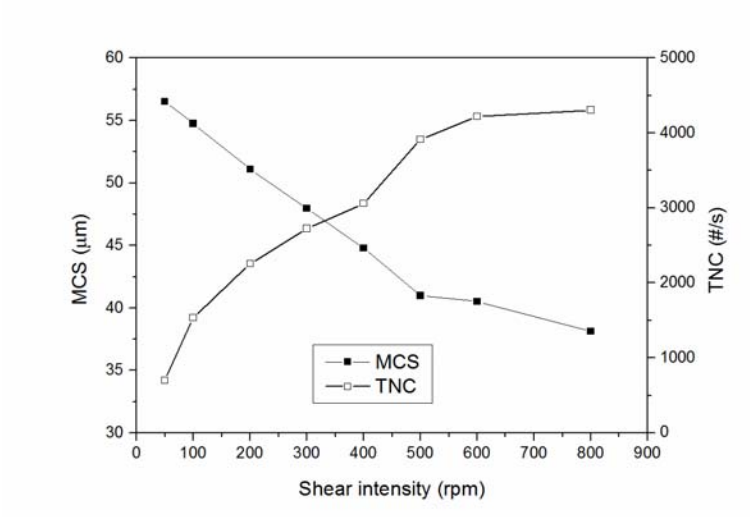
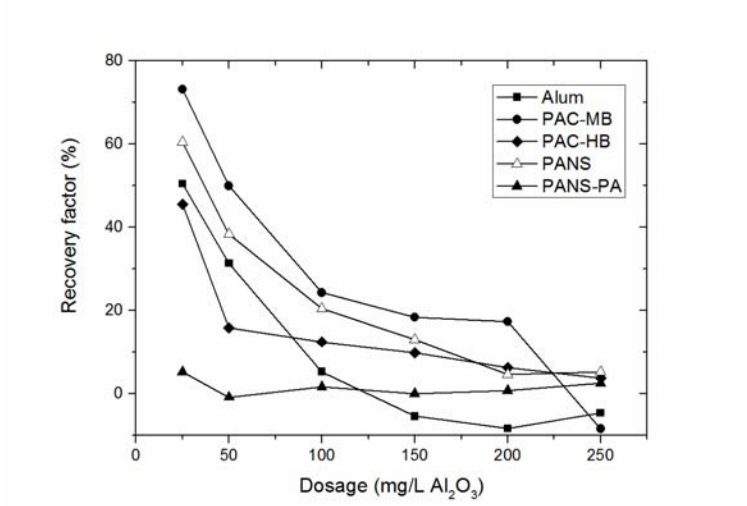


Figure 10.- Effect of shear intensity on MCS and TNC of the initial water.

As it was commented before, at low aluminum concentrations there is possible a partial charge neutralization mechanism, which makes the flocs to be partially reversible. However, as the dosage increases, the solubility of $Al(OH)_3$ is exceeded, and the main flocculation mechanism is sweep flocculation, which makes the flocs irreversible. The differences observed between PANS-PA and the other coagulants can be related either to its different nature or to the previous flocculation process. If we consider the PANS-PA nature, the addition of PA could induce a partial patching mechanism, which would generate flocs which are partially reversible (less reversible than charge neutralization but more reversible than sweep flocculation). Consequently, this product should be more reversible than other coagulants at the lowest dosages and similar at the highest dosages. However, this behavior was not observed. As the polyamines used in the composite flocculant are a mixture of polyamines of different molecular weights, some of them could act through patches formation (reversible flocs) but some of them through interparticles bridges formation (irreversible flocs). A possible explanation could be the highest concentration of suspended solids after deflocculation which promote interparticles bridging formation instead of patches [14-16].

Similarly to what strength factor represents in deflocculation, recovery factors were used to characterize the behavior of the flocs after refloccualtion. The results for the different treatments

517 are shown in Figure 11. Recovery factors decreased largely with the dosage for the pure
518 aluminum-based coagulants. At the lowest dosage tested (25 mg/L), the recovery factor varied
519 from 46% (PAC-HB) to 73% (PAC-MB), while at the highest dosage (250 mg/L), recovery
520 factor varied between -8% (PAC-MB) and 5% (PANS). In the case of PANS-PA, the recovery
521 factor was always close to zero, independently of the dosage tested, indicating its irreversibility.
522 Although the other coagulants reach a zero recovery factor at the highest dosage, there are
523 significant differences among them at the lowest dosages. At 25 mg/L, the recovery factors
524 varied in the following order: PAC-MB (73.2%) > PANS (60.5%) > alum (50.5%) > PAC-HB
525 (45.6%).
526



527
528 Figure 11.- Recovery factor for the different coagulants and used dosages.
529
530 The sharp decreases of recovery factors for alum and PAC-MB occurred at around 100 mg/L and
531 200 mg/L, respectively, which is in agreement with the dosages at which the restabilization was
532 observed in turbidity measurements. These sharp decreases in recovery factor are mainly related
533 to the pH suppression than to reach charge reversal as none of them achieved charge reversal, as
534 was previously demonstrated by cationic demand measurements.
535
536 As commented before, when charge neutralization is the predominant flocculation mechanism,
537 the reflocculation is almost total when the shear forces ends [24-25]. However, if sweep
538 flocculation is predominant, the flocs will likely to have a reduced recovery compared to a

539 coagulant treatment that primarily functions by charge neutralization [39]. As it can be seen from
540 the evolution of the recovery factor with the dosage, there is a continuous decrease in the
541 reversibility of the flocs formed, which could be explained by the increasing contribution of
542 sweep flocculation at increased dosages of the coagulant. If charge neutralization can be
543 considered the main flocculation mechanism at the lowest dosages tested (25-50 mg/L), at higher
544 dosages there is a combination of charge neutralization and sweep flocculation, the importance
545 of sweep flocculation becoming predominant at the highest dosages (> 150-200 mg/L), as
546 confirmed by the recovery factors < 5% obtained for these treatments.
547
548 In the case of PANS-PA, the recovery factor is around 0-5%, independently of the dosage tested.
549 Even at the lowest dosage tested, the recovery of the flocs is practically zero. This indicates that
550 the main flocculation mechanism of PANS-PA, although aluminum is present, is mostly
551 determined by the PA. The aluminum of the PANS part can produce a large amount of sweep
552 flocculation which can be agglomerated after by the polyamine. According to the previous
553 results obtained, the main flocculation mechanism of PA is bridges formation instead of patches
554 formation, independently of the dosage, which agrees with the larger flocs obtained by PANS-
555 PA during flocculation and the null reversibility of the flocs, typical situation for interparticles
556 bridge formation flocculation mechanism. If there are high concentration of suspended solids (as
557 occurs after deflocculation), bridges formation is promoted compared to patches formation even
558 for high charge density polyelectrolytes. During deflocculation, PANS-PA behaviour is more
559 close to patches formation than interparticles bridges formation, probably because the
560 concentration of particles is lower than after deflocculation.
561
562 In the case of recovery factor, basicity of the coagulants seems to play an important role. With
563 the exception of alum, the recovery factor of the polyaluminum coagulants is higher at lower
564 basicities: PAC-MB (73.2% strength factor, 37% basicity) > PANS (60.5% strength factor, 46%
565 basicity) > PAC-HB (45.6% strength factor, 85% basicity). The strength factor of alum is
566 intermediate (50%) although its basicity is 0% as there are significant differences in the action of
567 alum compared to polyaluminum coagulants. While in the case of alum, polymeric Al species are
568 not expected to be present at significant concentrations during coagulation, the opposite is true
569 for polyaluminum chlorides [8].

4. CONCLUSIONS

Significant differences in the removal efficiency of contaminants and flocculation behaviour have been found among the different aluminum-based coagulants. Alum and PAC-MB were the least efficient coagulants due to the high pH suppression after the treatment, PANS has an intermediate efficiency, and PAC-HB and PANS-PA were the most efficient coagulants. The higher basicity of the coagulant, the higher efficiency in removing contaminants was obtained. On the other hand, the high efficiency of PANS-PA is due to the presence of polyamines in its formulation which increases much its efficiency compared to their base PANS even although its basicity is intermediate.

At low dosages of coagulant (25-50 mg/L), the main flocculation mechanism for the coagulants is charge neutralization, while at high dosages, the contribution of sweep flocculation become more predominant. The hybrid coagulant has a rather different behaviour. The polyamines in PANS-PA seems to enhance patches formation during flocculation but interparticles bridges formation during reflocculation. This is reasonable according to the fact that polyamines used in its formulation are a mixture of high charge but different molecular weights and the concentration of small solids (as obtained after deflocculation) promotes interparticles bridging instead of patches formation.

The strength factor of the flocs formed by the pure aluminum coagulants was very similar and high (85-90%), independently of the dosages. The strength factor of the hybrid coagulant was much lower than those of the other coagulants, and decreasing with the dosage from 81% (at 25 mg/L) to 66% (at 250 mg/L). The larger flocs obtained during flocculation with PANS-PA are probably the cause for a reduced strength factor as the larger flocs are also the weakest. The possible flocculation mechanism of PA by the formation of patches (with very low shear resistance) is in agreement with the results obtained.

The recovery factors for the pure aluminum coagulants decreased with the dosage, from 46-73% (at 25 mg/L) to 0% (at 250 mg/L). At the lowest dosages, the contribution of charge neutralization is still important and there are high recovery factors (in pure charge neutralization

mechanisms the refloccualtion should be almost total). As the dosage of the coagulant increases, sweep flocculation (irreversible flocs) became predominant, and there is a parallel decrease in the strength factor of the formed flocs. In the case of PANS-PA, the recovery factor was always close to zero, independently of the dosage. This behaviour would be explained by interparticles bridges formation instead of patches formation at the reflocculation conditions, where the high concentration of small solids promote interparticles bridges formation compared to patches formation.

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PUBLICATION VI

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"Efficiency of chitosans for the treatment of papermaking process water by dissolved air flotation"

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Efficiency of chitosans for the treatment of papermaking process water by dissolved air flotation

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HIGHLIGHTS

- Papermaking process waters were treated with chitosans in dissolved air flotation.
- At neutral pH, native chitosans were more efficient than quaternary derivatives.
- A high synergy is obtained when native chitosans are combined with bentonites.
- Chitosan dosage can be reduced by half if bentonite is added at a ratio 1:2 by weight.
- FBRM technique allows monitoring flocculation and predicts separation efficiency.

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ABSTRACT

Interest has grown in bio-polymers as being environmental friendly alternatives to synthetic additives. In this work, two native chitosans with different molecular weights have been evaluated on a laboratory scale for their effectiveness for the removal of contaminants from papermaking process waters by dissolved air flotation (DAF). The use of chitosan quaternary derivatives and the use of the native chitosans in combination with anionic bentonite microparticles have also been tested. Results demonstrate a high efficiency of the native chitosan products at intermediate dosages and furthermore, their efficiency is enhanced by the combined addition of bentonite. For an equivalent removal of contaminants, the required dosage of chitosan is about half that the dosage required in absence of bentonite. Quaternary derivatives have not improved the efficiency of the native chitosan in this case. The optimum treatment would be 50 mg/L of nativechitosan and 100 mg/L of bentonite where this treatment is capable of the removal of 83–89% turbidity (residual turbidity 210–320 NTU), 68–71% dissolved turbidity (residual dissolved turbidity of 22–24 NTU), 18–22% total solids (residual total solids of 2750–2900 mg/L) and 19–23% COD (1440–1525 mg/L). The low molecular weight native chitosan is more efficient than the medium molecular weight chitosan in all cases. The Focused Beam Reflectance Measurement (FBRM) is used to assess the aggregation process and to predict the separation efficiency of DAF units either with single or dual systems. The efficiency predicted through the FBRM technique is very similar to that obtained later in the DAF tests.

1. Introduction

The pulp and paper industry is a large water consumer, the reduction of fresh water consumption being one of the most important issues in papermaking operations. One of the most frequently used strategy for reducing the fresh water consumption is the closure of the water circuits by reusing the process waters. However, as the mill closes the water circuits, there is a continuous accumulation of suspended and dissolved and colloidal material (DCM) in process waters, which increases nearly exponential with the reduction of fresh water consumption. While suspended solids are removed easily in the existing clarification systems, DCM is almost completely recycled into the process thus, limiting the closure of the circuits [1]. DCM negatively affects the production process causing blockings, scaling, slime formation, breaks and stickies deposits and also affects the quality of the final product by impairing itsphysical properties or by the presence of dirt and holes [2–4].

One of the most common processes used for the treatment of papermaking process waters is the dissolved air flotation (DAF), also called micro flotation. Water clarification by DAF is achieved

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in a rather quiescent environment by capture of both hydrophobic and hydrophilic solids on very fine bubbles generated by the release of air previously dissolved in pressurized water. DAF units efficiently remove 80–99% of suspended solids including fines, fillers, and a variety of contaminants such as ink particles and lipophilic extractives [5,6]. Moreover, with suitable chemicals, finely dispersed and colloidal organic particles (>0.2 μm) can also be agglomerated and removed. However, the best reductions of organic DCM obtained by micro flotation, measured as COD, are not higher than 10–30% and these removal efficiencies are really a great achievement as most COD is soluble [6–10]. On the contrary, inorganic and biological DCM are almost not affected by DAF.

A variety of chemicals are used in DAF systems where common chemicals including: aluminum based products such as alum, polyaluminum chloride, aluminum chlorohydrate, polyaluminum sulfate, etc.; ferric chloride; minerals such as bentonite or talc, and organic polymers such as polyacrylamides, poly(diallyl-dimethylammonium-chloride), polyamines, polyvinylamides, etc. [9]. Inorganic coagulants have been used for decades as they are cost effective and easy to handle, but these processes have a number of disadvantages: they are strongly pH-dependant, they consume alkalinity of the waters, high dosages of coagulants are necessary, high amounts of metal hydroxide sludge are produced, and in the case, of alum and aluminum salts, its use is now very controversial due to the possible impact of residual aluminum on Alzheimer's disease [11]. On the other hand, syntheticflocculants, mainly polyacrylamide-based cationic flocculants have been greatly used in the industry due to their economic advantages and easy tailorability by controlling the molecular weight, molecular weight distribution, chemical structure of polymers, nature and ratio of functional groups on polymeric backbone. The synthetic polymers are not biodegradable and their degraded products are considered hazardous because of the release of monomers that could enter in the food chain and cause carcinogenic effects [11].

For these reasons, the search for better alternatives to the conventional coagulants has become an important challenge [11,12]. Increasing demand for environmentally friendly technologies promotes the interest to natural polyelectrolytes where chitosan being the most promising cationic biopolymer for extensive application [13–15]. Chitosan is a polycationic biodegradable non-toxic high molecular weight linear copolymer of glucosamine and N-acetyl glucosamine, with a high charge density in the acidic to neutral solutions and it can be used as an eco-friendly coagulant/flocculant hybrid. The reactivity of chitosan for the coagulation and flocculation of suspended particles and colloids results from several mechanisms including: (i) electrostatic attraction, (ii) sorption, related to protonation of the amine groups of chitosan and chelatingcapacity due to the high content of hydroxyl groups, and (iii) bridging, related to the relative high molecular weight of chitosan [12].

In acidic to neutral solutions, the amino group in chitosan is protonated resulting in a high charge density and good solubility. However, this charge density is pH dependent where at neutral to basic conditions, chitosan loses its charge and precipitates from solution making it unusable. For these applications, quaternization is an alternative path to produce water-soluble chitosan derivatives with a wide operational pH range including neutral and slight basic conditions which are common in papermaking operations due to a permanent positive charge on the polymer backbone [16–19]. In addition, this would avoid the use of carboxylic acid solutions (such as acetic acid), which could increase organics content of treated waters, or inorganic acid solutions (such as chlorhydric acid) for preparing chitosans [20,21]. Another strategy toimprove the efficiency of chitosans is their low exploited combination with bentonites. The use of bentonites can improve the size and the density of the formed flocs which can result in an increase of its flocculation rate and at the same time can promote the adsorption of organics [22,23]. For a given level of contaminants' removal, the use of bentonites can help to reduce the required dosage of chitosan and thus, the treatment costs.

The objective of this study was first, to evaluate the efficiency of different chitosan treatments for the removal of dissolved and colloidal materials by the DAF process and second, to predict the efficiency of these treatments and their flocculation behavior using the Focused Beam Reflectance Measurement technique (FBRM). Apart from the efficiency of native chitosans, the possible efficiency improvement on using chitosan quaternary derivatives or by a combined addition of the native chitosans with anionic bentonite microparticles were also assessed.

2. Materials and methods

2.1. Materials

2.1.1. Process water

Process water samples were obtained from a DAF unit at Holmen Paper Madrid mill, producing newsprint from 100% recovered paper. This mill has a highly closed water circuit with three water loops, each one equipped with a DAF unit for the internal treatment of the process waters of the loop. The samples were taken from the inlet of the DAF unit located in water loop 2, which include the process waters from post-flotation, bleaching and thickening stages. The characterization of the process waters is shown in Table 1. Most of the contaminants, especially organic ones, are soluble: the dissolved COD is almost 83% of total COD and the suspended solids content is only around half of total solids. According to FBRM measurements, the mean chord size of the particles is 10.4 μm and 87.0% of them are smaller than 20 μm. All trials and analyses werecarried out within five days after taking the samples and the process water was always kept stored at 4 °C before use to avoid their degradation.

2.1.2. Chemicals

Four chitosan products were tested; two native chitosans and two quaternary derivatives and their main characteristics are shown in Table 2. The two native chitosans have a very similar deacetylation degree and cationic charge density (CCD), but differ in their molecular weights; one has a medium molecular weight (Ch.MMW) and the other has a low molecular weight (Ch.LMW). They were both supplied by Sigma–Aldrich Co. The two quaternary derivatives (Quat.5 and Quat.10) were prepared from the low molecular weight chitosan (Ch.LMW) using N-(3-chloro-2-hydroxypropyl) trimethyl-ammonium chloride (Quat-188) as the quaternizing agent. They were prepared following the method described in [16] and two weight ratios chitosan:Quat-188 were used; one is 1:5 for Quat.5 and the other is 1:10 for Quat.10, in order to obtain two differentquaternization degrees (Table 2). Anionic bentonite microparticles (Hydrocol® OT) were supplied

Table 1
Characteristics of papermaking process water.

pH	7.7
Conductivity, 25 °C (mS/cm)	2.13
Total solids (g/L)	6.59
Total suspended solids (g/L)	3.35
Turbidity (NTU)	2400
Cationic demand (meq/L)	1.28
COD (mg/L)	2280
SiO_2 (mg/L)	240
Total dissolved solids (g/L)	3.24
Dissolved turbidity (NTU)	89
Dissolved COD (mg/L)	1890
Dissolved chlorides (mg/L)	157

Table 2
Characteristics of chitosan products.

Chitosan product	$M_w \times 10^5$ (g/mol)	CCD* (meq/g)	Deacetylation degree (%)	Quaternization degree (%)	pH stock solution (1 g/L)
Ch.MMW	2.375	5.75	86.5	–	4.05
Ch.LMW	0.768	5.44	85.7	–	4.00
Quat.5	–	2.27	–	72	6.95
Quat.10	–	2.11	–	86	6.95

* Cationic charge density at the pH of the stock solutions determined by colloidal titration.

by Ciba Specialty Chemicals (Switzerland) and were tested together with the native chitosans. The bentonite (B) is a montmorillonite sodium salt with a specific area of about 100 m^2/g and a slight anionic charge (0.235 meq/g). According to FBRM measurements (described next), the median chord size of the bentonite is 17.5 μm; around 25% of the particles are lower than 10 μm, 60% of the particles are lower than 20 μm, 80% are lower than 30 μm and more than 95% are lower than 50 μm.

Chitosan products, both native chitosans and quaternary derivatives, were tested using dosages from 25 to 250 mg/L. According to the results obtained in previous studies [23,24], the bentonite was added in a fixed ratio chitosan:bentonite of 1:2 (wt./wt.) in dual systems.

2.2. Methodology

2.2.1. Dissolved air flotation tests (DAF tests)

They were carried out in a laboratory-cell model Flottatest FTH3 supplied by Orchidis Laboratories (France). The experimental protocol followed is shown in Fig. 1. The different dosages of chitosans and bentonite were added from 1.0 wt.% stock solutions to a 1 L volume of the process water sample. After flocculation, 200 mL of tap water saturated with air at about 6.5 bar was added for the flotation. Ten minutes after the addition of the air saturated water, a sample of the clarified water was collected from the bottom. A number of blanks were also carried out without adding any chemical so as to consider the dilution of the samples due to the addition of air-saturated water during flotation (20%) and the efficiency of DAF to remove contaminants without previous coagulation/flocculation. All the tests werecarried out at room temperature (~20 °C) by duplicate and the average error between replicates was always under 5%.

The efficiency of the different chemical treatments applied was evaluated by measuring turbidity, total solids, chemical oxygen demand (COD), cationic demand, pH, conductivity and silica (Fig. 1). Turbidity was measured according to ISO 7027:2001 with a LP 2000-11 nephelometer supplied by Hanna Instruments. The total solids were measured according to the Standard Method 2450 B [25]. COD was measured employing the Nanocolor® COD 1500 test method (Macherey–Nagel GmbH) and using a Thermo Aquamate UV–Vis spectrophotometer for the end point. Cationic demand was measured by colloidal titration using a Charge Analyzing System (CAS) supplied by AFG Analytic GmbH and using 0.001 N polydiallyl-dimethyl-ammonium chlorides (PDADMAC) as titrant. Reactive silica was measured by flow injection analysis through the silicomolybdate or molybdenum bluecolorimetric method using a FIA Compact Analyzer (MLE GmbH), according to DIN EN ISO 16264:2002. Finally, pH and conductivity of the samples were measured according to Standard Methods using a GLP-22 pH-meter and a GLP-32 conductivity meter, both supplied by Crison Instruments, S.A. [25]. All measurements were also carried out by duplicate. To obtain the dissolved and colloidal fraction of the samples, they were centrifuged at 4128 rpm (2000 g) during 15 min using a Universal 16 centrifuge supplied by Hettich Zentrifugen GmbH.

2.2.2. FBRM tests

FBRM technique monitors in real-time the chord length distribution and the number of particles in a suspension. The data can be used to analyze the flocs properties and the flocculation mechanisms allowing the selection of both the best chemicals and the optimal chemical dosages [26]. FBRM technique has been previously used for the chemical optimization of the DAF treatments in papermaking processes [8–10,27–29].

The measurements were performed using a M500L FBRM supplied by Mettler–Toledo (United States) at the same experimental conditions used in the DAF tests. First, sequential additions of the chitosan treatments were carried out. This procedure allowed the determination of the optimum dosages of the chitosans to obtain the maximum mean chord size of the flocs and the maximum number of destabilized DCM thus, acquiring a possible maximum efficiency in the DAF treatment. In these tests, the FBRM probe is submerged into 250 mL water being stirred at 180 rpm and after 30 s of system stabilization, the chitosan is continuously added at sequential additions of 25 mg/L every 30 s while maintaining the stirring speed. Second, the flocculation behavior with time was analyzed after the addition of a single dose of the chitosans. These dosages were selected according to the results of thestudy of the sequential additions of the chitosans and were the same as those tested in the DAF treatments for an effective comparison. In these tests, the probe is submerged into 250 mL water and after 30 s of system stabilization, the chitosans were added at a single dosage. After 90 s of the addition of the chitosan, the bentonite was added (when dual systems are used). Finally, the evolution of the system was monitored during 5 min. Stirring speed was maintained constant during the test at 180 rpm.

3. Results and discussion

3.1. Flocculation behavior study

The flocculation process was first studied to predict the effectiveness of the different chemicals for DCM removal by DAF where two different approaches were used.

3.1.1. Sequential additions of the coagulant

Fig. 2 shows the increase of the mean chord size when consecutive coagulant additions were used. Initially, the mean chord size is around 10 μm. The native chitosans increased the mean chord size up to a maximum of 34 μm in the case of Ch.MMW and to 23 μm in the case of Ch.LMW at dosages in the range 150–250 mg/L. The chitosan derivatives increased the mean chord size in a lower extent than does the Ch.LMW (17–20 μm) and their maximum efficiency occurred at higher dosages than those dosages of the native chitosans (275–350 mg/L). In this case, Quat.5 was slightly more effective than Quat.10. When native chitosans were used in combination with the bentonite, a clear synergistic effect was observed. In this case, the mean chord size of the flocs increased to 70–85 μm which means two to four times higher than those obtained with native chitosans alone. In addition, the maximum efficiency was obtained at slightly lower dosages than those dosages of the native chitosans alone; 150–200 mg/L versus 200–250 mg/L.

The evolution of total number of counts gives also valuable information about the efficiency of the different coagulants (Fig. 3). Initially, the total number of counts of the process water was around 2200 ± 100 (#/s). When successive dosages of coagulants are added to the sample, it is observed a clear increase in

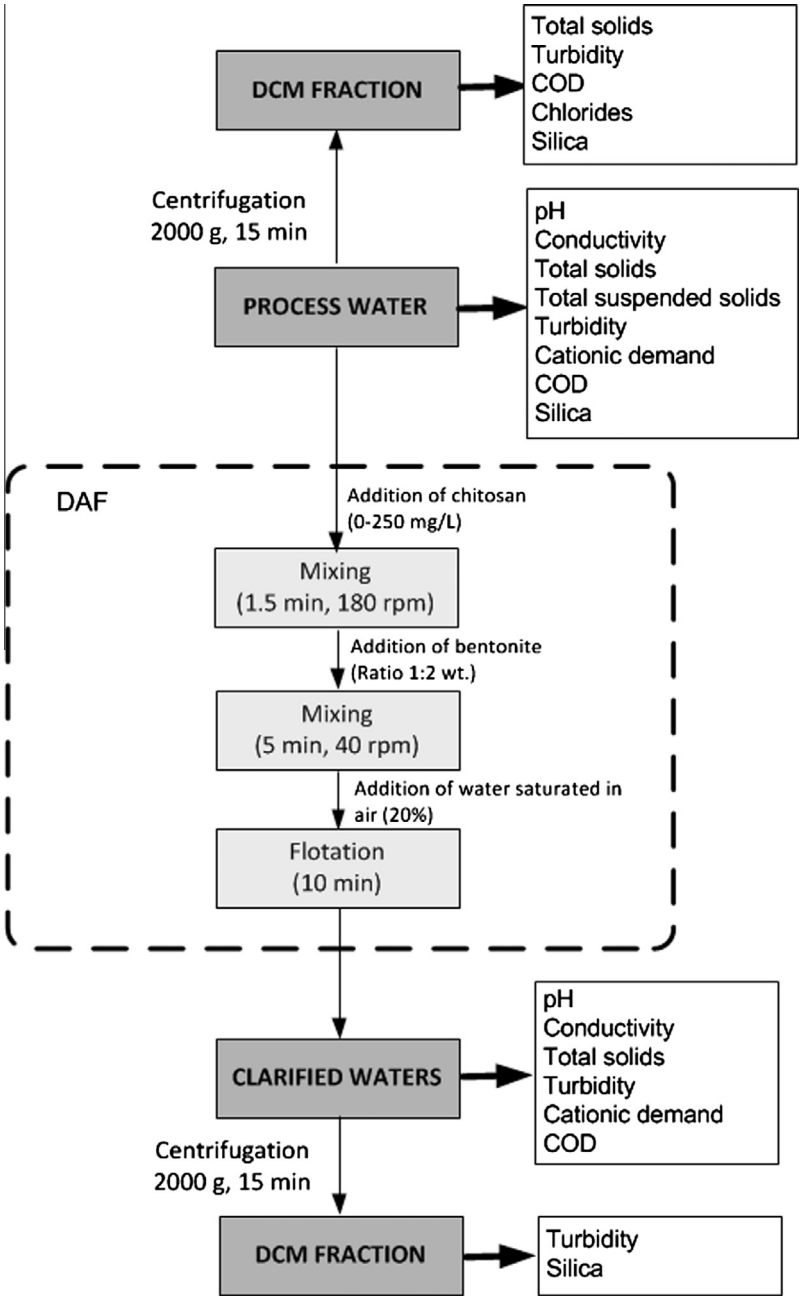

Fig. 1. Experimental protocol to evaluate the efficiency of different chemicals to remove DCM by dissolved air flotation.

the total number of counts. The reason is that the coagulant destabilizes the particles with a size lower than 1 μm (previously not detected by FBRM) and increases their particle size enough to be detected by the device (>1 μm). A higher increase in the counts number means more destabilized DCM. However, this increase must be analyzed together with the mean chord size of the resulting flocs to determine whether this size is large enough to be efficiently removed by DAF.

Native chitosans seem to be the most efficient coagulants as an effective increase in the total number of counts have been registered (up to 11,000–13,000 #/s) at the lowest dosages, i.e. 125 mg/L. Although quaternary derivatives increased the total number of counts to a higher extent (up to 11,000–16,000 #/s), considerably higher dosages (200–250 mg/L) were necessary. The dual systems chitosan–bentonite produced the lowest increase in the total number of counts although they were able to increase the total number of counts up to approximately 7000 #/s at only around 100 mg/L. At higher dosages, an important decrease in the number of counts occurred thus indicating that the previously destabilized particles are effectively aggregated to larger flocs (as demonstrated by the increase in the mean chord size at dosages higher than 100 mg/L). The increase in the mean chord size of the flocs formed bydual systems is considerably higher than those increases observed for single systems, therefore indicating that the microflocs obtained after the destabilization of DCM by chitosan can be effectively agglomerated to macroflocs by bentonite addition.

However, the other treatments especially quaternary derivatives are not effective in the aggregation of the previously destabilized particles. The case of native chitosans is intermediate. They produced an intermediate destabilization of DCM and an intermediate agglomeration of the previously destabilized DCM. After

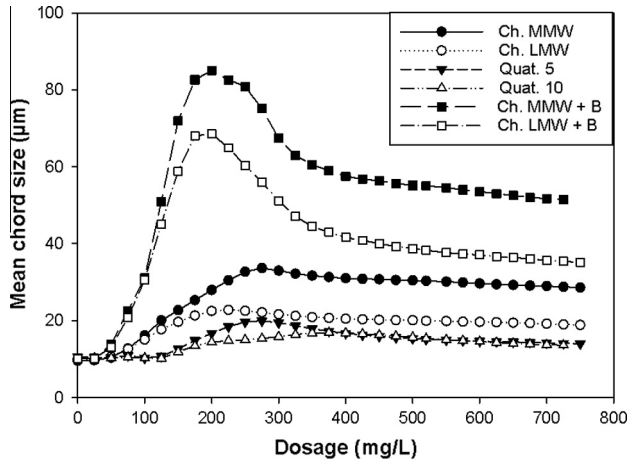

Fig. 2. Evolution of the mean chord size versus chemicals dosage.

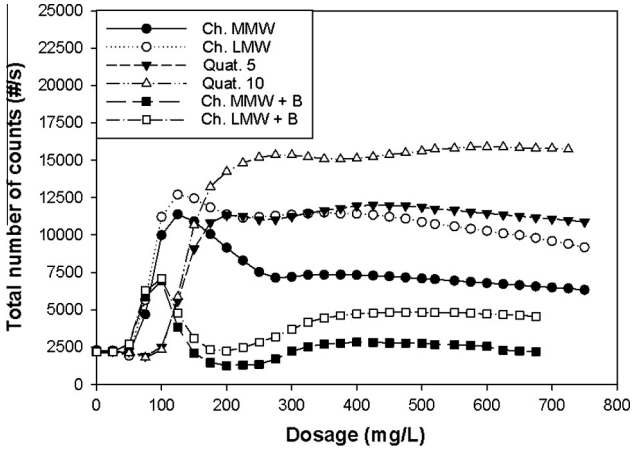

Fig. 3. Evolution of total number of counts versus chemicals dosage.

reaching the maximum total number of counts, there is a higher decrease in the number of particles (which means aggregation) with Ch.MMW than with Ch.LMW which could indicate that Ch.MMW is slightly more efficient than Ch.LMW. However, the number of particles previously destabilized by Ch.LMW is higher (around 13,000 #/s versus 11,000 #/s) which could be attributed to the lower increase in the mean chord size of the flocs. Therefore, it is difficult to select which native chitosan would be the most efficient in DAF treatments.

The analysis of the evolution of the number of counts between 1 and 10 µm (data not shown) have demonstrated the destabilization of DCM particles smaller than 1 µm. The trend in the number of counts lying between 1 and 10 µm is almost the same as that observed for the increase in the total number of counts evolution. Therefore, this demonstrates that the increase in total number of counts has been mainly due to the increase in the number of particles in this small size range.

3.1.2. A single addition of the coagulant

Comparing the mean chord size and the number of counts statistics for the different treatment systems and at the same dosages and conditions as those used for DAF tests, different behaviors are obtained. Fig. 4 presents the mean chord size of the aggregates depending on the coagulant dosages. On using single systems, the most efficient products in increasing mean chord size are native chitosans where Ch.MMW is more efficient than Ch.LMW. For both chitosans, the mean chord size of the particles increases at increased dosages observing a maximum value at around 150–200 mg/L which could be considered as the optimal dosage. At higher dosages of chitosan (i.e. 250 mg/L), the mean chord size decreases because the isoelectric point is reached and flocs destabilization takes place. At these dosages, the cationic demand of treated waters is 0–0.03 meq/L. When using chitosan derivatives, Quat.5 and Quat.10, the flocs size increase is smaller than those obtained with the original chitosan (Ch.LMW). In this case, the mean chord size also increases with the dosage, but no deterioration of the flocs size at the highest dosages has been observed. This is because the cationic demand of the waters treated with 250 mg/L of quaternary derivatives was still far from the isoelectric point (0.48–0.51 meq/L). Among the quaternary derivatives, Quat.5 seems to be slightly better than Quat.10, especially at dosages higher than 150 mg/L.

When bentonite is added together with the native chitosans (1:2 wt. ratio), their efficiency in increasing the size of the aggregates is clearly enhanced especially at intermediate dosages (around 100 mg/L). With this dual system it is possible to obtain considerably larger flocs than with the other treatments (mean chord size of 80–100 µm). At the same time, the dosage can be reduced to the half, 75–100 mg/L can be considered as the optimal dosages. When bentonite is added, Ch.LMW is slightly more efficient than Ch.MMW. This behavior of the Ch.LMW could be explained to fast interaction of chitosan molecules with DCM and formation first of small aggregates with cationic charge patches that further interact with anionic sides of other aggregates. At higher chitosan dosages, this phenomenon is counterbalanced by the cationic charge excess which leads to high dispersion rate of formed flocs (seealso Fig. 2).

The increase in total number of counts with time has been also analyzed (Fig. 5). The total number of counts increases with time for both the native and quaternized chitosans. This is due to the destabilization of the dissolved and colloidal material which is initially below the detection limit of FBRM device, but reaches a detectable size after aggregation (>1 µm). Up to dosages between 50 mg/L to 150 mg/L and even at 200 mg/L for quaternized chitosans, there is an important increase in the total number of counts. However, at the highest dosages, the number of counts generally decreased due to the aggregation of the previously destabilized DCM and thus, the mean chord size increased, as can be seen in Fig. 4. This could be a very positive effect due to theuse of chitosan products as they have the advantage of coagulating small particles [30] which cannot be separated otherwise by DAF system. Although flotation is generally promoted by large flocs (high mean chord size), but in some cases a low mean chord size with a higher number of counts indicate that DCM has been destabilized and aggregated forming small flocs that can be also removed subsequently by flotation [8,28,29]. Nevertheless, there is still a need

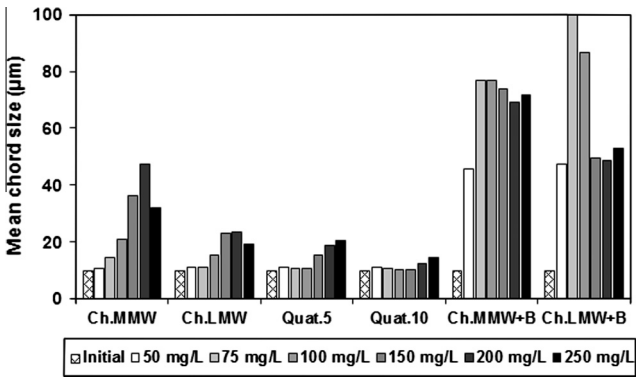

Fig. 4. Mean chord size for studied chemical systems, at different dosage levels.

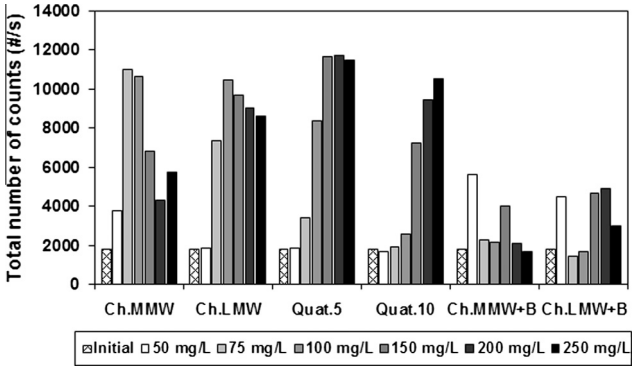

Fig. 5. Total number of counts for studied chemical systems, at different dosage levels.

to further increase the size of the flocs to be efficiently removed by DAF. When bentonites are added together with the native chitosans, there is no clear trend and it always depends on the data obtained for the mean chord size. Generally, the total number of counts remains similar to that of the process waters while the mean chord size is increasing largely at low and intermediate dosages. However, at thehighest dosages, when the mean chord size starts decreasing, there is a parallel increase in the total number of counts. Therefore, this increase confirms a slight higher efficiency of Ch.LMW than the Ch.MMW in increasing the floc size.

3.2. Dissolved air flotation tests

3.2.1. Effect of coagulants on turbidity

Turbidity of the waters was not significantly reduced by DAF when chemicals were not used. The removal of turbidity observed in the blank samples from 2400 NTU to 1840 NTU (22.9% removal), is justified by the dilution of the waters caused by the addition of 20% saturated air-tap water. This means that in an industrial DAF unit where the clarified water is the stream saturated with air, the removal of turbidity without any chemical treatment would be almost negligible, which is the case in the paper mill from which the samples were taken. Although around 50% of total solids are suspended solids, the size of these suspended solids is very small. According to FBRM measurements, mean chord size of particles (1–1000 μm) is around 10 μm and median is 7 μm, which is a very small size to be removed by DAF and especially for a lab DAF unit with a reduced hydrodynamic efficiency compared to the industrial DAFunits.

Most efficient products in removing the turbidity of clarified waters are the native chitosans (Fig. 6a), which reduced turbidity to 10–12 NTU (99.3–99.4% removal referred to the blank values) at the highest dosages. However, intermediate dosages such as 150 mg/L are high enough to obtain very high removal efficiencies (95.6–98.6%) with turbidity of the treated waters of 25–85 NTU. Differences between Ch.MMW and Ch.LMW are minor, but Ch.LMW is slightly more efficient than Ch.MMW despite that FBRM measurements indicated that Ch.MMW is able to produce larger flocs with similar destabilization of DCM. Previous studies showed that generally high molecular weight chitosans are more efficient than low molecular weight ones [20,31], which is not the case in this study according to the resultsobtained.

Quaternary chitosans are clearly less efficient in removing turbidity than native chitosans. Quat.5 is more efficient than Quat.10 thus, confirming the FBRM observations. With these products, a maximum removal of 94% (around 110 NTU of residual turbidity) was achieved at the highest dosage tested (250 mg/L). However, intermediate dosages of these products such as 150 mg/L, can only

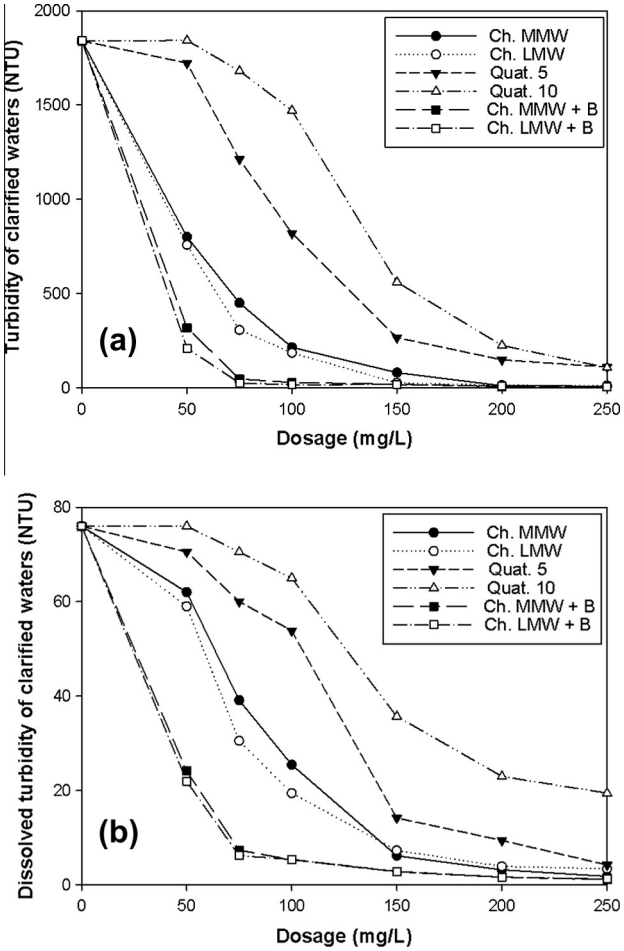

Fig. 6. Turbidity of clarified waters (a) and its dissolved fraction (b) versus chemicals dosage.

achieve turbidity removals in the 70–85% range. For a similar turbidity removal, quaternized chitosans require around double the dosage than that required for native chitosans. This is in agreement with the fact that quaternary chitosans have around half of the cationic charge of the native chitosans and can be an indication that charge neutralization flocculation mechanism is taking place to a large extent.

The addition of bentonite improved significantly the turbidity removal obtained by native chitosans especially at the lowest dosages of chitosan. The use of bentonite can slightly improve the removal obtained by the native chitosans up to 99.7% (residual turbidity of 5 NTU). However, the most important enhancement occurs at the lowest dosages. For example, at 50 mg/L, native chitosans reduced turbidity to 750–800 NTU (<60% removal) while the combination of chitosans with bentonite reduced turbidity to 200–320 NTU (80–90% removal) which could be a sufficient turbidity removal in industrial applications. Furthermore, the use of chitosan dosage of 75 mg/L with 150 mg/L bentonite is able to reduce the turbidity of clarified waters around 97–99% (residual turbidity of 25–50 NTU). To achieve similar results, however, the necessary dosages of native chitosans would be 150–200 mg/L.

The same trends have been observed for dissolved turbidity (Fig. 6b). Most efficient products are Ch.MMW and Ch.LMW both with and without bentonite addition. Maximum removal efficiencies of 94–98% referred to the blank are obtained at the highest dosages while with intermediate dosages, 90% removal efficiencies can be also obtained. Like the FBRM study, the quaternary chitosans were clearly of lower efficiency than the native chitosans.

Again Quat.5 is more efficient than Quat.10 while Quat.5 can obtain a maximum removal of dissolved turbidity of around 95% (residual turbidity of 4 NTU), maximum removal efficiency with Quat.10 is 75% (residual turbidity of 20 NTU).

3.2.2. Effect of coagulants on total solids

As expected, the total solids followed similar trends to turbidity measurements. The most efficient treatments in removing total solids from process water (Fig. 7) are native chitosans followed by their combination with bentonites and finally, quaternized derivatives. With Ch.MMW and Ch.LMW, total solids are reduced from around 3500 mg/L (blank value) to 2500–2600 mg/L which means 25–30% total solids removal. For these treatments, total solids removal is not improved significantly at higher dosages than 75–100 mg/L. Process water have 5500 mg/L of total solids: around 2800 mg/L of suspended solids and 2700 mg/L of dissolved solids. DAF treatments with native chitosans are able to eliminate almost all suspended solids (as seen with the turbidity of clarified waters aftertreatment) and around 100–200 mg/L of dissolved solids (4–8% removal of dissolved solids). Quaternary chitosans efficiency in removing total solids was lower than the native products. With the quaternized chitosans, maximum removal of total solids is 15–18% (residual 2900–3000 mg/L total solids) even at the highest dosage tested. This means that still 100–200 mg/L suspended solids and all the dissolved solids have not been removed. As it was observed with turbidity measurements, Quat.5 is slightly more efficient than Quat.10, but the differences are minimal. Contrary to native chitosans, the removal of total solids is continuously increased with higher dosages where the best results being obtained at the highest dosage (250 mg/L).

The use of bentonite in combination with the native chitosans has a minor effect on total solids of clarified waters and its effect varies depending on the chitosan considered. In the case of Ch.LMW, the addition of bentonite slightly improved its efficiency while in the case of Ch.MMW, this addition slightly impaired its efficiency. Although the addition of bentonite was very effective in removing turbidity of clarified waters, its effect on total solids is minor probably as dissolved solids are the main part of total solids and they are only slightly removed by the treatments. In addition, it could be possible that some of the bentonite added, due to its small size and high density, could not be aggregated or removed efficiently during the flotation process and thus, contributing to the total solids of clarified waters. This could justify that suspended solids removal (measured through turbidity) could be improved by bentonite addition but total solids removalcould be similar with or without bentonite addition.

3.2.3. Effect of coagulants on COD

The COD is a very important parameter in terms of process water contamination in papermaking. However, opposite to the turbidity or suspended solids which are generally removed in a large extent in the dissolved air flotation units (80–99%), COD removal is almost negligible in most of the cases. Only if an adequate chemistry is selected, DAF can also help to purge some organics from the water systems minimizing the accumulation of the DCM in water circuits [1].

The maximum COD removal efficiencies are in the 20–25% range as compared to the blank value (around 1900 mg/L), with residual COD values varying from 1400 to 1500 mg/L (Fig. 8). The most efficient products are Ch.MMW and Ch.LMW. As soluble COD of the process water is around 1900 mg/L (similar value to that of the blank), these treatments are able to remove 20–25% of dissolved COD which is an important achievement. As with other analytical parameters, the efficiency of quaternized chitosans is lower than other Ch.MMW and Ch.LMW-based treatments, however, at the highest dosages (200–250 mg/L), the efficiency in COD removal can achieve 20% (around 1500 mg/L residual COD). Although the maximum removal efficiencies are similar for both types of chitosans, 25% for native chitosans versus 20% forquaternary derivatives, there is an important difference: native chitosans achieve these maximum COD removal efficiencies at very low dosages (50–75 mg/L) while the maximum removal efficiency for quaternary derivatives is only achieved at dosages as high as 250 mg/L.

The use of bentonite in conjunction with the chitosan improved COD removal, especially at the smallest dosage of chitosan (50 mg/L), for both Ch.MMW and Ch.LMW. At this dosage, the use of bentonite improves COD removal from 14% to 19% for Ch. MMW and from 19% to 23% for Ch. LMW. However, the differences between using bentonite and not are lower and lower and lower at increased chitosan dosages. Although some authors argue that the preparation of native chitosans with acetic acid could increase the organic content of the treated water [20,21] and for this reason it is sometimes preferably to use acids such as chlorhydric acid, this effect has not been observed as relevant in this study probably due to the high COD levels found in this water.

3.2.4. Effect of coagulants on cationic demand

Along with the turbidity or COD, charge measurement is generally accepted as one of the most important indicators of the amount of detrimental substances in papermaking although not all interfering substances are anionic [32].

As shown in Fig. 9 the cationic demand of waters is efficiently reduced by the different chitosan-based treatments. The cationic

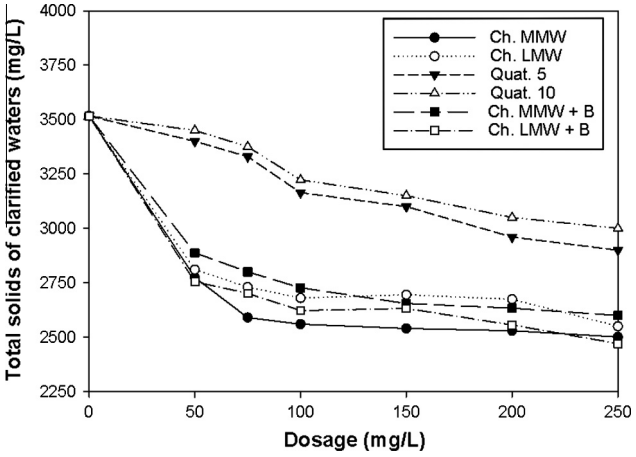

Fig. 7. Total solids of clarified waters versus chemicals dosage.

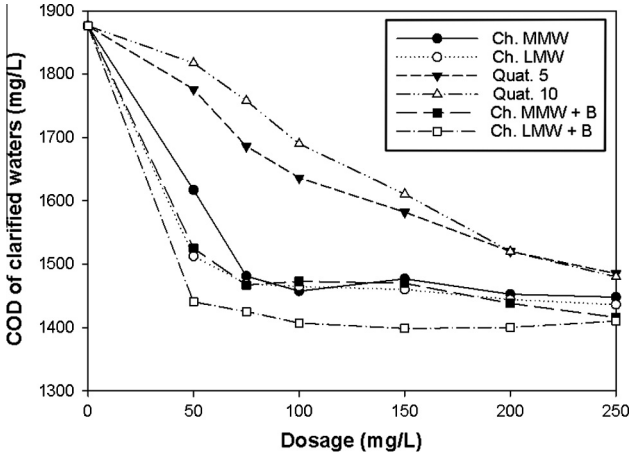

Fig. 8. COD of clarified waters versus chemicals dosage.

demand is decreased in parallel with the chitosan dosage and the cationic demand values come very close to zero at the highest dosage (250 mg/L) especially for Ch.MMW- and Ch.LMW-based treatments. With these treatments, the final cationic demand is around 0.04–0.10 meq/L (90–96% removal) and is even zero when only Ch.MMW is added. The effect of bentonite on cationic demand is producing only a small increase compared to the native chitosans based treatment which is in agreement with its small anionic charge. On the other hand, the quaternized derivatives reduced the cationic demand 48–52% (0.48–0.52 meq/L residual cationic demand). These observations are in agreement with the charge densities of theproducts. Ch.MMW and Ch.LMW have charge densities of 5.75 and 5.44 meq/g, respectively, while the quaternized products is around half, 2.27 meq/g in the case of Quat.5 and 2.11 in the case of Quat.10.

It is observed from Fig. 9 that the differences in neutralization efficiency between native chitosans based treatments and quaternary chitosans treatments is varying with the dosage. At the lowest dosages (50–75 mg/L), quaternary chitosans reduced more efficiently the charge than treatments based on native chitosans. At intermediate dosage (100 mg/L), the efficiency becomes similar, and at the highest dosages ($\geqslant$150 mg/L), the native chitosans based treatments become more efficient in reducing the cationic demand of waters than quaternary chitosans; the higher the dosage the higher difference between the cationic demand of the treatments based on native and quaternary chitosans.

The explanation is related to the effect of pH on the charge density of chitosans. While quaternary chitosans have an almost permanent positive charge on the polymer backbone, native chitosans have a charge density dependent on pH. Native chitosans must be dissolved either in acetic acid or hydrochloric acid thus, in acidic solutions where the amino groups in chitosans are protonated resulting in a high charge density and solubility of the native chitosans. However, at neutral to alkaline pHs, chitosan loses its charge and precipitate from solution [33]. As shown in Fig. 10, the cationic charge of native chitosans is sharply decreased at pHs higher than 6.5 and become almost zero at a pH 7.5–8.0. On the contrary, cationic charge of quaternary derivatives is almost constant from pH 4 to pH 7 and decreases only slightly atalkaline pHs (outside the experimental pH range). Even at high alkaline pHs as 10, quaternary derivatives still maintain their cationicity and their cationic charge is only 30–40% lower than this at pH 4.

pH of the blank (DAF treatment without any chemical) is 7.6 and at this pH theoretically the charge density of the quaternary chitosans would be higher than the native chitosans, and this result was observed at the lowest dosages of chitosans. However, as the dosage of native chitosans is increased (due to the acidic nature of the stock solution), the pH of the treated waters is continuously reduced. Although this decrease is not very noteworthy (0.6–0.8 pH units), this decrease is high enough for an important increase of the cationic charge of the native chitosans. At the highest dosage of native chitosans, pH of the treated waters can be reduced to around 6.8. Considering that the air-saturated water (tap water) added after flocculation having a pH around 7.6, the flocculation pH (before air-saturated water addition) could be even lower, around 6.6. At this pH, the charge density of native chitosans can be around double that of quaternary derivatives. This is thereason why the differences between quaternary derivatives and native chitosan based treatments on cationic demand are higher at the highest dosages. Furthermore, results from Fig. 10 shows that the charge density of Ch.LMW is higher than Ch.MMW at pH >6 which could explain why Ch.LMW could be more efficient than Ch.MMW.

The two main flocculation mechanisms of chitosans are charge neutralization and bridging formation and a combination of them usually occurs. However, in the case of native chitosans, due to its charge density dependence on pH, the importance of each has varied depending on the dosage. At the lowest dosages, the pH of waters is still high and the charge density of the chitosan is low where bridging formation is the main flocculation mechanism. At the highest dosages, the pH is low enough for having a high charge density and charge neutralization is the main flocculation mechanism.

3.2.5. Effect of coagulants on pH and conductivity

Regarding pH of the clarified waters, there are also slight differences between the native chitosans (with or without bentonite) and the quaternary derivatives. In the case of quaternary derivatives, pH is maintained almost constant even at the highest dosages tested. On the other hand, native chitosans reduced the pH of waters; this decrease being higher at higher dosages of chitosan. At the highest dosages of these chitosans, the pH reduction can be around 0.6–0.8 pH units. As commented before, the explanation of this behavior is related to the preparation method of the different chitosan products; native chitosans are prepared on acetic acid 0.1 M (pH around 4.0), and quaternary chitosans are directly prepared in distilled water therefore, their addition has no significant effect on the pH of clarified waters. Traditional treatments based on aluminum or iron salts usually produce higher pH reductions as they consume part of the alkalinity of thewaters to form the active species. Using organic coagulants such as chitosans, this can be minimized or even completely removed.

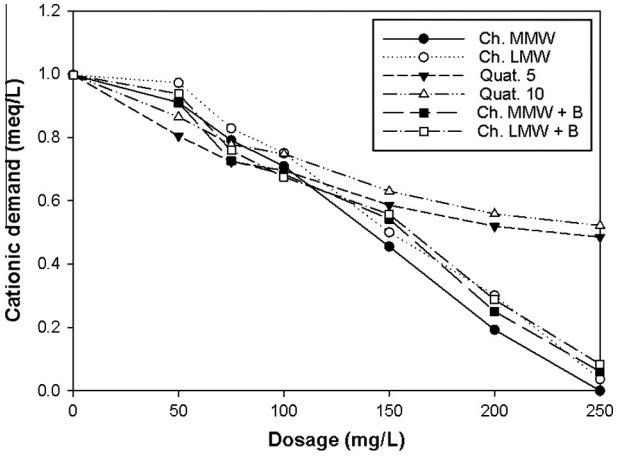

Fig. 9. Cationic demand of clarified waters versus chemicals dosage.

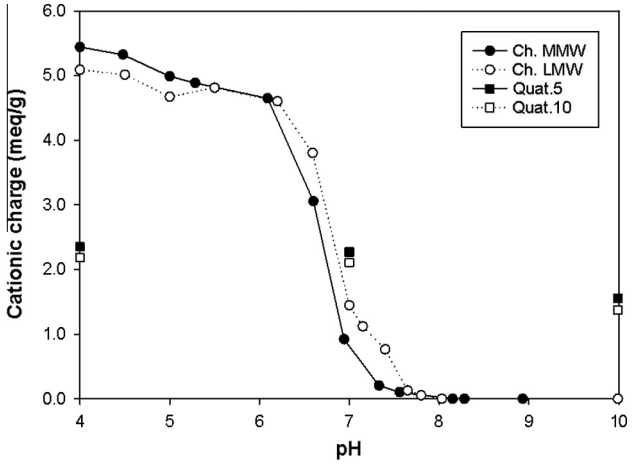

Fig. 10. Cationic charge of chitosans versus pH.

Conductivity of the waters only slightly increased with the different treatments. In the case of native chitosans with and without bentonite addition, the maximum increase was around 0.2 mS/cm (at 250 mg/L) as referred to the blank value. This increase is mainly due to the use of acetic acid in their preparation (stock solutions has around 0.4 mS/cm conductivity). Quaternized chitosans prepared in distilled water increased the conductivity only 0.05–0.1 mS/cm at the highest dosage tested (250 mg/L). One of the advantages of using organic versus inorganic coagulants as aluminum or ferric salts is the lower or even negligible conductivity increase of the treated waters. As inorganic DCM is not removed in conventional internal water treatments used in papermaking such as DAF units, the lower the increase of conductivity in the treated waters, the lower accumulation of inorganicDCM in water circuits [1].

3.2.6. Effect of coagulants on silica

DAF units are usually inefficient in removing inorganic compounds. However, in the analyzed paper mill, there is a high silica content in the water circuits varying in the range 150–250 mg/L (as SiO_2) depending on the water loop considered and its removal could be of interest due to future environmental discharge regulations. The results obtained indicated that only minor silica removals can be obtained with these treatments; always lower than 5–10%. Efficiency differences among the different treatments cannot be clearly assessed as these differences are very close to the experimental error of the silica measurement method. Although coagulation has been used in the literature to remove silica from papermaking waters, significant removals can be achieved only at high pHs and dosages [34–36] which is not the present case.

4. Conclusions

Native chitosans, Ch.MMW and Ch.LMW, have demonstrated to be efficient at intermediate dosages while Ch.LMW being more efficient than Ch.MMW. This is probably due to the higher charge density of Ch.LMW at a pH > 6. At 100 mg/L dosage, they resulted in the following removal efficiencies as referred to the blank: 88–90% turbidity (residual turbidity of 185–215 NTU), 60–75% dissolved turbidity (residual dissolved turbidity of 20–30 NTU), 24–27% total solids (residual 2550–2700 mg/L total solids) and 22% COD (residual 1455–1465 mg/L COD). Although the main disadvantage of commercial chitosan products is their insolubility at neutral and alkaline pHs, both chitosans have demonstrated to be efficient for treating the process waters even at the initial pH of 7.6. The high cost of chitosan could be compensated by the lower dosages necessary to obtain the same results as those obtainedwith the conventional products.

When native chitosans are tested in dual systems with bentonite, even 50 mg/L of chitosan added together with 100 mg/L bentonite is enough to achieve high removals of contaminants: 83–89% turbidity (residual turbidity of 210–320 NTU), 68–71% dissolved turbidity (residual dissolved turbidity of 22–24 NTU), 18–22% total solids (residual total solids of 2750–2900 mg/L) and 19–23% COD (1440–1525 mg/L). The low cost of the bentonite compared to chitosan would definitely reduce the cost of the treatment and for the same level of efficiency, the required dosage of chitosan is roughly half the dosage necessary if bentonites are not added (50 mg/L versus 100 mg/L). Again, the highest removal efficiency was obtained with the low molecular weight chitosan.

Quaternary derivatives obtained lower efficiency than the base chitosan used (Ch.LMW). The main reason for this is the lower charge density of the quaternary derivatives compared to the native chitosans at the operational conditions. Although the charge density of the native chitosans starts decreasing at pH 6.5 and becomes zero at around pH 7.5–8, the charge density of native chitosans is still higher than these of quaternary derivatives especially if we consider than the addition of the acidic solution of native chitosans reduced the pH of the treated waters in parallel. The pH of the treated waters was reduced from a pH of 7.6 (blank) to around pH 6.8 at the highest dosages of the native chitosans while the pH of the treated waters was around 7.7–7.8 independent of the dosages of the quaternized chitosans. In this application, the pH is just in the limit where the native chitosans can still be applied and there is no need for quaternary derivatives. The higherquaternization degree, the lower was the efficiency of the derivatives. In all the cases, Quat.5 was more efficient than Quat.10 probably by their slightly higher charge density (2.27 meq/g versus 2.11 meq/g).

The FBRM technique has proven to be a rapid and accurate method in providing information about polyelectrolyte-induced aggregation. The smallest chemical dose that efficiently aggregated DCM and also the dosages range to be tested in DAF tests, including the preliminary optimal dosage, were determined by FBRM technique. The data provided by FBRM are in agreement with the efficiency of chitosan and chitosan–bentonite systems to reduce turbidity, total suspended solids content and COD of the treated water in DAF tests. The FBRM predicted a higher efficiency of dual systems compared to single systems, a higher efficiency of these native chitosans compared to the quaternized derivatives and the higher efficiency of Quat.5 compared to Quat.10. The prediction of a higher efficiency of Ch.LMW compared to Ch.MMW, however, was not as clear as with the other treatments.

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PUBLICATION VII

I. Latour, R. Miranda, A. Blanco

"Silica removal in industrial effluents with high silica content and low hardness"

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RESEARCH ARTICLE

Silica removal in industrial effluents with high silica content and low hardness

Isabel Latour · Ruben Miranda · Angeles Blanco

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Abstract High silica content of de-inked paper mill effluents is limiting their regeneration and reuse after membrane treatments such as reverse osmosis (RO). Silica removal during softening processes is a common treatment; however, the effluent from the paper mill studied has a low hardness content, which makes the addition of magnesium compounds necessary to increase silica removal. Two soluble magnesium compounds ($MgCl_2$ $6H_2O$ and $MgSO_4$ $7H_2O$) were tested at five dosages (250–1,500 mg/L) and different initial pH values. High removal rates (80–90 %) were obtained with both products at the highest pH tested (11.5). With these removal efficiencies, it is possible to work at high RO recoveries (75–85 %) without silica scaling. Although pH regulation significantly increased the conductivity of the waters (at pH 11.5 from 2.1 to 3.7–4.0 mS/cm), this could be partially solved by using $Ca(OH)_2$ instead of NaOH as pH regulator (final conductivity around 3.0 mS/cm). Maximum chemical oxygen demand (COD) removal obtained with caustic soda was lower than with lime (15 vs. 30 %). Additionally, the combined use of a polyaluminum coagulant during the softening process was studied; the coagulant, however, did not significantly improve silica removal, obtaining a maximum increase of only 10 %.

Keywords Silica removal · Magnesium · Softening · Coprecipitation · Membranes fouling · Effluent reuse · Paper recycling

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Introduction

Nowadays, sustainable water management in paper mills is a must. One of the alternatives to improve sustainability is the reduction of the fresh water consumption through the regeneration and reuse of the effluent after an advanced treatment, usually including a reverse osmosis (RO) (Negaresh et al. 2013). With this treatment, it is possible to obtain high-quality water to replace fresh water use at critical points, such as in the high-pressure showers of the paper machine, where the highest quality is required (Ordoñez et al. 2010). Nevertheless, one of the bottlenecks for the implementation of this technology is the silica scaling on RO membranes, which is very hard to remove once it is formed (Koo et al. 2001; Hater et al. 2011). This limitation is more important in de-inking paper mills because they have high silica content in the effluent, which ranges from 50 to 250 mg/L as SiO_2 (Huuha et al. 2010; Latour et al. 2013). This causes severe scaling problems in RO membranes and other processes due to its low solubility at 100–140 mg/L (as SiO_2) at 25 °C (Sheikholeslami and Tan 1999). Silica scaling on RO treatments limits its recovery efficiency and the viability of the treatment (Salvador Cob et al. 2012), but it is not the only reason for the growing interest on silica removal, there are also stringent limits on the effluent quality set by the environmental legislation for silica: 50 mg/L in Finland, Canada, or the USA (Huuha et al. 2010). Therefore, there is a real industrial challenge in the paper sector, especially in recycling paper mill, the removal of silica from the effluent.

In de-inking paper mills, silica mainly comes from sodium silicate, which is a process additive used in de-inking and bleaching steps to achieve the optical properties required in the final product (Ferguson 1992a, b). Given its variety of functions, its removal in origin is very difficult. Although some alternatives have been studied (Hamäläinen et al. 2007), there is still not a satisfactory solution.

Silica and silicates derive from the orthosilicic acid. This is a weak polyprotic acid with pK_a values of 9.9, 11.8, and 12 (Ning 2002). Orthosilicic acid only remains monomer at 25 °C when the concentration is less than 2 mM. It polymerizes when its concentration in the solution is higher, resulting to larger molecules, which can reach a colloidal size. The rate of silicic acid polymerization is strongly pH dependent. The reaction is very fast in neutral and slightly alkaline solutions and extremely slow at low pH values of 2–3 (Ning 2002). More complex colloids can also be formed by its combination with organic and inorganic compounds. Silica and silicates chemistry is complex as different species with different behavior can be found in the system. The most common classification of silica-related species is based on their size; in this sense, they can be classified as soluble, colloidal, or particulate. Soluble silica includes polysilicic acid, small molecules as dimers, trimers, or oligomers. Colloidal silica is used to address more highly polymerized species or particles larger than 50 Å, although sometimes this denomination also includes species down to 10–20 Å. This category includes the colloidal particles formed by the combination with organic and inorganic species (Sheikholeslami and Tan 1999). Conversely, particulate silica is larger than colloidal size silica.

Silica scaling can occur through different mechanisms. First, deposition of silica compounds such as pure quartz scales, calcium silicate, magnesium silicate, and aluminum silicate when their solubility is exceeded. Colloidal silica deposition can also be found. In this case, colloids are formed in the bulk solution and then accumulate on the membrane surface blocking the pores. Finally, biogenic silica scaling caused by microorganisms can also appear on the membranes (Sheikholeslami and Tan 1999; Sheikholeslami and Bright 2002).

There are several silica removal processes but chemical methods are the most frequently used (Sheikholeslami et al. 2001; Zeng et al. 2007). Among them, silica removal during softening processes or by coagulation at high pH are the two most commonly used as they are able to treat large volumes of water at moderate costs. Both treatments are efficient with high silica concentrations such as those typically found in paper mill effluents.

The drawback of silica removal by coagulation for high silica-loaded effluents is the cost of the treatment due to the high dosages of coagulant required (Hermosilla et al. 2012; Latour et al. 2013). Conversely, silica removal during softening is promising although it is necessary to ensure that there is enough hardness present in the water in order to obtain high silica removal rates. Though calcium and magnesium are proven to be functional for silica removal, the higher ratio Mg/Ca, at constant total hardness, the higher silica removal is achieved (Chen et al. 2006). This is the reason why this study is focused on improving silica removal during the softening process by the addition of magnesium salts.

In the literature, there are several theories regarding the silica removal mechanisms (Sheikholeslami and Bright 2002; Chen et al. 2006; Parks and Edwards 2007; Hsu et al. 2008). Two main mechanisms have been proposed and probably both could occur simultaneously: adsorption of silica into fresh precipitated $CaCO_3$ and $Mg(OH)_2$ and coprecipitation of silica to form calcium and magnesium silicates with different stoichiometries.

Conversely, different authors studied the addition of coagulant to assist silica removal during the softening process (Sheikholeslami and Bright 2002; Al-Rehaili 2003; Chen et al. 2006; Zeng et al. 2007), yet, there is no agreement on whether coagulant addition significantly improves silica removal. Al-Rehaili (2003), for example, found necessary the addition of coagulants such as alum, sodium aluminate, or ferric chloride to improve the performance of the lime-soda ash process on silica removal. However, Sheikholeslami and Bright (2002) found that the addition of alum and ferric chloride only slightly increase silica removal during the softening process. Furthermore, Chen et al. (2006) studied that the addition of a polyaluminum chloride improved silica removal at pH 10, but it decreased at higher pH due to the anphoteric properties of the aluminum hydroxide.

This paper aims to generate new knowledge on the mechanisms and the efficiency of silica removal by softening in the effluent of a de-inking paper mill with high silica content and low hardness. These conditions differ from the ones considered in previous studies in which silica was removed during the softening process (Chen et al. 2006; Parks and Edwards 2007; Hsu et al. 2008). In those cases, the water to be treated had low silica content and high hardness. Given the low calcium and magnesium contents of the effluent, two magnesium-soluble salts ($MgCl_2$ $6H_2O$ and $MgSO_4$ $7H_2O$) were used to improve silica removal efficiency. In this study, the dosage, the operating pH, and the pH regulator were optimized. Moreover, the combination of $MgCl_2$ $6H_2O$ with a polyaluminum nitrate sulfate coagulant (PANS) was also studied to reduce treatment cost. The final objective of the present work is to achieve the silica removal necessary (80–90 %) to increase RO recovery from 20 to 60–80 %, to be able to make the effluent reuse process technically and economically feasible.

Materials and methods

Water samples

This study was carried out with the effluent of a Spanish paper mill using 100 % recovered paper to produce newsprint. The mill has an integrated wastewater treatment plant consisting of a primary treatment by dissolved air flotation and a secondary treatment based on an aerobic digestion of the waters on a

moving bed biofilm reactor (MBBR), followed by a secondary dissolved air flotation. Water samples were taken after these treatments, before the effluent discharge to an urban wastewater treatment plant. Samples were stored at 4 °C during the tests, and no sets of trials longer than 5 days were carried out. Table 1 summarizes the main characteristics of the effluent. Dissolved fraction was obtained by centrifugation at 2,000×g during 15 min.

Chemicals

Two magnesium compounds, $MgCl_2 \cdot 6H_2O$ and $MgSO_4 \cdot 7H_2O$, and two different pH regulators, NaOH and $Ca(OH)_2$, were tested. The four of them, reagent grade, were supplied by PANREAC. A polyaluminum nitrate sulfate - polyamine hybrid coagulant (PANS) supplied by Sachtleben Wasserchemie GmbH (Germany) was also used. This coagulant has 3.2 % aluminum content and 1.8 wt.% polyamine active content. Magnesium compounds, pH regulators, and the coagulant were prepared at 10 wt./vol.% with distilled water on a daily basis.

Methodology for jar tests

For each magnesium compound five dosages were tested (from 250 to 1,500 mg/L) at three different pH values: 10.5, 11, and 11.5. First, the best magnesium compound was selected using NaOH as pH regulator. Then, the pH regulator was optimized, comparing the efficiency of NaOH and $Ca(OH)_2$. Finally, the effect of the polyaluminum coagulant on the softening treatment with the most efficient magnesium salt was assessed.

Table 1 Characteristics of the paper mill effluent

Raw water	
pH	8.3
Conductivity (mS/cm)	2.20
Cationic demand (meq/L)	0.74
Total solids (mg/L)	1,990
Total suspended solids (mg/L)	83
BOD_5 (mg/L)	150
Turbidity (NTU)	120
Total alkalinity (mg/L $CaCO_3$)	675
Dissolved fraction	
Total solids (mg/L)	1,890
Silica (mg/L SiO_2)	180
COD (mg/L)	450
Sulfates (mg/L)	239
Chlorides (mg/L)	126
Calcium (mg/L)	33.5
Magnesium (mg/L)	2.8
Turbidity (NTU)	7.9

Figure 1 summarizes the jar test methodology followed to study the efficiency of the different treatments. First, the pH of the samples was adjusted by adding NaOH 10 wt./vol.% to 250 mL of sample. After 1 min of mixing at 800 rpm, the magnesium compounds were added from and mixed with the waters during 15 min at 800 rpm. After this period, the waters were allowed to settle for 1 h. Finally, the clarified waters and their dissolved and colloidal material (DCM) fraction, obtained by centrifugation at 2,000×*g* during 15 min, were characterized for different analytical parameters. All trials were carried out at room temperature (20 °C±2 °C) by duplicate, and the average error between replicates was always under 5 %.

The optimization of the pH regulator was carried out following the same jar test methodology but, in this case, the study was only carried out with the most efficient magnesium salt according to the previous results obtained, i.e., $MgCl_2 \cdot 6H_2O$. Three different dosages (500, 1,000, and 1,500 mg/L) were tested with the two pH regulators.

Finally, the effect of the combination of a polyaluminum coagulant with the magnesium compound was studied. In this case, $MgCl_2 \cdot 6H_2O$ was tested at 250 and 750 mg/L. The coagulant dosage used was fixed based on the preliminary tests (Latour et al. 2013), and it was 125 mg/L at the three

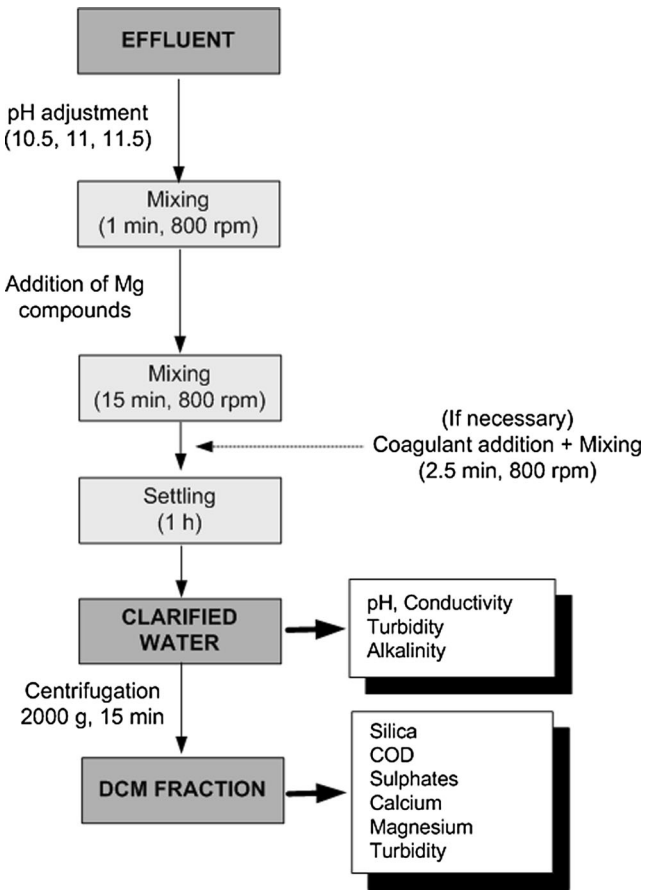

Fig. 1 Methodology for the evaluation of silica removal during softening

initial pH values tested. The objective was to partially replace the magnesium salt with the coagulant. For that purpose, lower dosages were used. As shown in Fig. 1, after the addition of the magnesium salt and mixing, 125 mg/L of coagulant were added and mixed during 2.5 min at 800 rpm. Then, samples were allowed to settle for 1 h as in the rest of the studies.

Mixing was carried out in a multiposition magnetic stirrer OVAN MulitMix Heat D. pH was measured using a GLP 22 pH meter (Crison Instruments, SA), according to Standard Method 4500 (APHA-AWWA-WEF 2005), and conductivity was determined with a GLP 31 conductivity meter (Crison Instruments, SA), according to the ISO 7888. Reactive silica was measured by flow analysis and photometric detection through silicomolybdate and reduction to molybdenum blue, using a FIA Compact (MLE GmbH) according to DIN EN ISO 16264 and expressed as milligrams per liter of SiO_2. Chemical oxygen demand (COD) was measured according to the Standard Method 5220-D (APHA-AWWA-WEF 2005). Alkalinity was measured by titration with sulfuric acid 0.1 N using a pH electrode connected to an automatic titrator, model Compact I (Crison Instruments, SA) to reach pH 4.5, according to the EPA 310.1 (1983) method. Sulfate content was determined using Nanocolor® sulfates method (Macherey-Nagel GmbH). Calcium and magnesium content were measured using a direct air-acetylene flame atomic absorption method according to ISO 7980:1986 in a SpectraA 220 spectrophotometer supplied by Varian. Finally, turbidity was measured with a LP 2000-11 nephelometer, supplied by Hanna Instruments, according to ISO 7027.

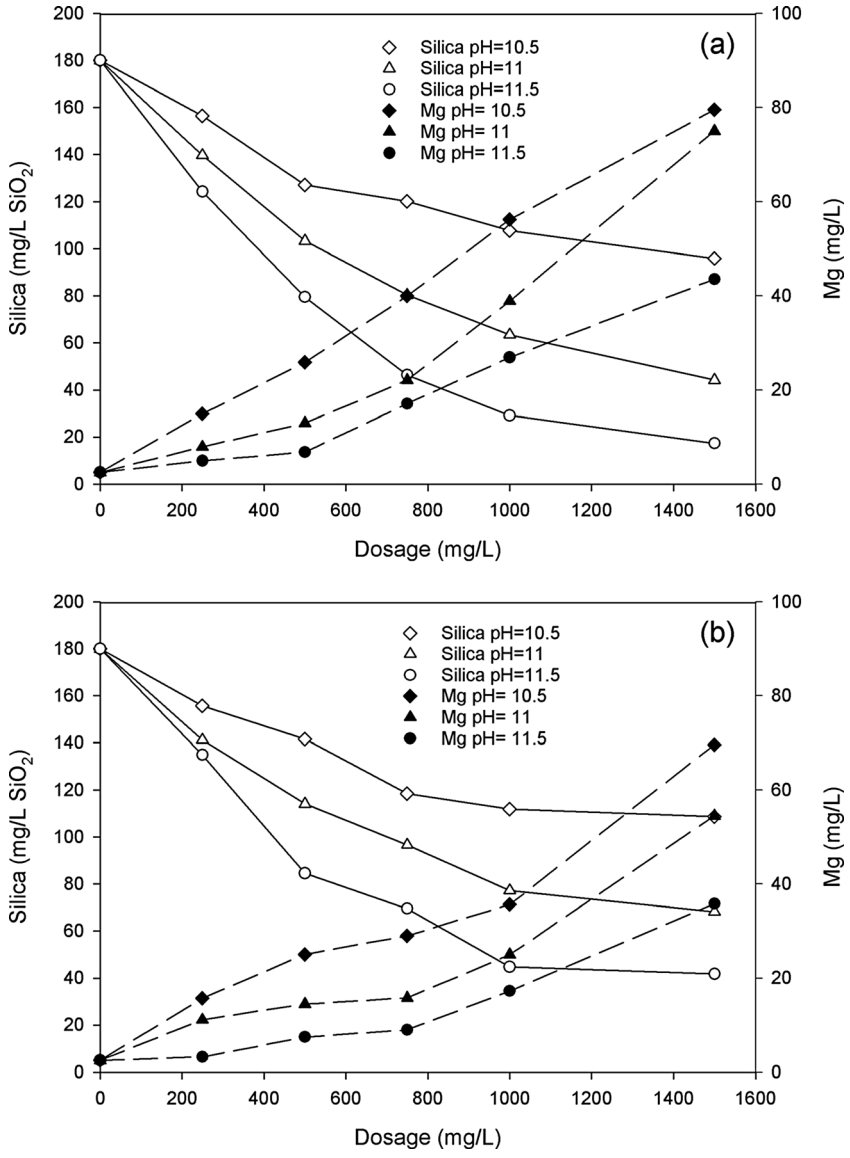

Fig. 2 Silica removal vs. dosage of **a** $MgCl_2 \cdot 6H_2O$ and **b** $MgSO_4 \cdot 7H_2O$, at different initial pH values

Results and discussion

Selection of the pH and magnesium compound

Figure 2 shows silica removal rates obtained with different dosages of $MgCl_2 \cdot 6H_2O$ and $MgSO_4 \cdot 7H_2O$ at three initial pH values (10.5, 11, and 11.5). Experiments at initial pH=8.3 (pH of the waters without any pH adjustment) and 9.5 were also carried out, however, as silica removal rates were lower than 20 %, even at the highest magnesium chloride dosage tested (1,500 mg/L), the results are not shown. Considering the high silica removal rates required to achieve the objectives of the present work, these pH values were discarded, and only pH values of ≥10.5 were further studied. The maximum removal rates were achieved at the highest pH (11.5) and dosage (1,500 mg/L), being $MgCl_2 \cdot 6H_2O$ more efficient (90 % silica removal) than $MgSO_4 \cdot 7H_2O$ (77 % silica removal) at these conditions. With 90 % silica removal, it would be possible to work on RO membranes at 80–85 % without silica scaling problems. In addition, it is worth to mention that silica removals around 60 % are also a treatment option as they would be high enough to work at intermediate RO recoveries (60–75 %), with the additional advantage of lower pH adjustment (pH=11 and 1,000–1,500 mg/L of the magnesium species) or a lower magnesium compound dosage (dosages, ≥750 mg/L at pH=11.5), which are translated in lower chemical costs, lower conductivity, and possibly avoiding the need of RO rejects post-treatment.

Figure 3 shows the millimoles of silica removed per millimole of initial magnesium contents. This ratio is almost the same for both magnesium species, which would explain that silica removal rates with $MgSO_4 \cdot 7H_2O$ were lower than those obtained with $MgCl_2 \cdot 6H_2O$ as $MgSO_4 \cdot 7H_2O$ has a magnesium content of 9.9 vs. 12.0 wt.% of $MgCl_2 \cdot 6H_2O$. It was observed that as pH was increased, more silica was removed per millimole of magnesium. With 250 mg/L of the magnesium salts, this ratio increased from 0.8 at pH=10.5 to 1.20 at pH=11 and 1.50 at pH=11.5. As dosage increased, these differences between the ratios at the three pH values became smaller. The explanation is that, despite the increase in silica removal with the dosage, there was an excess of magnesium in the water. Therefore, the final concentration of magnesium in the effluent increases with the dosage and decreases with pH. In these conditions, precipitation of magnesium hydroxide and magnesium silicates are favored (Al-Mutaz and Al-Anezi 2004).

Silica is removed at high pH values by two main mechanisms: precipitation of calcium and/or magnesium silicates with different stoichiometries and by adsorption/enmeshment in fresh precipitates of $Mg(OH)_2$ and/or $CaCO_3$. Although both mechanisms usually occur simultaneously, depending on the pH one mechanism is more important than the other. If silica is removed through the formation of magnesium silicates such as Mg_2SiO_4 (forsterite) or $MgSiO_3$ (enstatite), the ratio millimoles Si removed/millimole Mg removed would be 0.5 and 1, respectively. If adsorption on magnesium hydroxide was the main mechanism involved, this ratio would be smaller. Chen et al. (2006) and Hsu et al. (2008) reported that 0.04 mmol Si were removed/mmol of Mg removed. Figure 4 shows the ratios millimoles Si removed/millimole Mg removed at the three initial pH values and dosages tested. For both products, the Si/Mg removed decreased with the dosage indicating that the precipitation of $Mg(OH)_2$ was favored at higher magnesium concentrations. Conversely, the ratio Si/Mg increased with pH, and thus the precipitation of magnesium silicates. These results were in agreement with the fact that the SiO_4^{4-} becomes more predominant at pH values higher than 11, which would favor the precipitation of forsterite (Sheikholeslami and Bright 2002).

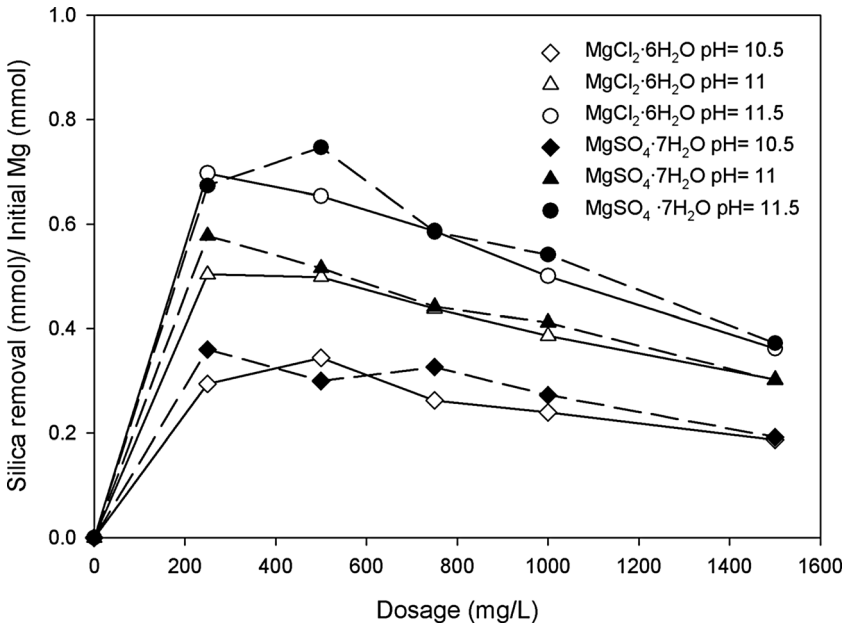

Fig. 3 Millimoles of silica removed per millimole per liter of initial magnesium at different initial pH values with $MgCl_2 \cdot 6H_2O$ or $MgSO_4 \cdot 7H_2O$

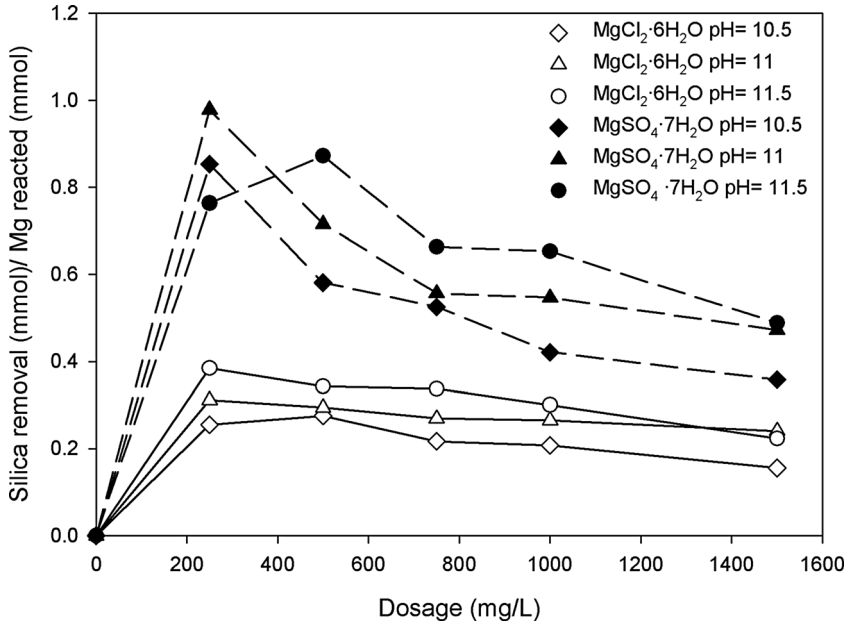

Fig. 4 Millimoles of silica removed per millimoles of magnesium reacted at different initial pH values with $MgCl_2 \cdot 6H_2O$ or $MgSO_4 \cdot 7H_2O$

Regarding the values of the Si/Mg ratio for the two magnesium salts tested, with $MgCl_2 \cdot 6H_2O$, the Si/Mg varied between 0.2 and 0.4, which indicates that Mg_2SiO_4 (forsterite) was the precipitated compound. This ratio is lower than 0.5 due to the precipitation of $Mg(OH)_2$ which, as mentioned before, removes silica in a ratio 0.04 Si/Mg. With $MgSO_4 \cdot 7H_2O$, the ratio Mg/Si was higher and varied between 1 and 0.5. In this case, the ratio 1:1 points at the precipitation of $MgSiO_3$ (enstatite) apart from the other two species. According to the Si/Mg ratios obtained, despite the fact that precipitation of $Mg(OH)_2$ contributed to the removal of silica, the precipitation of silicates was the main silica removal mechanism.

Alkalinity is an important parameter to understand silica removal mechanism during the softening process as it allows monitoring the precipitation of $Mg(OH)_2$, $CaCO_3$, and different calcium or magnesium silicates. As mentioned, in this particular case, silica removal through the precipitation of calcium carbonate or/and calcium silicates was not significant given the low average value of calcium removed (only 10 mg/L) under the different operational conditions, especially if it is taken into account the high dosages of Mg tested and the higher efficiency of Mg compared with Ca on silica removal. The results show that alkalinity followed the same tendency for both magnesium salts: it increased with the pH, as there were more hydroxide groups in the water, and decreased with magnesium dosage because more magnesium was available to precipitate with hydroxides forming $Mg(OH)_2$ or silicates. The final alkalinity of the water with the maximum dosage tested (1,500 mg/L) was around 1,000 mg/L $CaCO_3$ at pH=10.5, 1,100 mg/L $CaCO_3$ at pH=11, and 1,150 mg/L $CaCO_3$ at pH=11.5.

Conductivity is also critical for working at high RO recoveries. As mentioned, usual recoveries in RO systems for this application are around 60–80 %, thus the conductivity in the RO rejects are two to four times higher than in the feed water. In the specific case of this paper mill, the discharge limit value for conductivity in the effluent is 7.5 mS/cm, therefore higher values in the rejects would make necessary the post-treatment of these RO rejects, increasing the cost of the treatment chain.

Although the conductivity of the treated water was mostly increased due to pH regulation, the addition of magnesium salts also had a contribution to such rise. The conductivity increase caused by higher dosages of the magnesium salt was, however, lower at high pH values. This was because at higher pH values, the softening process was favored, thus more magnesium in form of magnesium hydroxide and magnesium silicate were removed and, to a lesser extent, calcium carbonates and silicates. The increase in conductivity, compared with the blank value at each initial pH, was 0.7 mS/cm at pH 10.5, 0.6 mS/cm at pH 11, and 0.4 mS/cm at pH 11.5 for $MgCl_2 \cdot 6H_2O$. In the case of $MgSO_4 \cdot 7H_2O$, this increase was 0.4, 0.3, and 0.1 mS/cm for pH=10.5, 11, and 11.5, respectively. This increase was smaller with $MgSO_4 \cdot 7H_2O$ compared with $MgCl_2 \cdot 6H_2O$. This is in agreement with the bibliography in which it was reported that the conductivity of 10 wt./vol.% dissolutions of $MgCl_2 \cdot 6H_2O$ and $MgSO_4 \cdot 7H_2O$ are 108 and 42.7 mS/cm, respectively (Wolf 1966; Haynes 2013).

In correspondence with alkalinity, pH decreased with the different treatments. This decrease was always more pronounced with $MgCl_2 \cdot 6H_2O$ for all the dosages and pH values tested. pH decrease was also more significant in those trials carried out at higher initial pH. The pH fall for the maximum dosage of the magnesium compound was 0.4, 0.7, and 0.9 at an initial pH=10.5, 11, and 11.5, respectively, with $MgCl_2 \cdot 6H_2O$. In the case of 1,500 mg/L of $MgSO_4 \cdot 7H_2O$, the decrease was 0.3, 0.5, and 0.7 at an initial pH of 10.5, 11, and 11.5, respectively. This is in agreement with the highest

magnesium content of $MgCl_2 \cdot 6H_2O$ and the highest silica removal achieved with this salt. To avoid scaling phenomena when mixing with other process waters, the pH of the treated water should be 7.5±1.0. In addition, the discharge limit of this paper mill establishes that the pH value of the final effluent, including RO rejects, should lie between 6.5 and 9.5. With all the treatments, the final pH was above the limit, being necessary to carry out a pH adjustment before discharge.

Another important parameter to consider when using membrane technologies is COD, as it contributes to the organic fouling of the membranes. The maximum COD removal efficiencies achieved with 1,500 mg/L of $MgCl_2 \cdot 6H_2O$ were 2, 10, and 14 % at pH=10.5, 11, and 11.5, respectively. Magnesium sulfate was slightly more efficient than magnesium chloride in COD removal, achieving the following COD removals at the maximum dosage (1,500 mg/L): 11 % at pH=10.5, 14 % at pH=11, and 16 % at pH=11.5.

Regarding turbidity, there was not a clear relation between the the turbidity of the treated water and the magnesium compound dosage and the initial pH level. Turbidity of clarified waters varied from 70 to 170 NTU, depending on the treatment, and dissolved turbidity of clarified waters from 7 to 15 NTU.

When selecting the best treatment for silica removal, the counterion of the magnesium salt used should be also taken into account as it could affect the membrane performance or the entire process. The use of magenisum sulfate could cause scaling problems due to the precipitation of calcium sulfate as initial sulfate content in the effluent was already high (239 mg/L). Conversely, the use of chlorides could cause corrosion problems. In the particular case of the paper mill studied, there is a discharge limit of 1,000 mg/L for sulfates and 2,000 mg/L for chlorides. As $MgCl_2 \cdot 6H_2O$ was more effective than $MgSO_4 \cdot 7H_2O$ on silica removal and, in this particular case, higher concentrations of chlorides are allowed in the effluent, the former was selected to optimize the pH regulator and to study the synergistic effect of the use of a coagulant and a magnesium salt.

Optimization of the pH regulator

As high pH values are required for silica removal, the selection of the pH regulator is a key factor to be considered, both in terms of costs and dissolved solids increase. The use of lime milk instead of caustic soda was analyzed. The main advantages of lime milk compared with caustic soda are that it is cheaper and increase less the conductivity of the treated waters. Additionally, it improved COD removal which was very low when NaOH was used as pH regulator. Alternatively, the volume of sludge generated was higher than in the case of NaOH.

As shown in Fig. 5, the maximum removal rates obtained with NaOH at each pH were 77 % at pH=10.5, 84 % at pH=11, and 91 % at pH=11.5 with 1,500 mg/L of $MgCl_2 \cdot 6H_2O$ in all the cases. Silica removal was increased when lime was used instead of NaOH. However, the difference in performance of the two products was less noticeable at higher pH values. Silica removal rates of lime were similar at the three pH values tested. With this pH regulator, the maximum removal rates achieved were 87, 90, and 93 % at pH=10.5, 11, and 11.5, respectively, with 1,500 mg/L of $MgCl_2 \cdot 6H_2O$. This is very important given the low dosage of pH regulator needed and therefore, the low increase in conductivity of the treated water. The higher removal rates obtained with lime milk seem to be due to the precipitation of $CaCO_3$, which also favors the

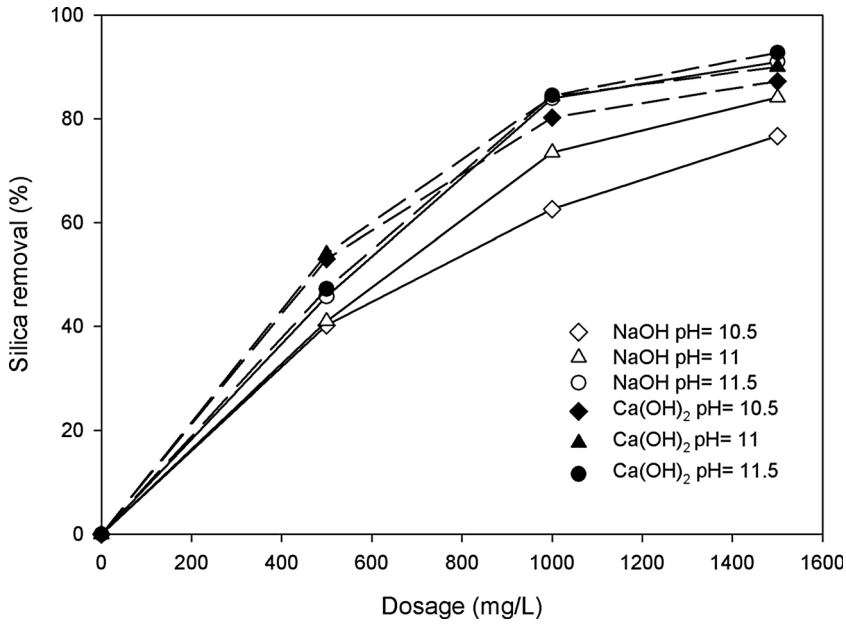

Fig. 5 Silica removal vs. $MgCl_2 \cdot 6H_2O$ dosage at different initial pH values with $Ca(OH)_2$ or NaOH as pH regulators

removal of silica (Sheikholeslami and Bright 2002). Another possibility is that silica was also removed through the formation of calcium silicates. It is interesting to notice that with 500 mg/L of $MgCl_2 \cdot 6H_2O$, the silica removal obtained at pH 11 with both pH regulators was higher than the one obtained at pH 11.5. This is because silica solubility increases with pH, and the removal rates achieved at that pH were not high enough to compensate the increase in the initial silica concentration at this pH.

Regarding the conductivity of the treated waters, it was always higher with caustic soda than with lime at all pH and dosages (Fig. 6). At pH 10.5, conductivity of the treated water varied between 3.9 and 4.8 mS/cm with caustic soda and only 3.0–3.3 mS/cm with lime milk, depending on the magnesium salt dosage. At pH 11, the conductivity ranges were 4.3–4.5 mS/cm for caustic soda and 2.7–2.9 mS/cm for lime milk. Finally, at pH 11.5, maximum increases in conductivity were obtained: conductivity of treated waters 4.6–4.8 mS/cm for caustic soda and 2.8–3.1 mS/cm for lime milk. The use of lime milk would allow working at 70 % recovery in the RO membranes without any post-treatment of the rejects for all dosages at the three pH values tested as the conductivities of the rejects would be lower than the discharge limit (7.5 mS/cm).

Although the use of lime milk can increase the turbidity of the waters, this effect was not relevant for the reuse of this effluent. The final turbidity with lime milk was higher than with caustic soda for all the dosages at the three pH values. The maximum turbidity was observed for the two pH regulators at pH 10.5 and 1,500 mg/L. Under these conditions, the final turbidity of the water was 180 NTU with caustic soda and 640 NTU with lime milk. In addition, the final turbidity at pH 11.5 and 1,500 mg/L of $MgCl_2 \cdot 6H_2O$, where maximum silica removal was obtained, was 140 NTU with caustic soda and 320 NTU with lime milk. High-turbidity-treated water could cause problems before a RO or UF unit. This limitation, however, could be solved with the use of a dissolved air flotation unit (DAF) or by increasing the settling time. In this respect, the use of a coagulant or small dosages of a flocculant would be enough for reducing turbidity without compromising the process feasibility and at a very low cost.

Regarding COD, higher removal rates were obtained with lime milk than with caustic soda at the three pH values and dosages. For both pH regulators, COD removal increased by increasing the pH and dosage (Fig. 7). However, a maximum COD removal of around 30 % was obtained with lime milk and only 15 % with caustic soda. This maximum removal obtained with caustic soda was smaller than those achieved with lime milk at lower pH values and the same dosage of $MgCl_2 \cdot 6H_2O$. This removal rates were 19 and 23 % at pH 10.5 and 11, respectively.

As it has been demonstrated, despite sludge generation being higher with lime than with caustic soda, it is preferred as pH regulator for the following reasons: silica and COD removal efficiencies with lime were higher than with caustic soda, the conductivity of the treated waters was considerably lower and lime milk is considerably cheaper than caustic soda.

Silica removal with $MgCl_2 \cdot 6H_2O$ assisted by the addition of a polyaluminum coagulant

Coagulation and particularly, coagulation with aluminum-based salts, has been recently recognized as an efficient silica-removal technique for the application considered in this

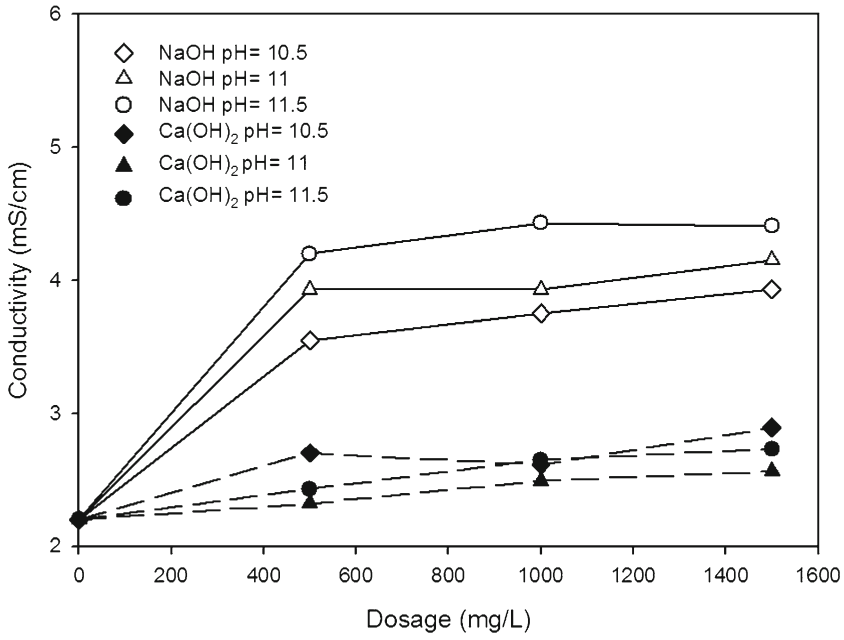

Fig. 6 Conductivity of treated waters vs. $MgCl_2 \cdot 6H_2O$ dosage at different initial pH values with $Ca(OH)_2$ or NaOH as pH regulators

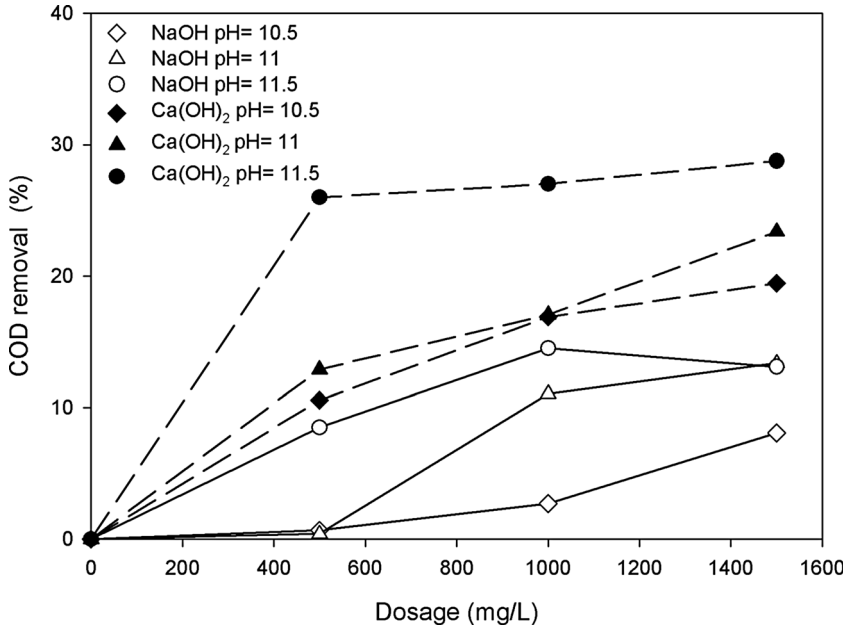

Fig. 7 COD removal vs. $MgCl_2 \cdot 6H_2O$ dosage at different initial pH values with $Ca(OH)_2$ or NaOH as pH regulators

work (Hermosilla et al. 2012; Latour et al. 2013). In view of that, the synergistic effect of silica removal with magnesium chloride and the subsequent addition of a polyaluminum nitrate sulfate coagulant were studied. The selected polyaluminum-based coagulant (PANS) showed to be very efficient for silica removal in the same effluent used in previous studies carried out by the authors (Latour et al. 2013). The approach followed was to obtain similar removal efficiencies lowering the dosage of $MgCl_2 \cdot 6H_2O$ by a polyaluminum coagulant while determining if there are any other synergistic effects in other quality parameters of the treated water. In this sense, a fixed dosage of 125 mg/L of the polyaluminum coagulant was tested with 250 and 750 mg/L $MgCl_2 \cdot 6H_2O$.

As shown in Fig. 8, the silica removal rates obtained with 250 mg/L of magnesium chloride and the coagulant were 27, 30, and 43 % at pH=10.5, 11, and 11.5, respectively. With 750 mg/L, the values of removal were 54 % at pH=10.5, 59 % at pH=11, and 77 % at pH=11.5. Zeng et al. (2007) achieved a similar silica removal rate (around 64 %) combining 750 mg/L of $MgCl_2 \cdot 6H_2O$ with 150 mg/L of a zinc coagulant ($ZnSO_4 \cdot 7H_2O$); however, the initial pH of the waters in this study was not provided but 600 mg/L of NaOH were added.

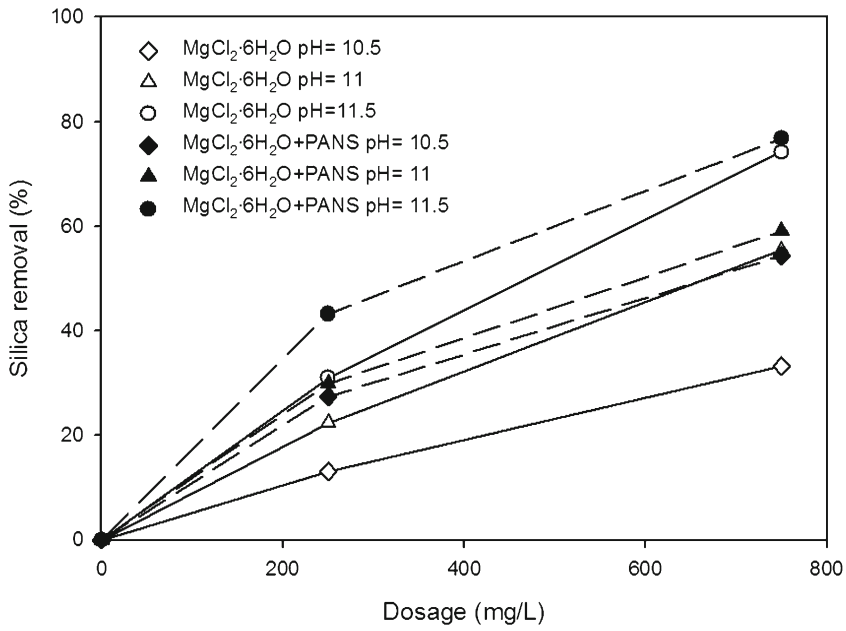

Fig. 8 Silica removal vs. $MgCl_2 \cdot 6H_2O$ dosage at three pH with and without further coagulation treatment

Comparing these results with the ones obtained with magnesium chloride used alone, it can be observed that silica removal increased with the addition of coagulant and this increase was higher at pH 10.5 (around 10 %), whereas it was 5 % at pH 11 and 11.5. Regarding COD removal, the addition polyaluminum coagulant did not have a significant effect on the results, being the differences smaller than 2 %. By contrast, conductivity was increased by the addition of the coagulant. It varied between 3.9 mS/cm at (pH 10.5 and 250 mg/L) and 4.6 mS/cm (pH 11.5 and 750 mg/L). When coagulant was not added, it varied between 3.7 mS/cm (pH 10.5 and 250 mg/L) and 3.6 mS/cm (pH 11.5 and 750 mg/L). The final conductivity of the water was around 1 mS/cm higher when $MgCl_2 \cdot 6H_2O$ was combined with coagulant than with $MgCl_2 \cdot 6H_2O$ alone for the same silica removal. Finally, the addition of coagulant failed to remove any dissolved turbidity though around 50 NTU were removed in the clarified fraction.

Conclusions

High silica removal rates (80–90 %) were obtained by adding soluble magnesium compounds (1,500 mg/L) at high initial pH (11.5) to the effluent. These silica removal rates would allow working in RO membranes at high recoveries (75–85 %) without silica scaling problems. $MgCl_2\ 6H_2O$ is preferred to $MgSO_4 \cdot 7H_2O$ because it is slightly more efficient on silica removal, due to its higher Mg content.

High pH required for high silica removal efficiencies is directly translated into an important increase of the conductivity of the waters that may require a further post-treatment of the RO rejects. This problem could be partially solved using $Ca(OH)_2$ instead of NaOH as pH regulator (final conductivity around 3.0 vs. 4.0 mS/cm). Additionally, the use of $Ca(OH)_2$ has the advantage of a lower cost, lower settling time, slightly higher silica removal (2–10 %, depending on the initial pH), and an additional 15 % COD removal.

The combination of $MgCl_2\ 6H_2O$ with a polyaluminum-based coagulant did not improve silica removal significantly (a maximum increase of 10 % was achieved). Alternatively, conductivity of the treated waters increase and the COD removal was not affected at all. Therefore, the use of the coagulant is not recommended.

According to the obtained ratios of Si removed/millimole Mg removed (around 0.5 and 1), it can be ascertained that the main mechanism involved on silica removal was the coprecipitation of silica with magnesium. These Si/Mg ratios are compatible with the formation of Mg_2SiO_4 (forsterite) or $MgSiO_3$ (enstatite).

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RESEARCH ARTICLE

Optimization of silica removal with magnesium chloride in papermaking effluents: mechanistic and kinetic studies

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Abstract The reuse of deinking paper mill effluent based on reverse osmosis is limited by silica scaling on the membranes. The removal of silica during softening processes is one of the most used approaches as it can treat large volumes of water at low cost, but when the water hardness is low, the addition of magnesium compounds is necessary. In the present investigation, $MgCl_2{\cdot}6H_2O$ was selected as magnesium source to analyze the effect of pH, dosage, temperature, and contact time on silica removal. Moreover, the silica removal mechanism was analyzed under different operational conditions. The results show that it is possible to obtain high silica removal rates (>70 %) at an intermediate dosage (750 mg/L of $MgCl_2{\cdot}6H_2O$) either at high pH (12.0) and ambient temperature (20 °C) or lower pHs, i.e., pH=10.5, but at higher temperatures 35–50 °C. The kinetic study demonstrates that contact times lower than 30 min are enough for silica removal with independence of the temperature. SEM-energy-dispersive X-ray spectroscopy (EDX) and Fourier transform infrared spectroscopy (FTIR) analysis of the solids obtained confirms that silica is removed through the formation of magnesium silicates. The EDX analysis showed that, independently of the operational conditions, the atomic Si/Mg ratio was around 0.7 which indicates that antigorite ($Mg_3Si_2O_5(OH)_4$) is the predominant specie formed.

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Keywords Silica removal · Magnesium · Precipitation · Membrane fouling · Paper recycling

Introduction

Nowadays, there is a growing interest in silica removal from industrial waters due to stringent legislation for discharge (i.e., 50 mg/L for Finland and Canada) (Huuha et al. 2010) and the increasing use of membrane treatments for effluent reuse (Pizzichini et al. 2005). These issues are particularly relevant in deinking paper mills since they are characterized by having a high concentration of silica in process waters and in the effluent (50–250 mg/L) (Huuha et al. 2010; Latour et al. 2013; Latour et al. 2014a; Latour et al. 2014b) resulting from the sodium silicate added to achieve the optical properties required in the final product (Ferguson 1992a; Ferguson 1992b; Lassus 2000). Due to the great variety of functions and good performance, its substitution is still difficult without affecting the quality of the final product. If silica is not removed, it is not possible to work with reverse osmosis (RO) membranes for effluent reuse at recoveries higher than 20 % (Ordoñez et al. 2010), which compromise the economic feasibility of the whole treatment chain.

Silica scaling in RO membranes is problematic and very difficult to remove even by chemical cleaning (Weng 1995; Neofotistou and Demadis 2004; Stathoulopoulou and Demadis 2008). There are many silica control techniques proposed in the literature including the use of antiscaling agents (Amjad et al. 1997; Neofotistou and Demadis 2004; Amjad et al. 2014), ion exchange resins, or electrocoagulation; however, the most important techniques, also for papermaking application, are silica removal during softening or by coagulation at high pH (Zeng et al. 2007; Demadis et al. 2012; Negaresh et al. 2013; Latour et al. 2014b, 2015a). These

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techniques allow treating large volumes of water with high silica content. Since coagulation has been widely studied (Hermosilla et al. 2012; Latour et al. 2013, 2015b; Miranda et al. 2015), the present study is focused on silica removal during softening.

When silica removal is carried out during the softening process, it is important to ensure that enough hardness is present in the water, especially magnesium hardness, which is more efficient than calcium hardness (Chen et al. 2006). Although this technique is effective, the main mechanism for silica removal is still not fully understood. Different studies claim that adsorption in freshly precipitated $Mg(OH)_2$ and $CaCO_3$ is the main silica removal mechanism, while others consider that co-precipitation of calcium and magnesium silicates is the main mechanism involved (Parks and Edwards 2007; Zeng et al. 2007; Hsu et al. 2008; Demadis et al. 2012).

In a previous study, it was found that the use of soluble magnesium compounds was a promising solution to obtain high silica removal rates treating the effluent from a deinking paper mill with high silica content and low hardness (Latour et al. 2014a). Among them, $MgCl_2{\cdot}6H_2O$ was the most efficient compound, achieving 90 % silica removal; however, these results were obtained under limited operational conditions (ambient temperature and 15 min of contact time). Based on these observations, the present study goes further, analyzing the effect of the operational temperature and contact time through a kinetic study. Moreover, the present study aims to generate a new knowledge clarifying the mechanism by which silica is removed in these conditions. For this purpose, the composition of the solids obtained after silica removal was analyzed by scanning electron microscopy-energy-dispersive X-ray spectroscopy (SEM-EDX) and Fourier transform infrared spectroscopy (FTIR) spectrophotometry.

Materials and methods

Materials

This study was carried out with the effluent of a Spanish paper mill using 100 % recovered paper to produce newsprint. This effluent is treated firstly by a primary and secondary treatment in the paper mill and then discharged for a further treatment in an urban wastewater treatment plant. The effluent used in this study is that being discharged to the urban wastewater treatment plan. Samples were stored at 4 °C during the tests, and no sets of trials longer than 5 days were carried out. Table 1 summarizes the main characteristics of the effluent. $MgCl_2{\cdot}6H_2O$, used as magnesium source, and $Ca(OH)_2$, used as pH regulator, both are analytical grade and were supplied by PANREAC. Lime milk was used as pH regulator due to its better performance compared to NaOH in previous studies (Latour et al. 2014a): slightly better efficiency in silica removal, significantly higher chemical oxygen demand (COD) removal, and less conductivity increase and pH decrease than NaOH. Both $MgCl_2{\cdot}6H_2O$ and $Ca(OH)_2$ were used as 10 wt.%/vol.% solutions prepared on daily basis.

Table 1 Characteristics of the paper mill effluent

Raw water	
pH	8.6
Conductivity (mS/cm)	1.62
Total alkalinity (mg/L $CaCO_3$)	644
Total suspended solids (mg/L)	75
Total solids (mg/L)	2050
Turbidity (NTU)	45
Dissolved fraction	
Silica (mg/L SiO_2)	160
COD (mg/L)	286
Sulfates (mg/L)	240
Calcium (mg/L)	52
Magnesium (mg/L)	12
Total solids (mg/L)	1945

Experimental procedure

Optimization of the operational conditions

The treatment was carried out at three different pHs (10.5, 11.5, and 12.0), at three temperatures (20, 35, and 50 °C) using $MgCl_2{\cdot}6H_2O$ at five dosages (from 250 to 1500 mg/L). These operational conditions were selected according to previous studies (Latour et al. 2014a; Latour et al. 2014b).

The experiments were carried out following a jar test methodology. First, the pH of the samples was adjusted by adding $Ca(OH)_2$ (10 wt.%/vol.%) to 200 mL of sample. After 1 min of mixing at 200 rpm, $MgCl_2{\cdot}6H_2O$ was added and mixed during 150 min at 200 rpm, and then, the waters were allowed to settle for 1 h. Finally, the clarified waters and the dissolved fraction, obtained by filtration through 0.45 μm pore size PTFE membrane filters, were analyzed. Settled solids were analyzed by FTIR spectrophotometry and SEM-EDX. All trials were carried out by duplicate with an average error between replicates under 5 %.

Kinetic study

The kinetic study was carried out at three intermediate $MgCl_2{\cdot}6H_2O$ dosages (500, 750, and 1000 mg/L) at two pHs (11.5 and 12.0) and three temperatures (20, 35, and

50 °C), according to the results obtained in the optimization of the operational conditions. First, the pH regulation was carried out by adding $Ca(OH)_2$, and after 1 min mixing, $MgCl_2{\cdot}6H_2O$ was added. Samples were taken at different times and immediately filtered through 0.45 μm PTFE membrane filter. These samples were characterized in terms of silica and magnesium concentration.

Analytical methods

pH was measured using a GLP 22 (Crison, S.A.) pH meter, according to Standard Method 4500, and the conductivity was measured with a model GLP 31 (Crison, S.A.) conductivimeter, according to Standard Method 2510 (American Public Health Association APHA, American Water Works Association AWWA, Water Environment Federation WEF 2005). Alkalinity was measured by titration with sulfuric acid 0.1 N using a pH electrode connected to an automatic titrator, model Compact I (Crison Instruments S.A.) to reach pH 4.5, according to EPA 310.1 method. Total solids and total suspended solids were measured according to the Standard Methods 2450 B and 2450 D, respectively (American Public Health Association APHA, American Water Works Association AWWA, Water Environment Federation WEF 2005). Turbidity was measured according to ISO 7027:2001 with a LP 2000-11 nephelometer supplied by Hanna Instruments. Reactive silica was measured by flow analysis and photometric detection through silicomolybdate and reduction to molybdenum blue, using a FIA Compact (MLE GmbH) according to DIN EN ISO 16264 and expressed as milligrams per liter of SiO_2. COD was photometrically measured by the Nanocolor® COD 1500 Method from Macherey-Nagel GmbH, according to ISO 15705:2003 using an Aquamate UV-Vis spectrophotometer supplied (Thermo Scientific Inc). Finally, calcium and magnesium content were measured using a direct air-acetylene flame atomic absorption method according to ISO 7980:1986 in a SpectraA 220 spectrophotometer supplied by Varian.

The FTIR analyses were carried out in a Nicolet Magna 750 spectrophotometer with a Spectratech IR-Plan Advantage Microscope. Spectra were recorded at 2 cm^{-1} resolution, and eight scans were taken for both the samples and the background. Samples were prepared with 0.6 mg of sample and 250 mg of KBr. The image analysis of the solids was carried out in a JEOL JSM-6400 SEM. This SEM is configured with an energy-dispersive X-ray analyzer (EDS system) which enables to perform elemental analysis. Samples for SEM-EDX analysis were coated with a thin graphite layer.

Results and discussion

Optimization of the operational conditions

Dosage, pH, and temperature optimization

The evolution of silica with the $MgCl_2{\cdot}6H_2O$ dosage under different conditions of pH and temperature is presented in Fig. 1. At 20 °C, pH 8.6 and 9.5 were also tested; however, silica removal rates were always smaller than 10 % (data not shown). One of the reasons behind these low silica removal could be that at these pH levels, silica, which derives from the orthosilicic acid, is not extensively ionized, and thus, it is not available to co-precipitate with magnesium as magnesium silicate, which is the main silica removal mechanism as it will be demonstrated later. Operational pHs >9.5 are necessary to have $H_3SiO_4^-$ and $H_2SiO_4^{2-}$ as the dominant species in the medium to promote silica removal (Huuha et al. 2010).

As a general trend, at all the pHs and temperatures tested, silica concentration decreased with the $MgCl_2{\cdot}6H_2O$ dosage. On the other hand, minimum silica concentration achieved varied with the operational pH and temperature.

At 20 °C, a significant increase on silica removal by increasing the initial pH was observed. At the highest dosage tested (1500 mg/L), silica removal was 34 % (residual silica 105 mg/L). This removal could be improved up to 80 % (residual silica 32 mg/L) at pH=11.5 and up to 90 % (residual silica 16 mg/L) at pH=12.0. The highest improvement on silica removal was obtained at dosages >500 mg/L at pH 11.5 and 12.0. This could be explained based on the stoichiometric dosage of the magnesium compound necessary to remove all the silica present in water through magnesium silicate precipitation. Considering silica precipitates as enstatite ($MgSiO_3$), with molar ratio Si/Mg=1, the stoichiometric dosage of $MgCl_2{\cdot}6H_2O$ to achieve a complete removal of silica would be around 430 mg/L taking into account the initial Mg in the water. This stoichiometric dosage would be higher if silica precipitates as Mg_2SiO_3 (forsterite) or $Mg_2Si_2O_5(OH)_4$ (antigorite), i.e., 870 or 650 mg/L, respectively. Hence, a dosage of 250 mg/L is much lower than that stoichiometrically required, insufficient to obtain high silica removal rates. It is also important to consider that not all the magnesium precipitates as magnesium silicates. The precipitation of $Mg(OH)_2$ (brucite) was also possible at the high pHs tested; however, according to the solubility constants of the different species (Table 2), the precipitation of magnesium silicates was more thermodynamically favored.

Operational temperature is a key parameter on silica removal as it affects not only the reaction kinetics but also the solubility of the different species. In this sense, magnesium silicates show inverse solubility (Demadis 2010; Milne et al. 2014); thus higher temperatures favors silica removal. At 35 °C, with 1500 mg/L of $MgCl_2{\cdot}6H_2O$, silica concentration

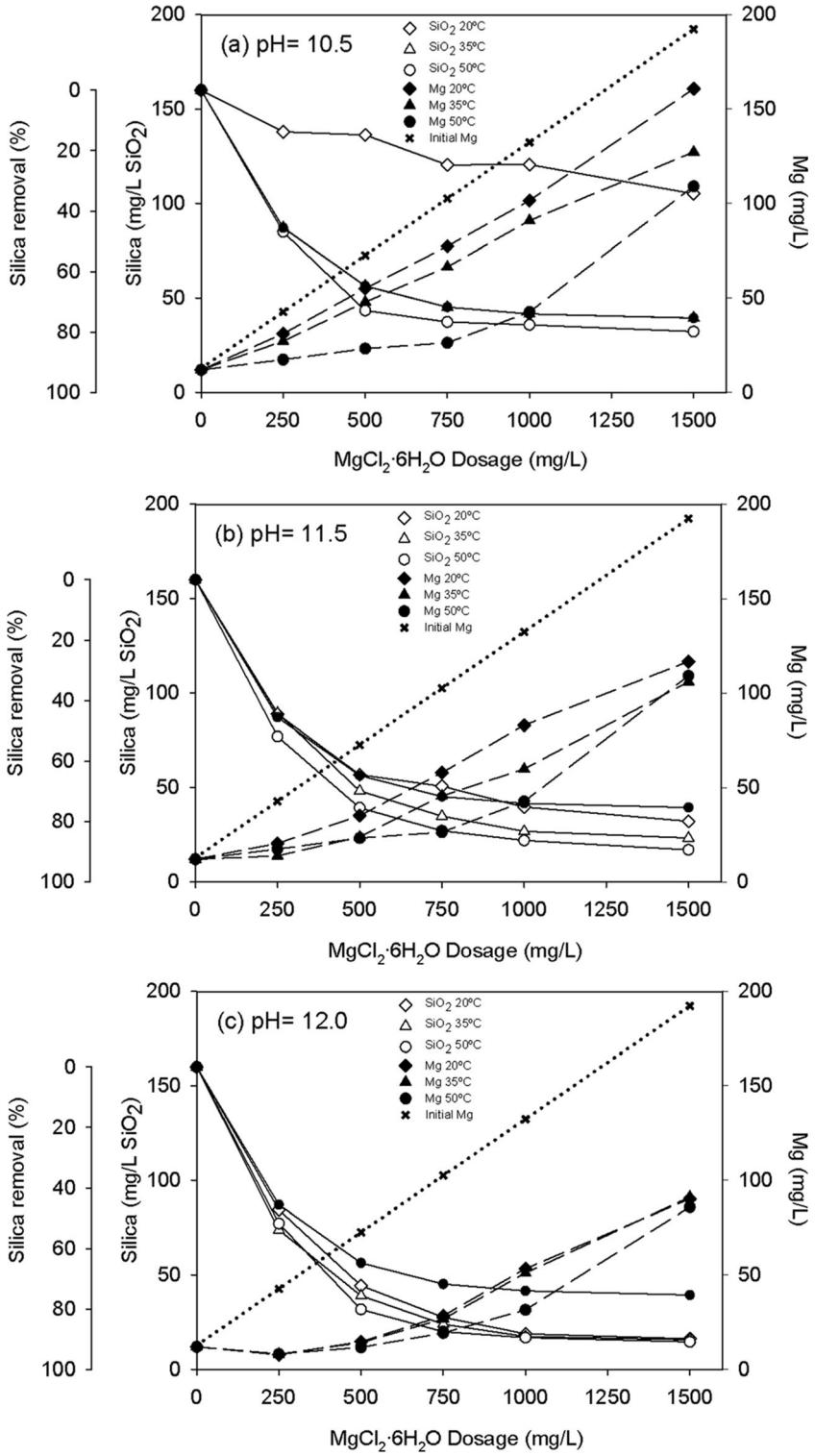

Fig. 1 Final silica and magnesium concentration vs. dosage at different temperatures and initial pHs: **a** pH=10.5, **b** pH=11.5, and **c** pH=12.0

was decreased down to 40 mg/L (75 % silica removal), 22 mg/L (86 % silica removal), and 16 mg/L (90 % silica removal) at initial pH 10.5, 11.5, and 12.0, respectively. Comparing these results with the ones obtained at 20 °C, it is possible to observe an increase on silica removal, especially at pH 10.5. This also occurred at 50 °C. In this latter case, the minimum silica concentration obtained was 32 mg/L (80 % silica removal), 16 mg/L (90 % silica removal), and 3 mg/L (98 % silica removal) at pH 10.5, 11.5, and 12.0, respectively. Higher temperatures favor

Table 2 Solubility constants of the most likely compounds to be formed

Specie	Equilibrium equation	pK_{ps}
Antigorite	$Mg_3Si_2O_5(OH)_4 + H_2O \rightleftharpoons 3Mg^{2+} + 2H_4SiO_4 + 6OH^-$	34.5
Forsterite	$Mg_2SiO_4 + 4H_2O \rightleftharpoons 2Mg^{2+} + H_4SiO_4 + 4OH^-$	26.9
Enstatite	$MgSiO_3 \rightleftharpoons Mg^{2+} + H_4SiO_4 + 2OH^-$	16.6
Brucite	$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$	11.6
$CaCO_3$	$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$	8.3
CaH_2SiO_4	$CaH_2SiO_4 + 2H_2O \rightleftharpoons Ca^{2+} + H_4SiO_4 + 2OH^-$	8.16
Lime	$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$	5.15

compounds to precipitate at lower pHs at constant magnesium concentration (Demadis 2010).

Figure 1 also shows residual magnesium after the different treatments at the three pHs tested. Initial magnesium was calculated as the initial magnesium in the water (12 mg/L) plus the magnesium added with $MgCl_2{\cdot}6H_2O$. As it was expected, the final magnesium increased with $MgCl_2{\cdot}6H_2O$ dosage (especially at dosages >500 mg/L), indicating the overdosing of the magnesium compound at the highest dosages. On the other hand, for a given initial $MgCl_2{\cdot}6H_2O$ dosage, final magnesium concentration decreased with the pH and temperature. This decrease is in agreement with the lower solubility of magnesium silicates and magnesium hydroxide at higher pHs and temperatures. At pH=10.5 and 20 °C, the highest concentrations of residual magnesium were obtained. At the maximum dosage of 1500 mg/L, residual magnesium was 160, 116, and 90 mg/L at 20, 35, and 50 °C, respectively. At pH=11.5 and >500 mg/L of $MgCl_2{\cdot}6H_2O$, residual magnesium increased linearly with the dosage, in parallel with silica removal.

As observed in silica concentration, variation of magnesium concentration with temperature was lower at higher pHs. It was also observed that at pH=12.0, the final magnesium concentration was similar at the three temperatures tested and it remained almost constant at around 15 mg/L at dosages <500 mg/L. With dosages over 750 mg/L, residual magnesium concentration started to increase. With 750 mg/L, silica removal rates were higher than 80 %, which leads us to think that the magnesium added could be close to the stoichiometric dosage and, consequently, there would be an excess on magnesium at higher dosages that could precipitate as $Mg(OH)_2$.

According to the solubility constants shown in Table 2, the precipitation of magnesium silicates is favored in waters with high silica contents, which is in agreement with the results obtained. Moreover, antigorite would be thermodynamically favored with respect to forsterite and enstatite for both high silica and magnesium concentrations. On the other hand, at high $MgCl_2{\cdot}6H_2O$ dosages, low silica and high magnesium concentrations were observed. In this case, brucite may play a relevant role. For example, at 50 °C with 1500 mg/L $MgCl_2{\cdot}6H_2O$, a 90 % silica removal was obtained, which is about the same silica removal (88 %) than that obtained when using 1000 mg/L of $MgCl_2{\cdot}6H_2O$. In these conditions, residual magnesium was 86 and 32 mg/L, respectively. Considering that silica removal rates are similar, magnesium consumption to remove silica as magnesium silicates would be the same. Increasing the $MgCl_2{\cdot}6H_2O$ dosage from 1000 to 1500 mg/L, magnesium in water would increase 50 mg/L, which is approximately the increase in residual magnesium observed (54 mg/L). That may indicate that the excess of magnesium added did not precipitate as $Mg(OH)_2$ at these pHs.

Although calcium is less efficient than magnesium for silica removal (Chen et al. 2006), as $Ca(OH)_2$ was used as pH regulator, silica removal assisted by calcium compounds should also be considered. Table 2 shows the dissolution equilibriums of different calcium compounds that may take place in the system. Although the precipitation of calcium silicates would be possible, especially due to the dissolution equilibrium of $Ca(OH)_2$, the solubility of calcium silicate is much higher than that of magnesium silicate. Therefore, when both calcium and magnesium are present in the water, silica would be preferably removed as magnesium silicate. Calcium silicate may precipitate in the case of waters with silica and low concentration of magnesium. That would be the case of working at dosages <500 mg/L $MgCl_2{\cdot}6H_2O$ that, as mentioned before, are lower than the stoichiometrically required to remove all silica. Moreover, dissolved calcium could also react with the alkalinity of the effluent and precipitate as calcium carbonate, as it is demonstrated in FTIR analysis section. Calcium in the treated waters varied between 5 and 25 mg/L when the initial calcium concentration is 52 mg/L in the effluent. The lower concentrations of dissolved calcium were obtained, as expected, at higher pHs.

Final conductivity and pH were also considered to compare the different treatments (Fig. 2). Conductivity is an important factor to take into account, especially if the water is going to be post-treated in a RO system. High conductivity levels may produce inorganic scaling on the membrane at high recoveries (Ordoñez et al. 2010; Latour et al. 2014a). Moreover, in the case of the paper mill studied, there is a discharge limit for conductivity of 7.5 mS/cm (Latour et al. 2014a); therefore, higher values in the RO rejects would make necessary a

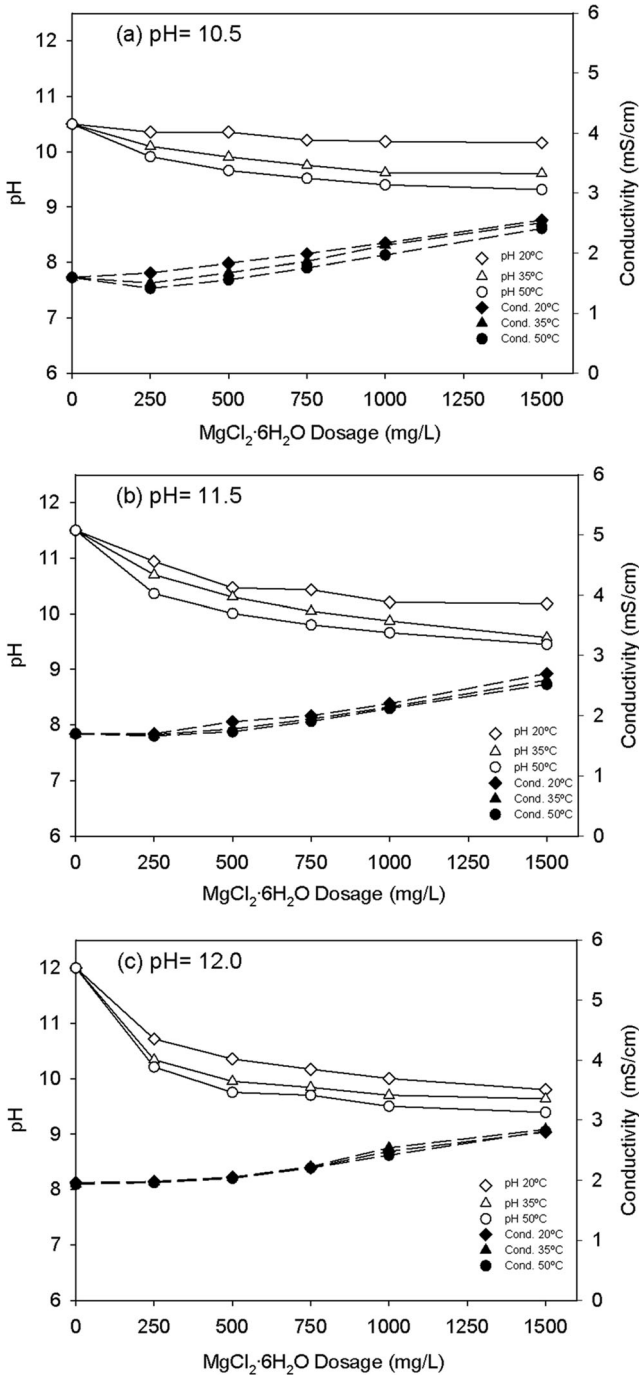

Fig. 2 Final pH and conductivity vs. dosage at different temperatures and initial pHs: **a** pH=10.5, **b** pH=11.5, and **c** pH=12.0

post-treatment. The conductivity increase after the treatment is determined by the pH regulation and the addition of the magnesium compound. The increase in conductivity caused by the pH regulation was lower than 0.5 mS/cm for the three pHs tested, which is considerably lower than the results obtained in previous studies when caustic soda was used as pH regulator (Latour et al. 2014a). On the other hand, the final conductivity also increased when increasing the $MgCl_2{\cdot}6H_2O$ dosage (around 1.0 mS/cm with 1500 mg/L). Final conductivity only varied slightly with the temperature. In all the treatments tested, final conductivity was lower than 2.5 mS/cm, which is the limit value to work at 75 % RO recovery without being necessary any post-treatment of the rejects and limiting the inorganic scaling on the RO membrane.

As stated previously, if silica is removed by co-precipitation with magnesium (as it will be demonstrated later), it has to be ionized, being high pHs required. At the operational pHs tested, the predominant silicate species is $H_3SiO_4^-$, which would react with Mg^{2+} and precipitate according to different stoichiometries (Table 2). The precipitation of the different magnesium silicates caused a pH decrease due to the consumption of OH^- (Table 2). The pH reduction observed varied in parallel with silica removal, and it was higher at the highest pHs and temperatures. At 20 °C, the pH fall for the maximum dosage of $MgCl_2{\cdot}6H_2O$ varied between 0.3 (initial pH=10.5) and 1.3 (initial pH=12.0). This decrease was higher at higher temperatures. It varied in the range of 0.75–1.3 pH units at 35 °C and 1.1–2.5 pH units at 50 °C.

Similarly to pH, alkalinity decreased with the different treatments. For an initial alkalinity of around 650 mg/L $CaCO_3$, the final alkalinity measured was always smaller being the decrease more pronounced at higher pH, temperature, and dosage. At 20 °C, the final alkalinity varied around 350–530 mg/L $CaCO_3$ with the maximum dosage tested (1500 mg/L). At 35 °C, the final alkalinity was smaller compared to the results obtained at 20 °C, with 1500 mg/L of $MgCl_2{\cdot}6H_2O$; it was around 350–475 mg/L $CaCO_3$. Finally, at 50 °C, final alkalinity was around 150–350 mg/L $CaCO_3$. This tendency is consistent with the trend followed by silica concentration and also with the precipitation of other species such as calcium carbonate.

Kinetic study

Based on the results obtained in the equilibrium tests, the kinetic study was carried out at three temperatures (20–50 °C), two pH levels (11.5 and 12.0), and three intermediate dosages of $MgCl_2{\cdot}6H_2O$ (500, 750, and 1000 mg/L). These conditions were selected as they allowed obtaining silica removal rates higher than 60 %.

Figure 3 shows the evolution of silica removal with time at different temperatures and dosages. In all the treatments, silica removal increased with the contact time until reaching a steady value which was different depending on the operational conditions. At 20 °C (Fig. 3a), silica was removed very fast for the first 30 min, reaching 75–85 % of the total removal. Afterwards, the removal continued increasing but at a lower rate. Maximum silica removal rates obtained varied in the range of 55–80 %, depending on the operational conditions. With 500 mg/L at both pH tested, silica removal rates were

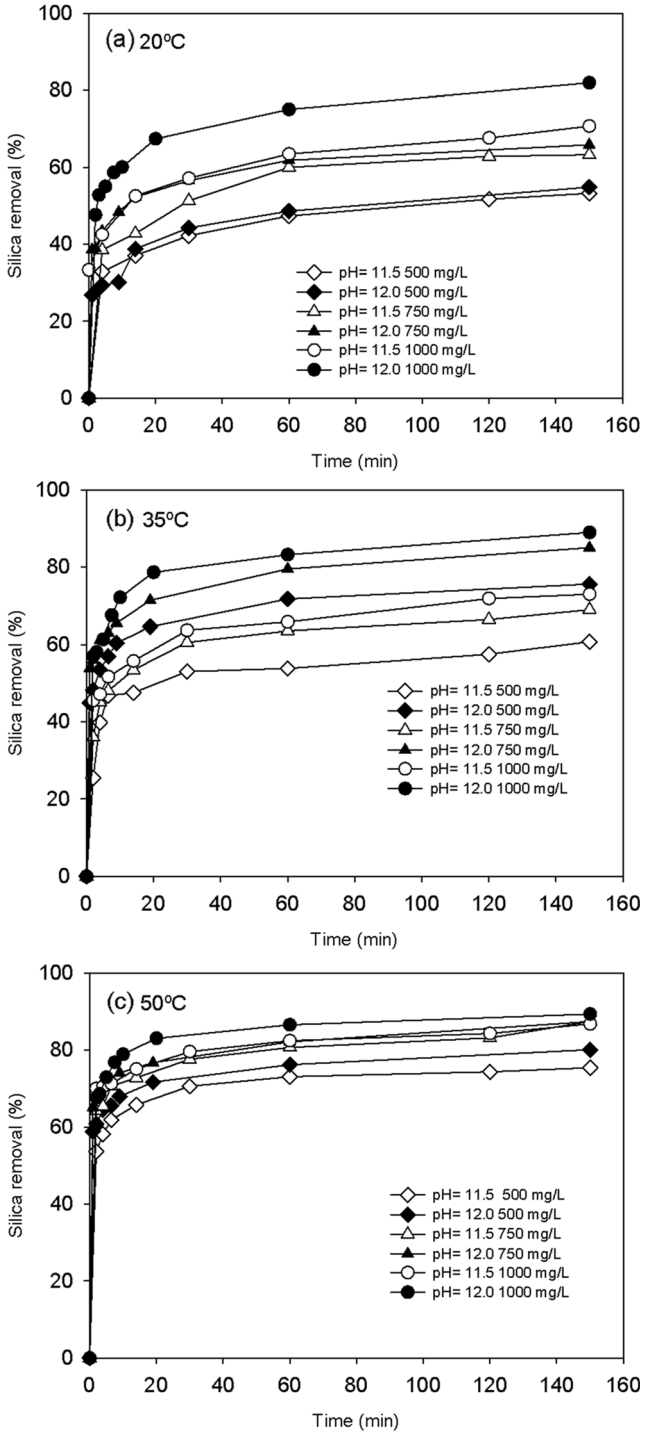

Fig. 3 Silica removal vs. time at different initial pHs and temperatures: **a** 20, **b** 35, and **c** 50 °C

very close at any time, indicating that at low dosages, the increase in pH did not enhanced the kinetics of the process. At 35 °C, silica removal kinetics were improved. In this case, 85 % of the total removal was achieved after 20 min. At this temperature, maximum silica removals varied between 65 and 90 %. Silica removals obtained at pH 12.0 were always higher than at pH 11.5 regardless of the dosage. Finally, at 50 °C, the removal was faster. In this case, 80 % of the total removal was achieved after 5 min and 85 % conversion was obtained after 15 min. At this temperature, differences in silica removal between at different pHs and dosages were lower than at lower temperatures; maximum silica removal varied between 75 and 90 %.

Figure 4 shows a simplified diagram of the main reactions involved in the silica removal process. Silica, which derives from the orthosilicic acid, can react with Mg^{2+} and precipitate as magnesium silicates. Silica may also react with Ca^{2+} from the lime used as a pH regulator to yield calcium silicates. The use of lime introduces also additional hydroxyl groups to the water which are consumed in the precipitation of different magnesium silicates and magnesium hydroxide. On the other hand, silica polymerization may also occur, especially at high temperatures; nevertheless, at the conditions of basic pH and magnesium concentration tested, the precipitation of silicates is favored compared to polymerization (Sheikholeslami et al. 2001). In some selected samples, total silica was measured by inductively coupled plasma optical emission spectrometry (ICP-OES). Silica concentration obtained (total silica) was around the same than these obtained for reactive silica (silicomolybdate method) indicating that silica polymerization was negligible at the contact times used and all the silica present was in the dissolved form.

Due to the complexity of the system studied, in which different species react and precipitate, the silica removal process was analyzed using a simplified kinetic approach based on a pseudo-order kinetic model. Different pseudo kinetic orders were tried to fit the data (first, second, and third pseudo kinetic order). Pseudo-*n*th order reaction kinetics were tested and discarded due to the poor fit of the experimental data ($R^2<$ 0.7) compared to the results obtained by the pseudo-second-order fit ($R^2>0.97$). The model best describing the experimental data are represented by [1]:

$$dC_{Si}/dt\cdot = \cdot k'\cdot\left(C_{Si}-C_{Sieq}\right)^2 \qquad ([1])$$

where k' is the pseudo-second-order rate constant (L/mol min), C_{Si} represents silica concentration at any time (mol/L), and C_{Sieq} is the silica concentration at t=150 min at each operational condition (≈equilibrium concentration). A plot of $1/(C_{Si}-C_{Sieq})$ vs. t gives the value of k' as the slope. Table 3 shows the values k' under the different operational conditions of pH, temperature, and $MgCl_2{\cdot}6H_2O$ dosage. In most of the cases, R^2 was around 0.98–0.99, indicating the goodness of the fit. The value of k' increased with the temperature and pH, while it not varied significantly with the $MgCl_2{\cdot}6H_2O$ dosage. The increase in k' with the temperature was observed with all the pHs and dosages. This increase was higher when increasing the temperature from 35 to 50 °C than

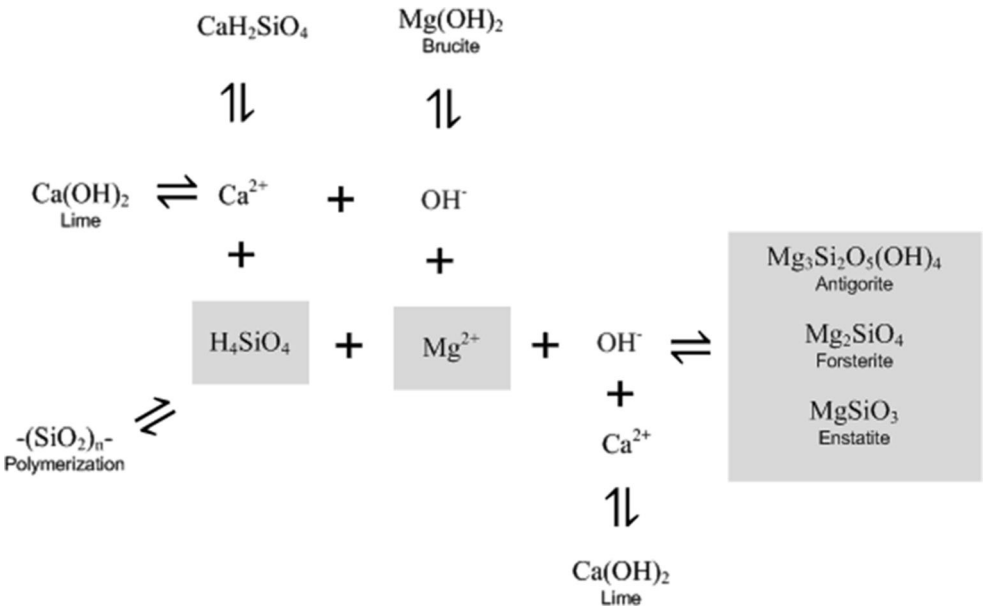

Fig. 4 Simplified scheme of the reactions that may occur during silica removal

in the temperature interval from 20 to 35 °C, e.g., at pH=11.5 and 1000 mg/L, the values of k' obtained were 43, 51, and 111 L/mol min. Regarding the effect of the pH in k', at 20°C and pH=11.5, k' varied from 43 to 51 L/mol min depending on the dosage, while at 20 °C and pH=12.0, k' values varied from 75 to 101 L/mol min, which were clearly higher than the ones obtained at pH=11.5. This indicates that at lower pHs, the kinetic is slower, probably because the dissolution of the $Ca(OH)_2$ is limiting the availability of alkalinity which is consumed in the precipitation of magnesium silicates. The apparent activation energy (Ea) was calculated at the different pHs and dosages, varying in the range of 10–20 kJ/mol. This low energy activation shows a fast kinetics for silica removal, independently of the different reactions which could take in place at the same time (Fig. 4). Previous studies carried out by the authors with sparingly magnesium salts as magnesium source (MgO) for silica removal showed slower kinetics, with the dissolution of the magnesium source as the limiting stage for silica removal (Latour et al. 2015a). This is not the case when using soluble magnesium salts as the $MgCl_2{\cdot}6H_2O$ used in the present study.

Table 3 Pseudo-second-order constants for silica removal under different operational conditions

pH	$MgCl_2{\cdot}6H_2O$ dosage (mg/L)	T (°C)	k' (L/mol min)	R^2
11.5	500	20	46±3	0.996
		35	66±4	0.954
		50	103±8	0.986
	750	20	51±3	0.985
		35	55±3	0.974
		50	138±2	0.980
	1000	20	43±1	0.998
		35	51±2	0.994
		50	111±2	0.999
12.0	500	20	101±4	0.991
		35	121±4	0.997
		50	135±2	0.999
	750	20	93±9	0.995
		35	99±2	0.993
		50	137±3	0.987
	1000	20	75±1	0.999
		35	93±7	0.974
		50	201±5	0.997

Solid characterization: assessment of silica removal mechanisms

To further understand the silica removal mechanism, a compositional analysis of the solids was carried out.

FTIR analysis

Figure 5 shows the FTIR spectra of some solids obtained under different operational conditions. The samples shown in Fig. 5 were selected as representative of the different operational conditions tested, i.e., low and high dosages of $MgCl_2{\cdot}6H_2O$ dosages, different pHs, and different temperatures. In all the samples analyzed, the same peaks and bands were observed independently of the operational conditions. The O–H vibration produced a wide band around 3434 cm^{-1} due to the hydration water and to calcium hydroxide. It is interesting to notice that at around 3700 cm^{-1}, it appears as small

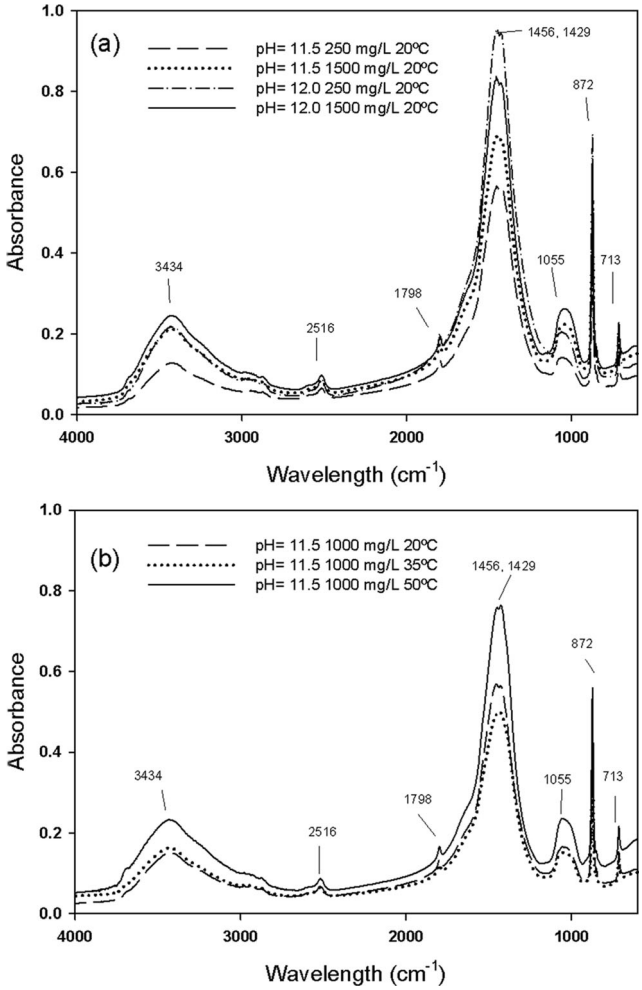

Fig. 5 FTIR spectra of the solids obtained after precipitation at **a** initial pH=11.5–12.0, 250–1500 mg/L, and 20 °C and **b** initial pH=11.5, 1000 mg/L, and 20-35-50 °C

shoulder with the OH stretching band corresponding to brucite and antigorite. There was a Si–O band at 1055 cm^{-1} that is associated with different silicates such as antigorite, forsterite, or enstatite. Carbonate bands were also detected at 2516, 1798, 1456–1429, 872, and 713 cm^{-1}. As lime milk was used as pH regulator, there were high concentrations of calcium carbonate in the solids; thus, the high intensity of the carbonate peaks masks the peaks and bands obtained of silicates.

Figure 5a shows the FTIR spectra obtained at 20 °C with two different dosages of $MgCl_2 \cdot 6H_2O$ at the two pHs tested. At both pHs, it was observed that the relative intensity of the band at 1055 cm^{-1} (Si–O) compared with the intensity of the peak at 872 cm^{-1} (carbonates) was always higher at the highest dosages. Moreover, at the same for the $MgCl_2 \cdot 6H_2O$, the relative intensity of the band 1055 cm^{-1} compared to the peak at 872 cm^{-1} was more intense at pH=12.0 than at pH=11.5. These observations are consistent with the results presented in Optimization of the operational conditions section, i.e., higher dosages and higher pHs increase silica removal. Furthermore, Fig. 5b shows the spectra obtained at different temperatures but the same pH and dosage. In this case, no significant differences were observed in the absorbance of the band at 1055 cm^{-1} compared to the peak at 872 cm^{-1}, indicating that silica removal was similar in both cases. However, the band at 1456–1429 cm^{-1} corresponding to $CaCO_3$ is more intense at 50 °C than at the lowest temperatures, which is in agreement with the inverse solubility of calcium carbonate.

SEM-EDX

Figure 6 shows some of the SEM images of the settled solids obtained under different operational conditions. As

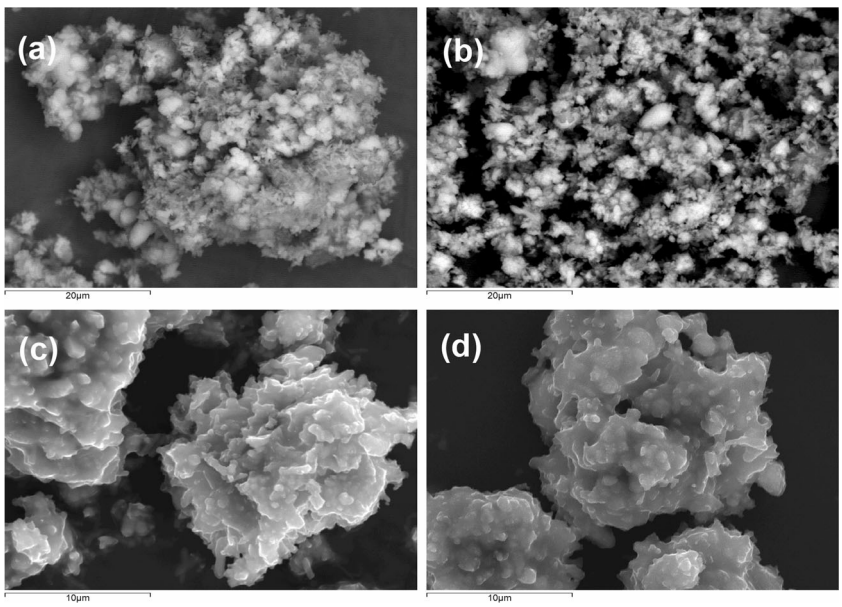

Fig. 6 SEM-EDX images of the typical solids obtained after the treatment at **a** pH=11.5, 250 mg/L, and 20 °C, ×2000; **b** pH=11.5, 750 mg/L, and 20 °C, ×2000; **c** pH=12.0, 250 mg/L, and 20 °C, ×4000; and **d** pH=12.0, 750 mg/L, and 20 °C, ×4000

Table 4 Composition of the solids obtained after precipitation

	Mg (atomic %)	Si (atomic %)	Ca (atomic %)	Si/Mg (atomic)
(a)	0.62	0.41	19.41	0.66
(b)	4.47	3.21	18.80	0.72
(c)	1.76	1.67	25.94	0.95
(d)	1.47	0.73	24.97	0.50

it can be seen, the solids were agglomerates of amorphous particles of different composition. Table 4 shows the EDX analysis of the solids presented in Fig. 6. The solids were mainly composed by Mg, Si, O, and Ca. Atomic Si/Mg ratios varied between 0.5 and 1, which is in agreement with the precipitation of a mixture of forsterite (Mg_2SiO_4), enstatite ($MgSiO_3$), and antigorite ($Mg_3Si_2O_5(OH)_4$). Besides magnesium silicates, due to the addition of lime milk as pH regulator, particles with high calcium concentration were detected, being these compatible with $Ca(OH)_2$, $CaCO_3$, or calcium silicate (Table 4).

Figure 7 shows Si (atomic %) vs. Mg (atomic %) of the solids analyzed by EDX at different operational conditions of dosage, pH, and temperature. It could be observed that the Si/Mg atomic ratio for the different solids was very similar, independently of the operational conditions. A linear fit of the data obtained an average 0.69 atomic Si/Mg ratio which is very close to the atomic Si/Mg ratio of the antigorite ($Mg_3Si_2O_5(OH)_4$, Si/Mg=0.67). This result is in agreement with the K_{ps} data presented in Table 2 where antigorite was the most insoluble magnesium silicate and therefore the most likely to precipitate. This result is also in agreement with Gunnarsson et al. (2005), who also obtained a Si/Mg=0.7 when studying the precipitation of magnesium silicate in synthetic water under different operational conditions of pH and temperature. Although the average Si/Mg ratio was 0.69, particles with ratios from 0.50 to 1 were also observed (Table 3 and Fig. 7). These lower ratios could be attributed to other magnesium silicate stoichiometries (e.g., forsterite, Si/Mg=0.5) or to the presence of other magnesium compounds such as $Mg(OH)_2$ or $MgCO_3$. Higher Si/Mg ratios could be associated to the presence of polymeric silica or magnesium silicates with higher silica/magnesium stechoimetries (e.g., enstatite, Si/Mg=1).

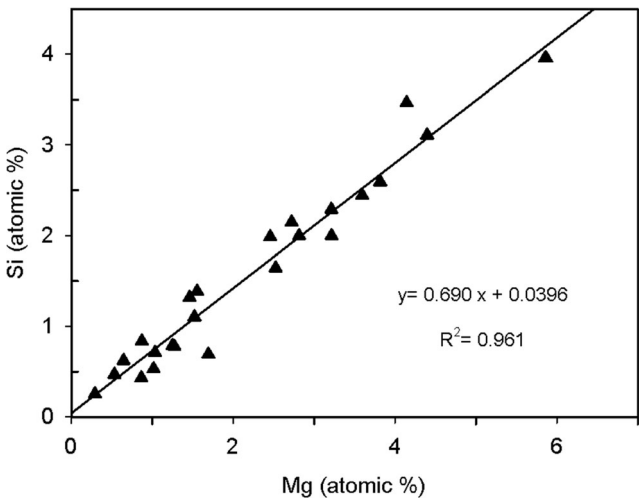

Fig. 7 Si (*atomic*) vs. Mg (*atomic*) of the solids under different operational conditions

Based on the constant Si/Mg atomic ratio obtained and the large values of Si removed per Mg removed, it can be ascertained that the main silica removal mechanism would be precipitation as antigorite. If adsorption on fresh formed magnesium hydroxide were the main mechanism involved, the Si/Mg ratio observed in the solids would be much lower. In the literature, it was reported a molar ratio Si/Mg of around 1:22 for pure adsorption of silica on $Mg(OH)_2$ (Chen et al. 2006; Hsu et al. 2008). The fast kinetics of the process also suggests that precipitation is favored to adsorption at these experimental conditions.

Conclusions

High silica removal rates are (>80 %) with different combinations of high pH or high temperature conditions with different dosages of magnesium chloride. At 20 °C, 80 % silica removal is obtained with 1500 mg/L of $MgCl_2{\cdot}6H_2O$ working at pH 11.5–12.0. Higher operational temperatures increase silica removal up to 80 % at pH=10.5 and up to 90 % at pH 11.5–12.0 with 1500 mg/L of $MgCl_2{\cdot}6H_2O$. Finally, 90 % removal is achieved by decreasing the dosage down to 750 mg/L at pH=12.0 and 50 °C.

The silica removal process is fast even at ambient temperature (20 °C), achieving >80 % of the total silica removal with contact times lower than 30 min. Higher temperatures improve the kinetics, being possible to achieve 85 % of the total silica removal in 20 min at T=35 °C and 15 min at T=50 °C, respectively. The silica removal process shows a good fit to a pseudo-second kinetic model.

FTIR spectra and SEM-EDX analysis support the precipitation of magnesium silicates as the main silica removal mechanism. The Si/Mg ratio detected by SEM-EDX is around 0.69, independently of the operational conditions, meaning that the primary mechanism in the removal of silica is formation of antigorite ($Mg_3Si_2O_5(OH)_4$). The constant Si/Mg atomic ratio and the fast kinetics also support that adsorption on $Mg(OH)_2$ and $CaCO_3$ mechanism is negligible at the operational conditions tested.

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PUBLICATION IX

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Silica removal with sparingly soluble magnesium compounds. Part I

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ABSTRACT

The main bottleneck in the treatment and reuse of effluents from deinking paper mills that employ reverse osmosis (RO) is the high silica content, which causes membrane fouling that limits the recovery of the treatment. Silica removal with magnesium compounds enables to treat large volumes of water with high removal efficiencies at low cost. Although soluble magnesium compounds are efficient, their use is limited since they increase the conductivity in the treated waters. Therefore the use of sparingly soluble magnesium compounds might be a promising alternative. Three sparingly soluble magnesium compounds (MgO, $Mg(OH)_2$ and $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$) were studied in this paper at three pHs (10.5, 11.0 and 11.5) and five dosages (250–1500 mg/L) at ambient temperature (~20 °C). Only 40% silica removal was obtained, which is not high enough to work at regular RO recoveries without scaling problems. To increase silica removal, the slurries of sparingly soluble compounds were pre-acidified with concentrated sulphuric acid and tested at the same conditions. In this case, high removal rates were obtained (80–86%) at high pH (11.5), even at ambient temperature. These removal rates would allow working at 75–80% recovery in RO units without scaling problems. This pre-acidification, together with the use of $Ca(OH)_2$ as pH regulator limited the increase of the conductivity of the treated waters to only 0.2 mS/cm. Additionally, the use of $Ca(OH)_2$ instead of NaOH as pH regulator increased the chemical oxygen demand removal from 15% to 25%.

1. Introduction

Paper industry is one of the leading industries in water management and sustainable water use. Although different alternatives have been developed to optimize the use of water in papermaking, there are still some unresolved aspects that limit their implementation at industrial scale. The closure of water loops through the internal reuse of water is limited by the accumulation of contaminants, especially dissolved and colloidal material (DCM), which affects the paper machine runnability and the final product quality [1]. To further reduce water consumption it is therefore necessary to treat and reuse the paper mill effluents. Membrane treatments, such as ultrafiltration (UF) and reverse osmosis (RO) [2,3], allow to produce the water quality required to reuse the effluent. However, effluents from deinking paper mills are characterized by high silica content, ranging from 50 to 250 mg/L as SiO_2 [2,4,5]. This makes the removal of silica a key factor for the reuse of the effluent to work on the RO membrane at recoveries higher than 20% [3] without scaling problems. Membrane fouling caused by silica is a bottleneck as silica scaling in RO membranes is severe and, once it is formed, it is very difficult to remove by chemical cleaning [6,7]. This scaling causes decline in water production rates, low permeate quality, unsteady-state operation conditions, higher energy consumption and serious damages in the membranes that shorten their lifetime, limiting the technical and economic feasibility of the whole treatment chain [8,9]. Furthermore, the environmental legislation sets stringent limits to the level of silica allowed in the effluents: 50 mg/L in Finland, Canada and United States [5]. Therefore, there is a need to develop cost effective technologies to treat large volumes of high silica content industrial waters.

In papermaking, silica cannot be reduced at its source since sodium silicate, is necessary to: (i) stabilize the hydrogen peroxide for bleaching; (ii) take advantage of its buffering and saponification properties; (iii) assist ink particles dispersion and influence their size; (iv) collect ink; (v) reduce fibre losses; and (vi) avoid the flotation of fibres [10,11]. Several attempts have been made to reduce its use [12,13]; however, due to its great variety of functions and low cost, its substitution is still very difficult in deinking papermaking operations.

Silica can be found in crystalline and amorphous forms. There are various forms of crystalline silica, but the most abundant one is quartz, having a very low solubility in water, around 6 mg/L

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(as SiO_2) at 25 °C. On the other hand, amorphous silica has a solubility of 100–140 mg/L (as SiO_2) at 25 °C [14,15]. Moreover, amorphous silica can be classified as dissolved, colloidal and particulate silica. Dissolved silica includes polysilicic acid and oligomeric species such as dimers, trimers or oligomers. Colloidal silica stands for more highly polymerized species. Particulate silica is larger than the colloidal one [16]. Both soluble and colloidal silica cause scaling problems on reverse osmosis membranes [7]. When the concentration of soluble silica exceeds its solubility, it precipitates on the membrane surface alone or with other products. In the case of colloidal silica, fouling occurs due to the accumulation of the colloids formed in the bulk solution, and accumulates on the membrane surface [16,17].

Although there are many silica removal techniques proposed in the literature [18], it is usually carried out during softening processes or by coagulation at high pH [2,4,5,19,20].

Coagulation with aluminum-based salts is very effective at ambient temperature, but high dosages (2500–5000 mg/L) are required to achieve high removal rates and the use of hybrid coagulants which increases considerably the treatment cost [4]. On the other hand, when silica removal is carried out during softening, it is necessary to ensure that enough hardness is present in the water. Thus, the addition of magnesium compounds is a preferred option, since higher silica removal is achieved with a higher Mg/Ca ratio at constant total hardness [21].

Previous studies have shown that 80–90% silica removal can be achieved adding $MgCl_2{\cdot}6H_2O$ and $MgSO_4{\cdot}7H_2O$ at high pH (11.5) with dosages of 1500 mg/L at ambient temperature. This high pH level needed was directly translated into an important increase in the conductivity of the waters, which could make necessary the post-treatment of the RO rejects and may compromise the economic feasibility of the whole effluent reuse treatment. However, this problem could be partially solved with the use of $Ca(OH)_2$ as pH regulator [22]. Another approach would be the use of sparingly soluble magnesium compounds instead of soluble magnesium as tested in previous studies [22].

Part I of this study aims to gain new knowledge in the use of sparingly soluble compounds to treat high silica content industrial effluents at ambient temperature. The treatments with MgO, $Mg(OH)_2$ and $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$) were optimized in terms of dosage, pH and type of pH regulator. Additionally, the possibility of increasing silica removal rates through pre-acidification of the slurries was studied. The objective was to achieve the silica removal necessary (80–90%) to increase RO recovery from 20% to 60–80%, in order to make the effluent reuse process technically and economically feasible. Part II focuses on equilibrium and kinetic studies at different temperatures of the most efficient sparingly soluble magnesium compound (MgO) and the main silica removal mechanisms.

2. Materials and methods

2.1. Water samples

This study was carried out with the effluent of a Spanish paper mill that uses 100% recovered paper to produce newsprint. The mill has an integrated wastewater treatment plant consisting of a primary treatment by dissolved air flotation and a secondary treatment based on an aerobic digestion of the waters on a moving bed biofilm reactor, followed by a secondary dissolved air flotation. Water samples from the final effluent were taken before its discharge to an urban wastewater treatment plant. Samples were stored at 4 °C during the tests and no sets of trials longer than five days were carried out. Table 1 summarizes the main characteristics of the effluent considered.

2.2. Chemicals

Three sparingly soluble magnesium compounds of analytical grade, MgO (solubility 0.086 g/L, 20 °C), $Mg(OH)_2$ (solubility 0.012 g/L, 20 °C) and $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$ (solubility 0.0375 g/L, 20 °C) were studied. Slurries of 10 w/v% were prepared with distilled water on a daily basis. When necessary, pre-acidification of the slurries was carried out with H_2SO_4 (96%). Two different pH regulators were used to increase the pH to the desired values: NaOH and $Ca(OH)_2$, both of analytical grade and also prepared 10 w/v% in distilled water on a daily basis. All products were supplied by PANREAC (Barcelona, Spain).

2.3. Methodology for jar-tests

For each magnesium compound, 6 dosages were tested (from 250 to 1500 mg/L) at 3 different pHs: 10.5, 11.0 and 11.5. These pHs were selected according to previous studies with the same type of water [22]. Magnesium compounds were tested using NaOH as pH regulator. Once the most efficient compound was selected, pH regulator was varied, comparing the efficiency of NaOH and $Ca(OH)_2$.

First, the pH of the samples was adjusted by adding NaOH (10 wt.%) to 250 ml of sample. After 1 min of mixing at 200 rpm, the magnesium compound being tested was added and mixed for a period of 15 min at 200 rpm, according to previous studies [22], and then, the waters were allowed to settle for 1 h. Finally, the clarified waters and the dissolved fraction, obtained by centrifugation at 2000 g during 15 min in a Hettich Zentrifugen Universal 16, were characterized. All trials were carried out at room temperature (20 °C ± 2 °C) by duplicate. The average error between replicates was always under 5%.

The optimization of the pH regulator was carried out following the same jar-test methodology, using the most efficient magnesium compound according to results obtained, i.e. pre-acidified MgO. Three different dosages (500, 1000 and 1500 mg/L) were tested with the two pH regulators at three pHs (10.5, 11.0 and 11.5).

Mixing was carried out in a multiposition magnetic stirrer OVAN MulitMix Heat D. The pH was measured using a model GLP 22 (Crison, S.A), according to Standard Method 4500 [23], and the conductivity was measured with a model GLP 31 (Crison, S.A.), according to the ISO 7888. Reactive silica was measured by flow analysis and photometric detection through silicomolybdate and reduction to molybdenum blue, using a FIA Compact (MLE

Table 1
Characteristics of the paper mill effluent.

Raw water	
pH	8.3
Conductivity (mS/cm)	2.20
Cationic demand (meq/L)	0.74
Total solids (mg/L)	1990
Total suspended solids (mg/L)	83
COD (mg/L)	430
BOD_5 (mg/L)	150
Turbidity (NTU)	141
Total alkalinity (mg/L $CaCO_3$)	735
Dissolved fraction	
Total solids	1890
Turbidity (NTU)	6.5
Silica (mg/L SiO_2)	190
COD (mg/L)	355
Sulphates (mg/L)	237
Chlorides (mg/L)	126
Calcium (mg/L)	26.5
Magnesium (mg/L)	2.7

GmbH) according to DIN EN ISO 16264 and expressed as mg/L of SiO_2. Chemical oxygen demand (COD) was measured according to the Standard Method 5220-D [23]. Alkalinity was measured by titration with sulphuric acid 0.1 N using a pH electrode connected to an automatic titrator Compact I (Crison Instruments S.A.) to reach pH 4.5, according to EPA 310.1 (1983) method. Sulphate content was measured using Nanocolor® sulphates method (Macherey–Nagel GmbH). Calcium and magnesium content were measured using a direct air-acetylene flame atomic absorption method according to ISO-7980:1986 in a SpectrAA 220 spectrophotometer supplied by Varian. Turbidity was measured with a LP 2000-11 nephelometer, supplied by Hanna Instruments, according to ISO 7027. Finally, an image analysis of the precipitate particles was carried out in a Jeol JSM-6400 Scanning Electron Microscope (SEM). This SEM is configured with an energy dispersive X-ray analyzer (EDS system) which enables the SEM to perform elemental analysis of the solid.

3. Results and discussion

3.1. Silica removal with sparingly soluble magnesium compounds

Fig. 1 shows silica removal rates obtained with different dosages of MgO, $Mg(OH)_2$ and $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$ at three initial pHs (10.5, 11.0 and 11.5). MgO was the most effective product, achieving silica removal rates of 40% at pH 10.5 and dosages over 1000 mg/L. With this product, silica removal decreased when increasing the initial pH. Maximum removal rates, obtained at pH 11.0 and 11.5 with 1500 mg/L of MgO, were 32% and 12%, respectively. On the other hand, silica removal rates achieved with $Mg(OH)_2$ and $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$ were lower than 20% and 10%, respectively, for all the dosages at the three pHs tested. With these two products, silica removal only slightly increased along with the pH and dosage. $Mg(OH)_2$ showed similar removal rates at pH 10.5 and 11.0 and slightly higher removals at pH = 11.5. The variations in silica removal rates with $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$ were very small and within the experimental error for all the pHs and dosages tested.

The low removal rates obtained with the three products could be attributed to the low solubility of these magnesium compounds and, consequently, the low concentration of dissolved magnesium that is available to react and precipitate either as fresh $Mg(OH)_2$ or magnesium silicates of different stoichiometries [22]. The higher efficiency in silica removal by MgO can be explained through its higher solubility (0.086 g/L) and its higher magnesium content of 60.3 wt.%. This is translated into around 52 mg/l of dissolved magnesium at equilibrium. Using MgO, silica removal increased with the dosage and decreased with pH because MgO solubility decreases at higher pH. The final Mg contents in the water was around 12 mg/L at pH = 10.5, 4 mg/L at pH = 11.0 and 2.5 mg/L at pH = 11.5. Although silica removal increases with pH, the solubility of the sparingly soluble compounds decreases. In this sense, magnesium concentration in the treated water remained constant, which could indicate that magnesium is being consumed to co-precipitate with silica and the dissolution equilibrium moves towards the dissolution of more magnesium oxide. With $Mg(OH)_2$ and $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$, the final dissolved magnesium in the water did not vary with the dosage and pH, remaining constant at 12.5 mg/L and 2.5 mg/L, respectively. Although working at lower initial pHs would increase the amount of dissolved magnesium, silica solubility decreases at lower pHs and thus silica removal.

COD is another important parameter to take into account as it contributes to the organic fouling of the membrane. As shown in Fig. 2, the maximum COD removals were around 15% with all the products. These removal rates were similar to the ones obtained with soluble magnesium salts ($MgCl_2{\cdot}6H_2O$ and $MgSO_4{\cdot}7H_2O$) at similar conditions as reported in a previous study [22]. Although significant, this decrease in COD values may not have a significant impact on the organic fouling in subsequent membrane treatments.

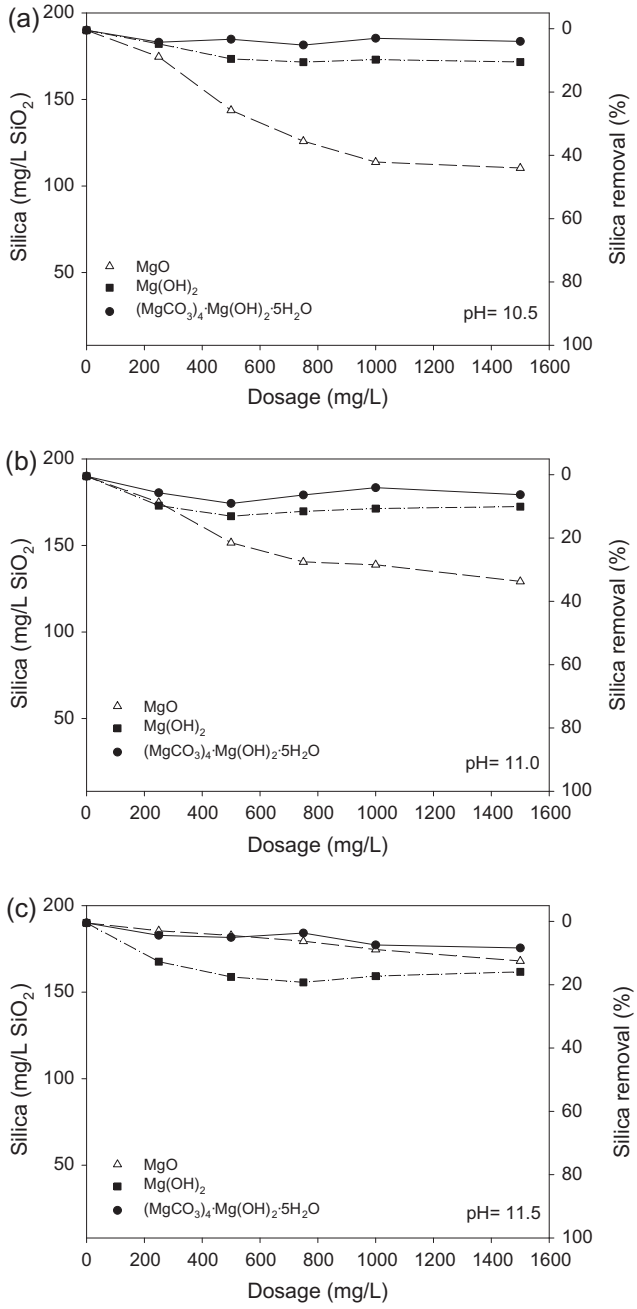

Fig. 1. Silica removal vs. dosage at different initial pH with MgO, $Mg(OH)_2$ and $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$.

Soluble magnesium salts can achieve high silica removal rates working at high pHs, however, the high final conductivity of the treated waters is a limitation. In the particular case of the paper mill studied, the conductivity of the final effluent cannot exceed 7.5 mS/cm for its direct discharge to the sewage system without any post-treatment. The increase of conductivity in the treated water is mainly caused by the initial pH adjustment and, to a lower extent, by the magnesium compound dosage. In this sense, the use of sparingly soluble magnesium compounds has the advantage of not increasing the conductivity due to their low solubility. The conductivity increase caused by the pH regulation was 0.8, 1.0 and

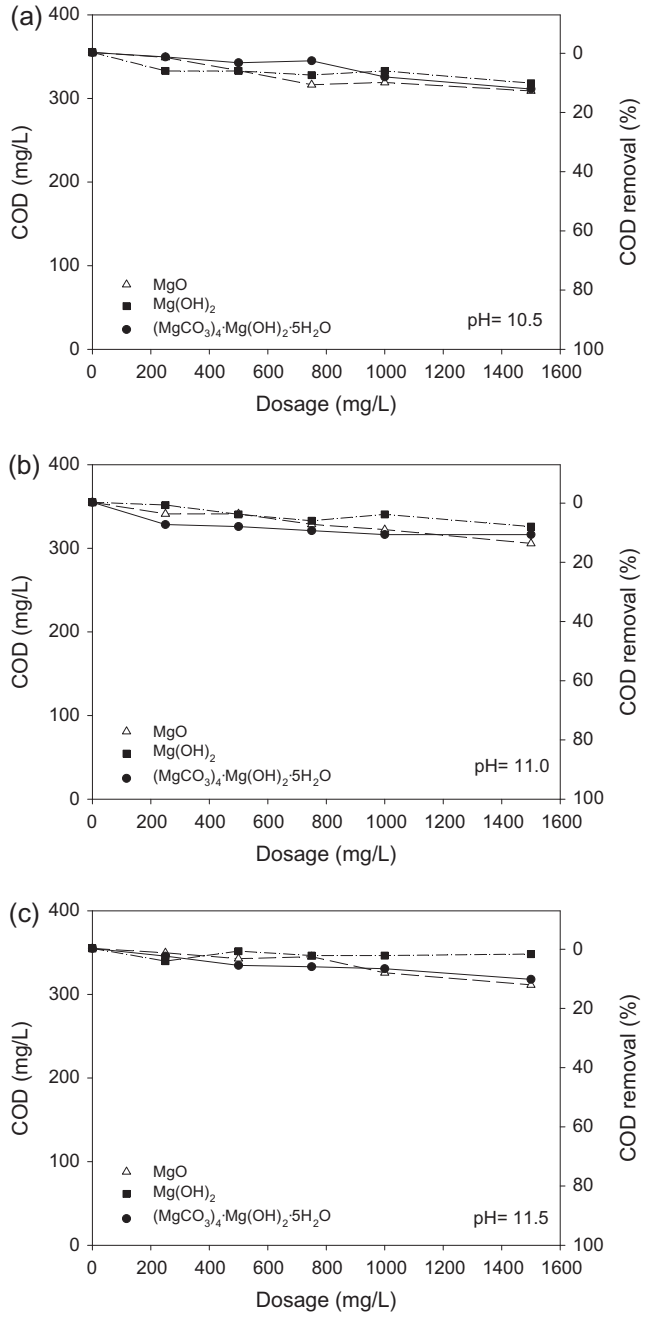

Fig. 2. COD removal vs. dosage at different initial pH with MgO, $Mg(OH)_2$ and $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$.

1.5 mS/cm at the initial pH values of 10.5, 11.0 and 11.5, respectively. On the other hand, the increase in conductivity induced by the three magnesium compounds tested was around 0.1–0.2 mS/cm at the three pH levels, regardless the dosage used. Thus the final conductivities with the three magnesium compounds were around 2.9, 3.3 and 3.6 mS/cm at pH = 10.5, 11.0 and 11.5, respectively.

Monitoring the final alkalinity and pH of the water allows studying the silica removal process, as the precipitation of $Mg(OH)_2$ and/or silicates consumes alkalinity and so the final pH of the water is lower. With the sparingly soluble magnesium compounds, the final pH and alkalinity remained almost constant. The pH variation with the 3 products at the 3 pHs and with the maximum dosage was always smaller than ±0.1 pH units with the exception of $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$ at pH = 11.5 (±0.3 pH units). This was due to the fact that the low silica removal rates achieved and the hydroxide groups consumed were re-established through the dissolution of the magnesium compounds to maintain the equilibrium.

Regarding turbidity, it increased with the magnesium compound dosage, due to the higher concentration of the sparingly soluble magnesium compound in the treated water, and there were small variations with pH and the magnesium compound used. The turbidity of the clarified waters ranged from 60 to 300 NTU, depending on the treatment, and dissolved turbidity varied from 6 to 9 NTU.

The low solubility of magnesium compounds used resulted in a low concentration of dissolved magnesium and, consequently, in small silica removal rates. Different strategies could be used to increase silica removal, e.g. to increase the working temperature to kinetically favour the dissolution of the magnesium compounds, to increase the contact time or to increase the dissolved magnesium by pre-acidifying the magnesium compound slurries before use. A controlled pre-acidification of the slurries was selected as it is a cheap option to increase dissolved magnesium and could increase the final water conductivity in a lesser extent than soluble magnesium compounds when treating waters at ambient temperature.

3.2. Silica removal with pre-acidified magnesium compounds

3.2.1. Characteristics of pre-acidified slurries

Three levels of acidification were tested for the 10 w/v% slurries of each sparingly soluble salt: 9.8, 19.6 and 57.6 g of H_2SO_4/L of slurry. Table 2 summarizes the main characteristics of the slurries with and without pre-acidification. Dissolved magnesium was measured after 30, 60 and 90 min in each slurry at the three acidification levels and only variations in dissolved magnesium below 1% were observed for all the products, indicating the stability of these products. The highest pre-acidification level (57.6 g of H_2SO_4/L of slurry), was selected to carry out further studies as it was the one allowing enough dissolved magnesium for a possible complete silica removal for the three sparingly soluble salts. Although higher levels of pre-acidification could be even more efficient, they would increase the conductivity and sulphates concentration in the slurries, and this is exactly what we tried to avoid using sparingly soluble compounds compared to soluble salts such as $MgCl_2{\cdot}6H_2O$ and $MgSO_4{\cdot}7H_2O$.

3.2.2. Silica removal with pre-acidified slurries

Silica removal was significantly increased using the slurries pre-acidified with 57.6 g of H_2SO_4/L of slurry. As shown in Fig. 3, maximum removal rates were obtained at the highest pH (11.5) and dosage (1500 mg/L), being 86% silica removal for both MgO and $Mg(OH)_2$ and around 80% silica removal for $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$.

Silica removal increased with pH and dosage, as there are more hydroxide groups, dissolved silica and dissolved magnesium available to precipitate as magnesium silicates or $Mg(OH)_2$ where silica is adsorbed/entrapped. At the lowest magnesium compound dosage, the increase in silica removal with the increasing initial pH was lower than at the higher dosages. For example, with 250 mg/L of MgO, silica removal was 11%, 13% and 17% at pH = 10.5, 11.0 and 11.5, respectively. On the other hand, with 1500 mg/L of MgO, silica removal increased from 47% at pH = 10.5 to 76% at pH = 11.0 and 86% at pH = 11.5 with the same product. This indicates that at low dosages, the level of dissolved magnesium is the limiting factor, while in conditions of abundance of the magnesium compound pH (i.e. the availability of hydroxide groups) is the limiting factor. At pH = 10.5, $Mg(OH)_2$ and $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$

Table 2
Characteristics of the slurries with and without pre-acidification.

Magnesium compound	pH	Conductivity (mS/cm)	Dissolved magnesium (g/L)	SO_4^{2-} (g/L)
MgO	11.5	0.2	4.9	0.0
p.a. MgO	9.8	20.4	18.9	54.2
$Mg(OH)_2$	10.3	0.5	5.6	0.0
p.a. $Mg(OH)_2$	9.5	31.3	19.4	54.0
$(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$	9.9	0.4	0.87	0.0
p.a.$(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$	8.3	25.6	15.2	54.3

*p.a. means pre-acidified slurry.

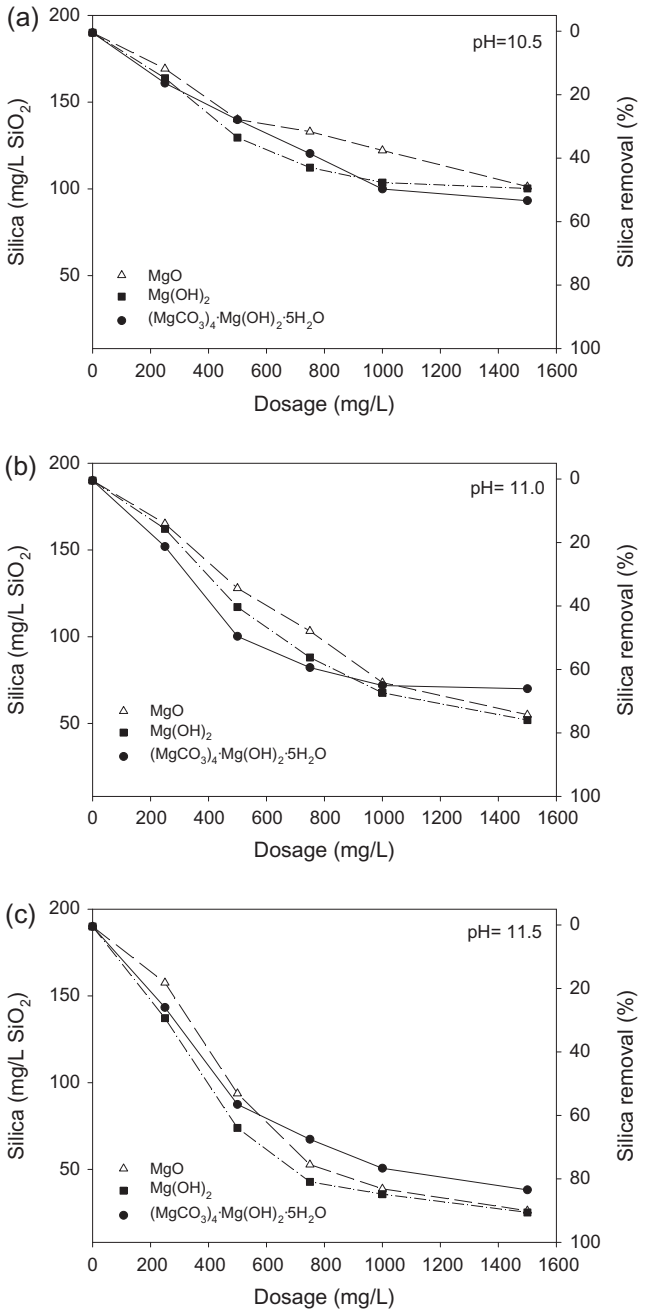

Fig. 3. Silica removal vs. dosage at different initial pH using pre-acidified MgO, $Mg(OH)_2$ and $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$.

were more efficient than MgO, which was opposite to their behavior at pH = 10.5 without pre-acidification (Fig. 1a) where MgO was the most efficient product. Silica removal rates obtained with 1500 mg/L of pre-acidified $Mg(OH)_2$ were 47%, 73% and 86% at pH = 10.5, 11.0 and 11.5, respectively. Finally, with 1500 mg/L of pre-acidified $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$, silica removal rates were 51% at pH = 10.5, 63% at pH = 11.0 and 70% at pH = 11.5. Comparing these silica removal values with the ones obtained without pre-acidification, 70% improvement was obtained at the optimum conditions (pH = 11.5 and 1500 mg/L dosage), indicating that pre-acidification of sparingly soluble salts allows obtaining high silica removal efficiencies even at ambient temperature.

The maximum silica removal rates obtained after pre-acidification were similar to the ones obtained in previous studies [22] using soluble magnesium compounds with a similar effluent having approximately the same silica contents. In this case, silica removal rates of 90% and 77% were obtained with $MgCl_2{\cdot}6H_2O$ and $MgSO_4{\cdot}7H_2O$ with a similar magnesium compound requirement (Table 3). Although pre-acidified salts required also 4.7 mg/L H_2SO_4 per mg/L of silica removed, this addition would not increase significantly the cost of the treatment as H_2SO_4 as it is a cheap product (46 €/t) [24]. Additionally, MgO, $MgCl_2{\cdot}6H_2O$ and $MgSO_4{\cdot}7H_2O$ have similar prices (250–350 €/t) [24], which makes the use of pre-acidified MgO competitive it terms of costs compared to soluble magnesium salts. Moreover, the price of $Mg(OH)_2$ (750 €/t) is approximately twice as expensive than the other magnesium compounds while its use would not further improve silica removal.

The results obtained with pre-acidified magnesium compounds were also competitive with others reported in the literature (Table 3). Negaresh et al. [2], for example, achieved 90% silica removal with higher magnesium compound requirements while Zeng et al. [20] obtained 67% silica removal using a similar amount of magnesium compound but also adding a zinc coagulant.

The analysis of the solids formed by SEM–EDX (Fig. 4), also confirmed by other studies in the literature [22,25], indicates that Si/Mg ratio in these solids varied between 0.5 and 1 (Table 4), which is in agreement with the formation of a mixture of forsterite (Mg_2SiO_4) and enstatite ($MgSiO_3$). Without pre-acidification, the magnesium contents in the water was the limiting factor for silica removal; however, according to the precipitates formed and the level of dissolved magnesium in the acidified slurries, the magnesium concentration dissolved after pre-acidification was not the limiting factor for any of the products to achieve high silica removal. Therefore, similar silica removals were obtained for all the magnesium compounds used.

Fig. 5 shows the final magnesium concentration in the treated water with and without pre-acidification of the magnesium compounds. With the non-pre-acidified slurries magnesium concentration depends on the solubility of the sparingly soluble salts at each operational pH and on the magnesium content in the molecule. Thus MgO and $Mg(OH)_2$, according to their magnesium contents (60.3% and 41.7% respectively), showed higher final magnesium concentrations than $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$ (25.0% Mg content). On the other hand, final Mg concentration with MgO decreased with the operational pH and, in the case of $Mg(OH)_2$ and $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$, magnesium solubility remained constant.

Pre-acidified MgO was the product resulting in the highest magnesium concentration in the treated water, it varied between

Table 3
Magnesium requirements for silica removal.

References	Initial SiO_2 (mg/L)	Silica removal (%)	pH or NaOH (mg/L)/(mg/L SiO_2 removed)	Treatment (mg/L)/(mg/L SiO_2 removed)
Present study	190	86	pH = 11.5	MgO: 9.1 H_2SO_4: 4.7
		86	pH = 11.5	$Mg(OH)_2$: 9.1 H_2SO_4: 4.7
		80	pH = 11.5	$(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$): 9.8 H_2SO_4: 4.7
Latour et al.[22]	180	90	pH = 11.5	$MgCl_2{\cdot}6H_2O$: 9.2
		77	pH = 11.5	$MgSO_4{\cdot}7H_2O$: 10.6
Negaresh et al.[2]	120	90	pH = 10.9	$MgSO_4{\cdot}7H_2O$: 23.3
Zeng et al. [20]	140	67	NaOH: 6.7	$MgCl_2{\cdot}6H_2O$: 8.9 $ZnSO_4{\cdot}7H_2O$: 1.7

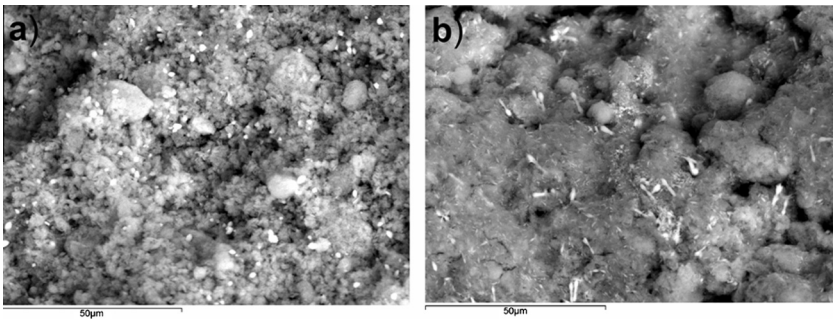

Fig. 4. SEM–EDX images of the typical solids obtained after the treatment.

Table 4
Composition of the of the solids obtained after precipitation.

Solid	O (wt.%)	Mg (wt.%)	Si (wt.%)	P (wt.%)	Ca (wt.%)	Si/Mg (molar)
a)	46.6	28.3	24.2	1.0	7.9	1.03
b)	48.7	30.5	16.5	1.0	3.4	0.47

54 and 70 mg/L at the maximum dosage. In the case of $Mg(OH)_2$ and $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$, at the maximum dosage and at the three pHs tested, magnesium in the treated water was lower around 15 mg/l.

The final magnesium concentration in the water is higher with pre-acidified MgO than with the other two magnesium compounds due to the higher equilibrium concentration of magnesium at the operational pH. Although the levels of dissolved magnesium in the slurries were similar for MgO and $Mg(OH)_2$ (Table 2), both slightly higher than for $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$, after precipitation of magnesium silicates, the levels of dissolved magnesium were mainly governed by the solubility equilibrium of these compounds, as the operational pH was much higher than the pH of the pre-acidified slurries. According to the solubility of magnesium in water at 20 °C, its concentration in water would be around 52 mg/L for MgO, 5 mg/L for $Mg(OH)_2$ and 9.4 mg/L for $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$. These values are very close to the ones observed in the treated water with small differences between the theoretical conditions (pure water and 20 °C) and the real ones. The fact that the final magnesium concentration with $Mg(OH)_2$ was higher than with $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$ was due to the operational pH, which was more similar to the pH of the slurry in the case of $Mg(OH)_2$ than in the case of $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$.

Considering that silica solubility is around 120–140 mg/L, maximum silica removal of 86% obtained with both MgO and $Mg(OH)_2$ would allow working at 75–80% recoveries in the RO membranes without silica scaling problems. In the case of using $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$, it would be possible to work in the range of 70–75% recoveries as a lower maximum silica removal rate was obtained (80%). However, it would also be possible to work at intermediate recoveries (60–65%) under softer conditions away from the optimum (pH = 11.5 and 1500 mg/L dosage). For example, selecting pH = 11.0 to work with 1500 mg/L of MgO or $Mg(OH)_2$ would reduce significantly the treatment cost and the conductivity of the waters treated. Another possibility would be working at pH = 11.5, but at lower dosages like 750–1000 mg/L of MgO or $Mg(OH)_2$, or even with 1000 mg/L of $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$, which also reduces the costs, but not much the conductivity of the water treated.

On the other hand, working at 60–80% recovery rates involves an increase in the conductivity of the RO rejects of around 2.5–5 times with respect to that of the feed water. Taking into account the discharge limit for conductivity in the effluent (7.5 mS/cm), the conductivity of the treated water should be in the range of 1.5–3.0 mS/cm to avoid the need of a reject post-treatment. Although the conductivity of the treated water was mostly increased due to pH adjustment, as shown in Fig. 6, the increase in conductivity with respect to blank values was higher when pre-acidified compounds were used due to the increase of dissolved magnesium and sulphates. In contrast, the increase in conductivity was lower at higher pH due to the precipitation of dissolved species such as $Mg(OH)_2$ and magnesium silicates. At pH = 11.5 the increase in conductivity compared to the non pre-acidified magnesium compounds was lower than at pH = 10.5. (0.1–0.2 mS/cm at pH = 11.5 versus 0.6 mS/cm at pH = 10.5). With 1500 mg/L of MgO, the final conductivity was 3.6 mS/cm at pH 10.5 and 11.0 and 3.9 mS/cm at pH 11.5. In the case of $Mg(OH)_2$, the final conductivity was 3.5, 3.6 and 3.8 mS/cm for pH = 10.5, 11.0 and 11.5, respectively. Finally, with $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$, the highest conductivities obtained were: 3.7 mS/cm at pH = 10.5, 3.8 mS/cm at pH 11.0 and 3.9 mS/cm at pH 11.5. The use of pre-acidified magnesium compounds compared to soluble ones has the important advantage of increasing less the conductivity of the waters, i.e. 0.5 mS/cm in the conditions of maximum silica removal (pH = 11.5 and 1500 mg/L dosage) [22]. This would imply

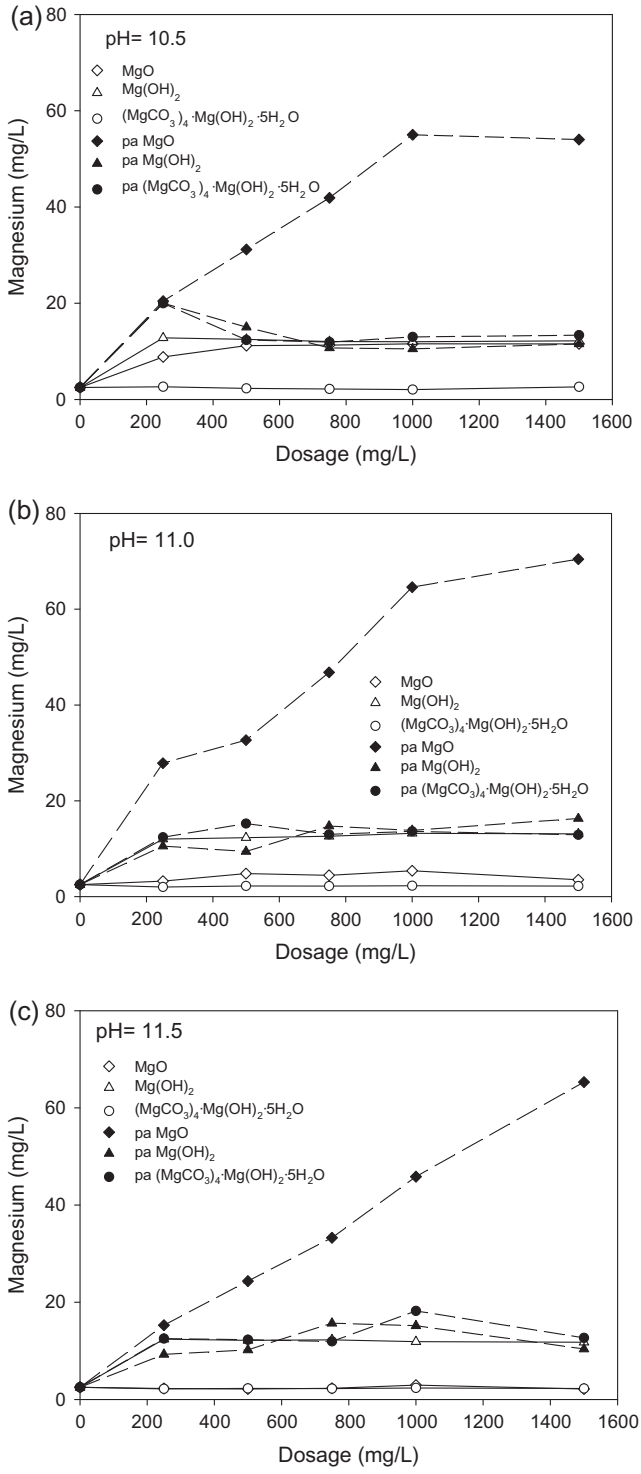

Fig. 5. Final magnesium vs. dosage at different initial pH using MgO, $Mg(OH)_2$ and $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$ with and without pre-acidification.

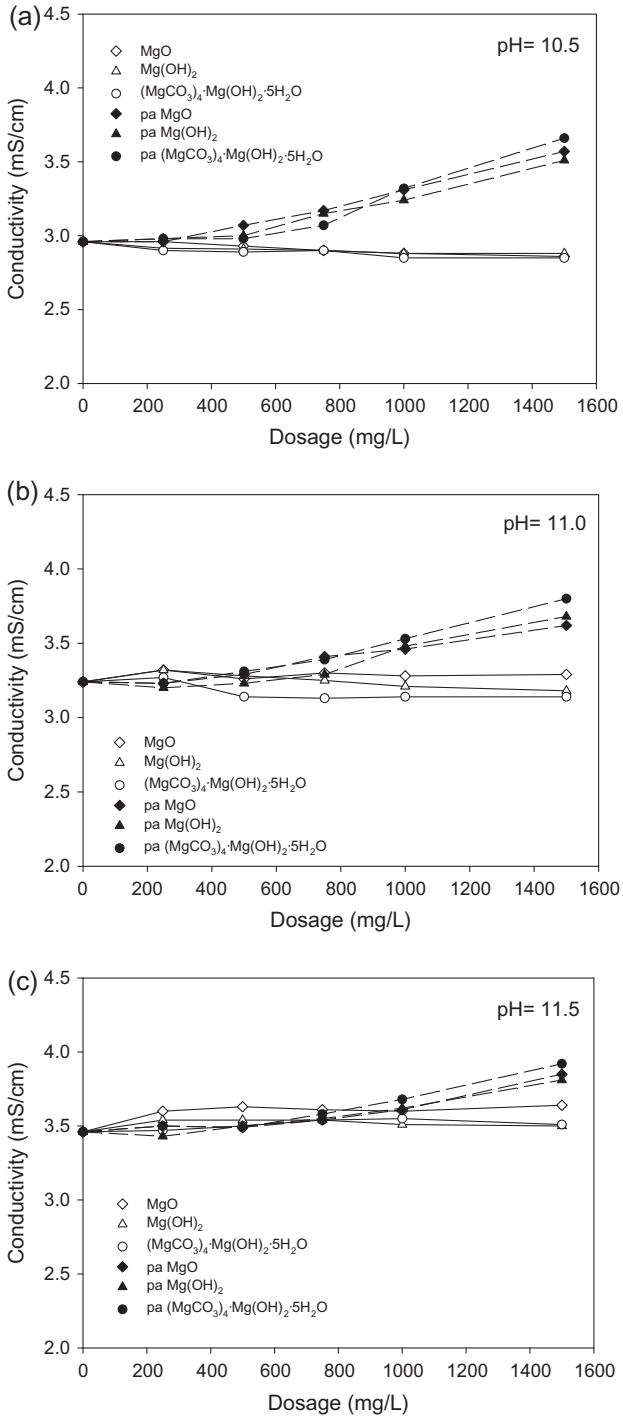

Fig. 6. Final conductivity vs. dosage at different initial pH using MgO, $Mg(OH)_2$ and $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$ with and without pre-acidification.

1.25–2.5 mS/cm lower conductivity in the RO rejects, which is a great achievement related to the RO rejects management and treatment.

Alkalinity is another important parameter to understand the silica removal mechanism during the softening process as it allows monitoring the precipitation of $Mg(OH)_2$, $CaCO_3$ and different calcium or magnesium silicates. In this case, silica removal by precipitation of calcium carbonate or calcium silicate is considered negligible compared to the removal by magnesium due to its higher efficiency on silica removal [21] and the high concentration of dissolved magnesium present in the water. pH and alkalinity varied in parallel with silica removal: the higher the silica removal, the higher the decrease in pH and alkalinity. The final pH and alkalinity were determined by two facts: the pH adjustment before the addition of the magnesium compound and the pH decrease caused by the precipitation of $Mg(OH)_2$ or the precipitation of magnesium silicates. Regardless the compound, pH decrease was greater with pre-acidification than without. When focusing on pre-acidified compounds, at pH = 10.5 and 11.5, $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$ was the product with the highest pH decrease and at pH = 11.0, the

decreases obtained with $Mg(OH)_2$ and $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$ were very close. pH should also be in the range 7.5 ± 1.0, to avoid a pH "shock" when reusing the treated water within the process which could produce organic and inorganic deposits, especially microstickies and secondary stickies [26]. Additionally, according to the discharge limit of the paper mill studied, the RO rejects should have a pH between 6.5 and 9.5. With all the treatments, the final pH was over these limits and that would require a final pH-adjustment. Alkalinity of the treated waters increased with the initial pH of the water and decreased with the magnesium compound dosage. Alkalinity consumption was lower than 100 mg/L $CaCO_3$ with the three pH values and maximum dosage of magnesium compounds, presenting little variation as in the case of pH.

Sulphates contents was in all cases the sum of sulphates present in the original water and the sulphates added with each dose due to pre-acidification with H_2SO_4. Sulphates added to water with each dosage were 130, 250, 380, 500 and 750 mg/L at the 5 dosages tested (250–1500 mg/L), respectively.

Regarding COD, its removal increased with the dosage when using the pre-acidified compounds, but the variation in COD removal with the same dosage at different pH conditions was lower than 2%. The maximum COD removal efficiencies achieved with 1500 mg/L of the pre-acidified magnesium compounds were: 19% with MgO, 19% with $Mg(OH)_2$ and 16% with $(MgCO_3)_4{\cdot}Mg(OH)_2$.

Turbidity showed small variations with pH and dosage. It decreased slightly with the initial pH of the water and increased with the magnesium compound dosage. The final turbidity in the clarified water varied between 90 and 200 NTU while dissolved turbidity in the treated water was in the range of 6–10 NTU.

3.3. Optimization of the pH regulator

As high pH is required for silica removal, the selection of the pH regulator is a key factor, both in terms of costs and treated water characteristics, such as conductivity and COD. The convenience of using lime milk as pH regulator instead of caustic soda was studied using pre-acidified MgO as magnesium source. The main advantages of lime compared to caustic soda is that it is cheaper but also, as it is a sparingly soluble compound, it produces a milder conductivity increase which, for this particular application, is very important. Another advantage is that it improves the COD removal [22]. By contrast, the use of lime milk also brings along some disadvantages such as the higher generation of sludge or the increase in the turbidity of the treated water.

First, the effect of the pH regulator on the silica removal was tested. As shown in Fig. 7, silica removal was increased when using lime milk. Silica removal was around 11% higher with lime milk at the lower pH values (10.5 and 11.0) and 5% at pH = 11.5. With NaOH, the maximum removal rates obtained at each pH were 55% at pH 10.5, 68% at pH 11.0 and 74% at pH 11.5, using 1500 mg/L of pre-acidified MgO. On the other hand, maximum silica removal rates obtained with lime milk were 66%, 78% and 82% at pH = 10.5, 11.0 and 11.5, respectively, using the highest dosage of pre-acidified MgO. This higher removal rates were probably due to the precipitation of $CaCO_3$ that, despite proven to be less effective than magnesium compounds, still contributes to silica removal in some extent, which could even be the most important effect for waters with high calcium and low magnesium hardness [15]. Another possibility is that silica was also removed through the formation of calcium or calcium–magnesium silicates.

As expected, the final conductivity of the treated waters was always significantly higher with caustic soda than with lime milk at all pH levels and MgO dosages (Fig. 8). With caustic soda, conductivity varied between 3.6 and 3.7 mS/cm at pH 10.5, 3.8–4.1 mS/cm at pH 11.0 and 4.2–4.3 mS/cm at pH = 11.5. On the other hand, conductivity ranges with lime milk were: 2.2–2.3 mS/cm at pH 10.5, 2.3–2.4 mS/cm at pH 11.0 and 2.4–2.6 mS/cm at pH 11.5.

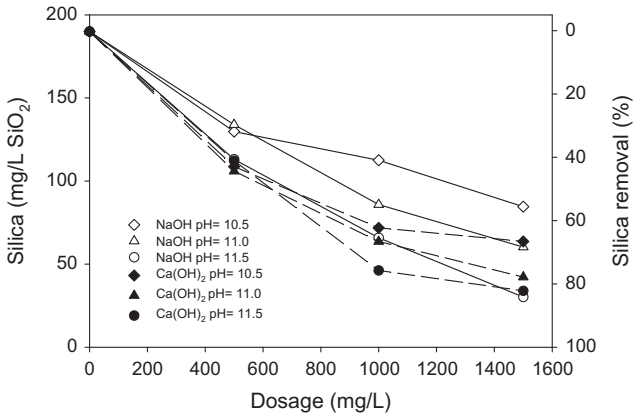

Fig. 7. Silica removal vs. pre-acidified MgO dosage at different initial pH with $Ca(OH)_2$ or NaOH as pH regulators.

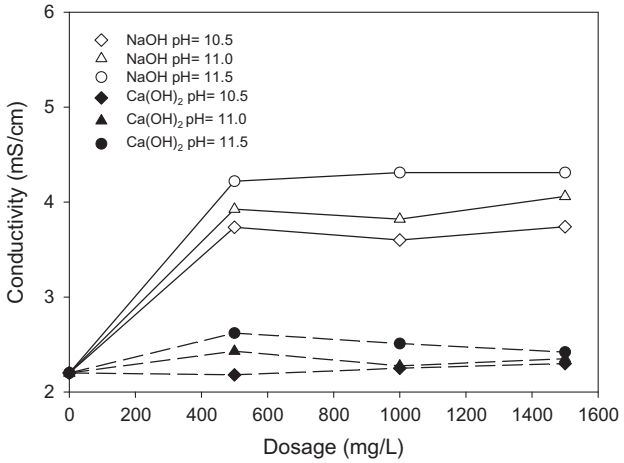

Fig. 8. Conductivity of treated waters vs. pre-acidified MgO dosage at different initial pH with $Ca(OH)_2$ or NaOH as pH regulators.

Turbidity in the clarified water did not vary significantly with the pH or MgO dosage. With NaOH, the turbidity of the clarified water was around 100 NTU, whereas the final turbidity of the water using lime was around 200 NTU, compared to 141 NTU in the raw water. Turbidity of treated waters when using lime milk as pH regulator could reduced following different approaches such as using dissolved air flotation, increasing the settling time or with small dosages of flocculant in the settling tank. Moreover, prior to the RO the water is usually pre-treated in a membrane system such as UF. Although this last step would minimize the potential problems that may appear on the RO, this operation must be carefully optimized to select the correct flux and backwash interval.

Regarding COD, higher removal rates were obtained with lime milk than with caustic soda at all pH levels and $MgCl_2{\cdot}6H_2O$ dosages. For both pH regulators, COD removal increased by increasing the dosage of the Mg compound (Fig. 9). In the case of lime milk, with the maximum dosage of $MgCl_2{\cdot}6H_2O$, 25% of COD was removed at all pHs. On the other hand, with caustic soda, the maximum COD removal was 10% at pH = 10.5 and 15% at both pH 11.0 and 11.5.

As it was demonstrated, despite the higher sludge generation and more accentuated turbidity increase, lime milk is preferred as pH regulator because it allowed: a greater silica removal (82%

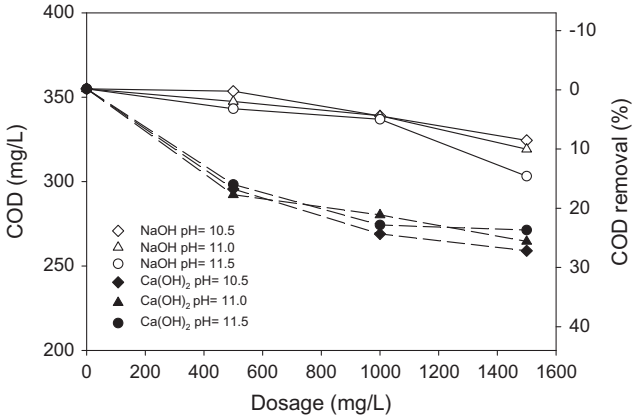

Fig. 9. COD removal vs. pre-acidified MgO dosage at different initial pH with $Ca(OH)_2$ or NaOH as pH regulators.

vs. 74%), greater COD removal (25% vs. 10%), and a considerably lower conductivity of the treated waters (2.4 vs. 4.6 mS/cm). Moreover, lime milk is cheaper than caustic soda.

4. Conclusions

Silica removal during softening is a cheap treatment to treat large volumes of water with high silica contents; however, the high operational pH required and the counter-ions of calcium and magnesium salts added are directly translated into a high conductivity of the treated water which causes operational problems in the RO and the need of a further the post-treatment of RO rejects before water discharge.

The use of sparingly soluble compounds has the advantage of adding less conductivity to water while causing no further scaling problems as they do not add counter ions to total dissolved solids. Nevertheless, silica removal obtained with these species was very limited at ambient temperature and at 15 min contact time due to the slow dissolution kinetics of these compounds. At these conditions, a maximum of 40% silica removal was obtained with 1500 mg/L of MgO at pH 11.5. With $Mg(OH)_2$ and $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$, removal rates lower than 20% and 10% were achieved, respectively. These low removal rates would not allow working at the high RO recoveries necessary (65–80%) without silica scaling problems, making the process not technically viable.

Pre-acidification of the magnesium compounds increased the dissolved magnesium content, and, thus, silica removal: a 86% silica removal was obtained with both MgO and $Mg(OH)_2$ and a 80% with $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$. However, previous acidification increases the conductivity of the treated waters compared to the direct use of the sparingly soluble compounds. This problem was solved by using $Ca(OH)_2$ as pH regulator instead of NaOH. In the most favourable conditions (pH 11.5 and 1500 mg/L of pre-acidified MgO), the final conductivity of the treated water was 4.3 mS/cm with caustic soda and 2.4 mS/cm with lime milk for an initial conductivity of the waters of 2.2 mS/cm. The use of lime milk as pH regulator has the additional advantage of increasing COD removal (25%) compared to 15% obtained with NaOH. As showed in the study, the use of pre-acidified MgO with $Ca(OH)_2$ as pH regulator allowed obtaining high silica removal rates with a low increase in conductivity and at low cost even at ambient temperature. These aspects make the softening an economically competitive technique compared to other silica removal techniques such as coagulation, as the latter requires high dosages of complex hybrid coagulants to obtain similar removal rates.

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Silica removal with sparingly soluble magnesium compounds. Part II

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ABSTRACT

Silica scaling is one of the main bottlenecks in the reuse of papermaking effluents by reverse osmosis. The low hardness of deinking paper mill effluents makes necessary the addition of magnesium compounds to increase silica removal at high pH. Based on the results obtained in Part I, MgO was selected as the most efficient magnesium source. Its efficiency was tested at different dosages (150–10,000 mg/L), pH values (8.2–9.5) and temperatures (25–50 °C) and the optimization of the reaction time was also carried out. Silica removals over 95% were obtained at the 4 pHs and 3 temperatures with MgO dosages over 500 mg/L; however, MgO can only be applied if water temperature is higher than 35 °C, as the dissolution of MgO is limited. Moreover, the analysis of the solids obtained (SEM–EDX and FTIR) showed that the main mechanism for silica removal was co-precipitation of magnesium silicates (forsterite and antigorite) while adsorption was less significant.

1. Introduction

One alternative to reduce fresh water consumption in the paper industry is the reuse of the final effluent after an extensive treatment, usually involving a final reverse osmosis (RO) stage [1,2]; however, this treatment is not feasible when treating effluents with high silica content, as those typically found in deinking paper mills, due to severe scaling in the membranes. If silica is not previously removed, it is not possible to work on the RO at recoveries higher than 20% [2], thus comprising the economic feasibility of the whole treatment chain. Moreover, there are also stringent limits for silica in the effluents (i.e. 50 mg/L for Finland and Canada) that makes silica removal of a growing interest not only for deinking paper mills but also for other industries even if effluent reuse treatments based on RO membranes are not used [3].

The main origin of the high silica levels in paper mill effluents (50–250 mg/L SiO_2) is the sodium silicate used as process additive [1,3,4]. Due to its great variety of functions, mainly focused on the deinking and bleaching steps, its substitution is very difficult without affecting the quality of the final product [5–7]. Therefore, it has to be removed from the process water. The limitations of silica removal by coagulation at high pH [3,8] and by softening using soluble magnesium compounds [9] motivated the study of sparingly soluble magnesium compounds [10].

In part I of this work, the use of different sparingly soluble magnesium compounds (MgO, $Mg(OH)_2$ $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$) was studied. At ambient temperature (~20 °C) and 15 min contact time, a maximum 40% silica removal was achieved with the most efficient (MgO). In order to increase dissolved magnesium concentration and thus silica removal, pre-acidification of the slurries of the sparingly soluble magnesium compounds was tested. Results demonstrated this pre-acidification is a competitive approach to increase silica removal. Under the optimal conditions (1500 mg/L dosage, pH = 11.5), 86% silica removal was obtained with both MgO and $Mg(OH)_2$. Although pre-acidified magnesium compounds increased less the conductivity of the treated water than soluble ones, final conductivity was still high. Therefore, there is a need of generating new knowledge on the direct use of sparingly soluble magnesium compounds to treat high silica loaded waters and the optimal conditions for their application.

In this sense, part II of the article studies the effect of the operational temperature and the contact time on silica removal using MgO, which was the most efficient compound in part I. With this aim, different jar-tests were carried out. Based on the results obtained, the optimal conditions (maximum silica removal and minimum conductivity increase) were selected. An additional novelty of this paper is the elucidation of the mechanism involved in silica removal which is unclear in the literature [11–13].

2. Materials and methods

2.1. Materials

This study was carried out with the effluent of a Spanish paper mill before its discharge to an urban wastewater treatment plant.

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This mill produces newsprint using 100% recovered paper. Table 1 summarizes the main characteristics of the effluent. Dissolved fraction was obtained by filtration through 0.45 μm pore size PTFE membrane filters. Samples were stored at 4 °C during the tests and no sets of trials longer than five days were carried out. MgO, used as magnesium source, and NaOH, used as pH regulator, both analytical grade, were supplied by PANREAC. MgO and NaOH were prepared 10 wt./vol.% on a daily basis.

2.2. Methodology

2.2.1. Optimization of pH, dosage and temperature

First, the treatment was optimized in terms of pH and dosage at ambient temperature (25 °C). MgO was tested at 10 dosages (from 50 to 10,000 mg/L) and at 4 different initial pHs: 8.2 (initial pH of effluent), 9.5, 10.5 and 11.5. These pHs and dosages were selected according to previous studies carried out by the authors with a similar effluent [9,10]. Next, the effect of the temperature on silica removal was studied. In this case, 4 dosages of MgO (150, 250, 500 and 1000 mg/L) were tested at 3 temperatures (25, 35 and 50 °C) without pH regulation.

For these tests a jar-test methodology was used. First, when necessary, the pH of the samples was adjusted by adding NaOH to 200 mL of sample. After 1 min of mixing at 200 rpm, MgO was added and mixed during 24 h at 200 rpm and then the waters were allowed to settle for 1 h. Finally, the clarified waters and its dissolved fraction were characterized. Jar-tests were carried out in a multiposition magnetic stirrer OVAN MulitMix Heat D. All trials were carried out by duplicate and the average error between replicates was always around 5%.

2.2.2. Optimization of the contact time

The optimization of the contact time was carried out at the optimal dosage of MgO (500 mg/L) and at the 4 initial pHs (8.2, 9.5, 10.5 and 11.5) and the 3 temperatures (25, 35 and 50 °C) used previously. In this case, the pH regulator was firstly added to 600 mL of sample and after 1 min mixing, MgO was added. Samples were taken at different time periods and immediately filtered through 0.45 μm PTFE filter to remove the solids present in the water and stop the reaction. These samples were characterized in terms of silica and magnesium concentration. After a number of consecutive samples, with silica concentration approximately constant the experiment ended.

2.3. Analytical methods

The pH was measured using a model GLP 22 (Crison, S.A), according to Standard Method 4500, and the conductivity was measured with a model GLP 31 (Crison, S.A.), according to Standard Method 2510 [14]. Alkalinity was measured by titration with sulfuric acid 0.1 N using a pH electrode connected to an automatic titrator, model Compact I (Crison Instruments S.A.) to reach pH 4.5, according to EPA 310.1 method. Total solids and total suspended solids were measured according to the Standard Method 2450 B and 2450 D respectively [14]. Turbidity was measured according to ISO 7027:2001 with a LP 2000-11 nephelometer supplied by Hanna Instruments. Reactive silica was measured by flow analysis and photometric detection through silicomolybdate and reduction to molybdenum blue, using a FIA Compact (MLE GmbH) according to DIN EN ISO 16264 and expressed as mg/L of SiO_2. COD was photometrically measured by the Nanocolor® COD 1500 Method from Macherey–Nagel GmbH, according to ISO 15705:2003 in an Aquamate UV–Vis spectrophotometer supplied Thermo Scientific Inc. Calcium and magnesium content were measured using a direct air-acetylene flame atomic absorption method according to ISO-7980:1986 in a SpectraA 220 spectrophotometer supplied by Varian.

Precipitated solids were anaylized by FTIR spectrophotometry and SEM–EDX. The FTIR analyses were carried out in a Nicolet Magna 750 spectrophotometer with a Spectratech IR-Plan Advantage Microscope. Spectra were recorded at 2 cm^{-1} resolution and 16 scans were taken for both the samples and the background. Samples were prepared with the same amount of sample and KBr, i.e. 0.6 mg of sample and around 250 mg of KBr. Finally, the image analyses of the precipitate particles were carried out in a JEOL JSM-6400 Scanning Electron Microscope (SEM). This SEM is configured with an energy dispersive X-ray analyzer (EDS system) which enables to perform compositional analysis.

Table 1
Characteristics of the paper mill effluent.

Raw water	
pH	8.2
Conductivity (mS/cm)	2.55
COD (mg/L)	380
Total alkalinity (mg/L $CaCO_3$)	721
Total suspended solids (mg/L)	75
Total solids (mg/L)	2050
Turbidity (NTU)	125
Dissolved fraction	
Silica (mg/L SiO_2)	260
COD (mg/L)	360
Sulfates (mg/L)	250
Calcium (mg/L)	33.9
Magnesium (mg/L)	6.8
Total solids (mg/L)	1975

3. Results and discussion

3.1. Optimization of the operational conditions

3.1.1. Optimization of pH, dosage and temperature

Fig. 1 shows silica removal rates obtained at 25 °C with different dosages of MgO, at four initial pHs. As observed, silica removals over 95% were obtained at dosages higher than 500 mg/L, independently of the initial pH.

With 50 mg/L of MgO, silica removal was around 20–25% at the 4 pHs. These low removal rates could be attributed to the low dosages of MgO used. Considering silica precipitates as enstatite ($MgSiO_3$), with molar ratio Si/Mg = 1, the theoretical maximum silica removal rate that could be achieved using 50 mg/L MgO would be 28% which is very close to the obtained results. This maximum

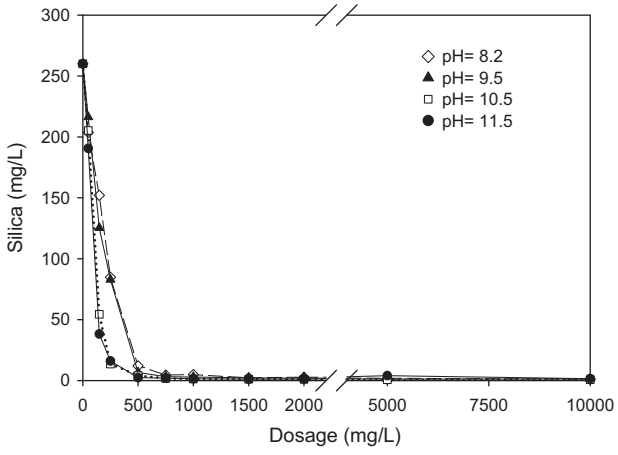

Fig. 1. Silica removal vs. MgO dosage at 25 °C and different initial pHs.

silica removal that would be even lower if Mg_2SiO_3 (forsterite) or $Mg_2Si_2O_5(OH)_4$ (antigorite), which was also detected in previous studies, were the main magnesium silicates formed as they have lower molar Si/Mg ratio [9,10].

As observed in Fig. 1, there were two different tendencies on silica removal at low dosages. With 150 mg/L of MgO, silica removal rates were 42%, 52%, 80% and 85% at pH 8.2, 9.5, 10.5 and 11.5 respectively. With 250 mg/L silica removal was 68% at the lowest pHs (8.2, 9.5) and 94% at the highest pHs (10.5, 11.5). Furthermore, at dosages higher than 500 mg/L silica removal was higher than 90% and there were not significant differences among the initial pHs tested.

It is well known that pH is a critical parameter to consider when silica is removed during softening as there are different dissolution-precipitation equilibriums involved. Silica, which derives from the orthosilicic acid, has to be ionized to be removed by co-precipitation with magnesium. Orthosilicic acid is a weak polyprotic acid with pK_a values of 9.9, 11.8 and 12 [15,16]. At pH higher than 10 most of the silica is ionized as $H_3SiO_4^-$ and allows high removal rates.

The operational pH during silica removal with MgO is determined by two main aspects. First, the pH regulation performed with NaOH before the addition of the MgO. Second, the dissolution equilibriums of MgO, which is controlled by the dissolution and precipitation of $Mg(OH)_2$ (Eq. (1) and (2)). At lower pHs, the MgO dissolution is enhanced while impaired where dissolved magnesium is rather limited. Furthermore, dissolved magnesium can precipitate as magnesium silicates of different stoichiometries or react with the hydroxyl groups and precipitate as $Mg(OH)_2$.

$$MgO(s) + H_2O \leftrightharpoons Mg^{2+} + 2OH^- \quad (1)$$

$$Mg^{2+} + 2OH^- \leftrightharpoons Mg(OH)_2(s) \quad (2)$$

As shown in Eq. (1), MgO dissolution generates hydroxyl groups that increase the pH of the water. Final magnesium concentration in the treated water was around 50 mg/L, which is approximately the solubility of magnesium according to MgO dissolution equilibrium in water at ambient temperature, indicating that an equilibrium state was achieved. When silica is removed by precipitation of magnesium silicates, the equilibrium shown in Eq. (1) is shifted to the right, dissolving MgO and thus increasing dissolved magnesium and OH^- concentration and thus the pH. This fact can also be observed in Fig. 2 which shows final pH of the treated waters and also the blanks (pH regulation was carried out but MgO was not added) obtained after 24 h. It is interesting to notice that final the pH steeply increased while silica removal was increasing. Nevertheless, at dosages over 500 mg/L when silica removal was as high as 90%, pH remained almost constant. That could be explained as at dosages over 500 mg/L there is not silica available to co-precipitate with magnesium and thus no more MgO was dissolved and no more OH^- groups were released (Eq. (1)).

It is worth noting that, as occurred in the case of silica removal, there were two distinct trends for the lowest (pH 8.2 and 9.5) and the highest initial pHs tested (10.5 and 11.5). Nevertheless, contrary to silica removal at dosages over 500 mg/L, final pH values were not the same at the four pHs tested. In the case of pH 8.2 and 9.5, final pH increased and remained constant at around pH = 11.0 at dosages lower than 2000 mg/L. On the other hand, at pH = 10.5 and 11.5, the final pH was around 11.5. In the case of the three highest dosages tested, it could be observed that at initial pH 8.4 and 9.5, final pH continued increasing with the toward the equilibrium pH of a MgO solution (pH = 11.5) [10].

As commented before, at dosages lower than 500 mg/L, at pH = 8.2 and 9.5 silica removals were lower than in the case of initial pH = 10.5 and 11.5. These differences on silica removal were determined by the operational pH. At initial pH 8.2 and 9.5 the pH increase caused by the dissolution of MgO is not high enough to achieve pH > 10. At pHs higher than 10, most of the silica is ionized as $H_3SiO_4^-$ and thus available to be removed by co-precipitation.

One of the advantages of using MgO as magnesium source is that the increase in conductivity is smaller than using soluble magnesium compounds or pre-acidified sparingly soluble magnesium compounds [9,10]. In the present study, the main increase in conductivity was caused by the addition of NaOH as pH regulator. The conductivity increase was 0.2 mS/cm, 0.7 mS/cm and 1.2 mS/cm to raise the pH to 9.5, 10.5 and 11.5, respectively. On the other hand, the conductivity increase caused by MgO was lower than 0.5 mS/cm for all the dosages and pHs tested. The final conductivity of the waters treated with 500 mg/L of MgO, which was selected as the optimum dosage, was 3.0, 3.2, 3.7 and 4.2 mS/cm at pH = 8.2, 9.5, 10.5, and 11.5, respectively.

Fig. 3 shows the temperature effect on silica removal. Temperatures tested varied from 25 to 50 °C. No significant improvement on silica removal was observed after increasing the initial temperature from 25 °C to 35 °C. At these temperatures, silica removal rates higher than 95% were obtained with 500 and 1000 mg/L of MgO; however, at 50 °C, higher removal rates were achieved with lower dosages, at 125 mg/L MgO silica removal was 83% and 97% with 500 mg/L. This demonstrates it is possible to use MgO with high removal efficiency with temperatures

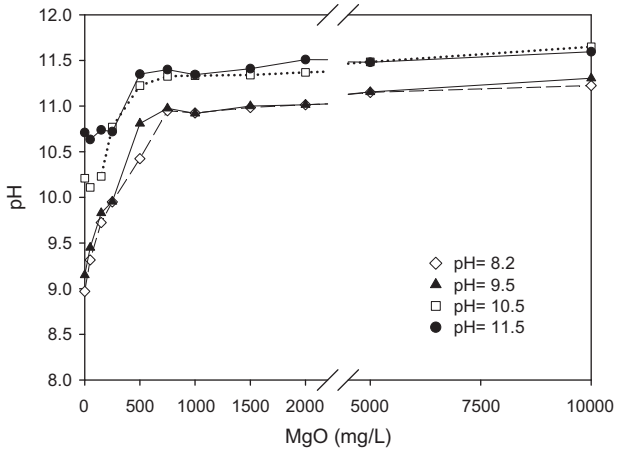

Fig. 2. Final pH vs. MgO dosage at 25 °C and different initial pHs.

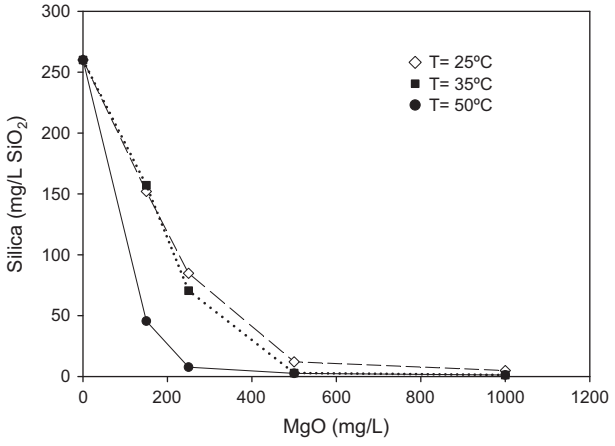

Fig. 3. Silica removal vs. MgO dosage at initial pH 8.2 and 3 different temperatures (25 °C, 35 °C and 50 °C).

ranging from 25 °C to 50 °C which are lower than the traditionally used in warm softening (50–60 °C) and hot-softening (110–115 °C) [17]. As the effluent of the paper mill could be treated either before or after the cooling towers used to reduce the effluent temperature while heating the fresh water entering to the process, working in the range of 25–50 °C would not be a problem in the paper mill as before the cooling towers the effluent temperature is around 50 °C. Additionally, working at higher temperatures would not be economically viable as it would be necessary to heat large volumes of water.

Operational temperature is a very important parameter to be optimized when silica is removed during softening as precipitation of the different species starts at lower pHs when the temperature is high enough [18]. This fact has been observed in this study since silica removal rates obtained at 150–250 mg/L were similar at 50 °C without pH regulation than those obtained at pH 10.5 and 11.5 at 25 °C. This is of a great importance as the pH regulation is the main contribution to the conductivity increase in the treated waters.

Due to the high reaction time used (24 h), silica polymerization might have occurred, especially at high temperatures; however, at the conditions of basic pH and magnesium concentration tested, the precipitation of silicates is favored compared to polymerization [19]. On the other hand, if silica polymerization would be the main mechanism, the final concentration achieved should be similar to equilibrium solubility of pure silica, which varies at each temperature. In order to minimize the polymerization, reaction times required under the different conditions were optimized (Section 3.1.2). Based on the results obtained in these equilibrium tests, 500 mg/L of MgO was used in the optimization of the reaction time study as this dosage allows achieving maximum silica removal at the 4 pHs and 3 temperatures tested.

3.1.2. Optimization of the contact time

Fig. 4 shows the evolution of silica concentration at 3 temperatures (25, 35 and 50 °C), and 4 initial pH levels (8.2–11.5) with time. Silica concentration is expressed as $[SiO_2]/[SiO_2]_0$ being $[SiO_2]_0$, the initial silica concentration in the effluent (260 mg/L).

At 25 °C, two different trends on silica removal were observed, one corresponding to pH = 8.2, 9.5 and 10.5 and the other one to pH = 11.5. At initial pHs ranging 8.2–10.5 and $t \leqslant 45$ min, silica conversion was lower than 20% while at $t = 45$ min there was a sharp increase to 40% removal. At $45 < t < 180$ min, conversion variation was lower than 5%. At $t > 180$ min silica removal continued increasing, achieving 50% conversion at $t = 240$ min. These different stages may indicate that the mechanism for silica removal involves a series of three steps, two fast (I and III) and one slow (II). The step I corresponds to the co-precipitation of silica with the dissolved magnesium at each pH. The precipitation of magnesium silicates shifted MgO dissolution equilibrium to the right dissolving more magnesium thus silica removal concentration remained constant (stage II). Finally in the step III the same tendency than in step I was observed, silica co-precipitates with dissolved magnesium. On the other hand, at pH = 11.5, silica removal was higher than those obtained at the three other initial pHs at $t > 180$ min. Second, although the same three steps were identified, the transition between these steps was smoother. At pH = 11.5, 50% removal was achieved after 180 min and 70% at $t = 300$ min. Although silica removal was favored at pH = 11.5, if large reaction times are used ($t = 21$ h) the same final concentration is obtained, independently of the initial pH. One explanation for the evolution of silica concentration is that at pH < 11.5, MgO solubility is limiting silica removal, as the magnesium concentration and the pH increase caused by MgO dissolution are low. Consequently, silica might not be ionized.

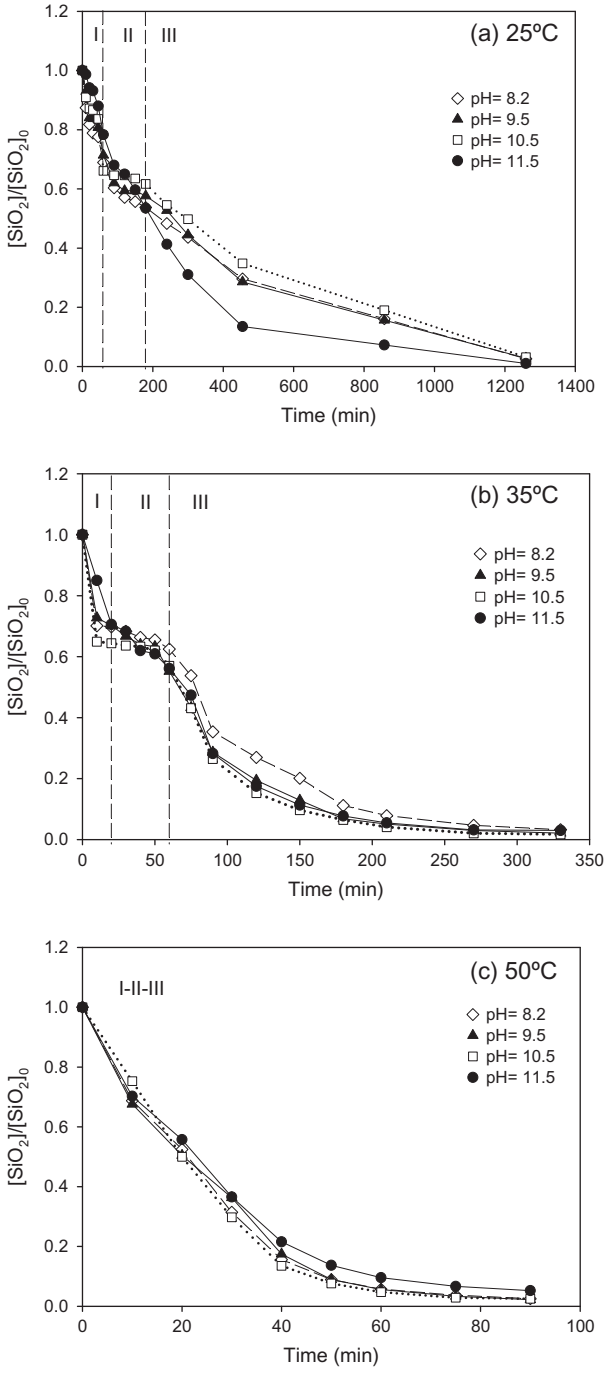

Fig. 4. Silica concentration vs. time at different initial pHs and temperatures: (a) 25 °C, (b) 35 °C and (c) 50 °C.

At $T = 35$ °C, there were not significant differences among the 4 initial pHs tested. This is a very interesting aspect since MgO dissolution increases the pH, allowing silica ionization and thus silica removal at lower pHs or even without pH regulation. The evolution with time observed was similar to this obtained at $T = 25$ °C at pH = 11.5 and even the three different stages are more clearly distinguished. At 35 °C silica removal is faster. After 10 min, silica conversion is around 35%, then silica concentration remained constant until $t = 60$ min, then silica started to decrease achieving 75% conversion at $t = 120$ min and 95% at $t = 180$ min.

At $T = 50$ °C, as occurred at $T = 35$ °C, no differences were observed in the removal of silica with the initial pH of the waters.

In this case, there was not any stage where the silica concentration remained almost constant. Contrary to this, silica concentration continuously decreased with time. Stage II was not observed at all, and stage I and III were merged. The higher MgO solubility at high temperatures avoided the MgO dissolution to be the limiting step in the silica removal process. Removals higher than 80% were achieved in 40 min. Moreover, 90% conversion could be obtained after 60 min. This conversion is significantly higher than those obtained at 25 °C and 35 °C. After 60 min, at 25 °C and 35 °C, only 30% and 45% were achieved respectively. As commented in Section 3.1.1, temperature is a key parameter that makes different species precipitate at lower pH [18].

3.2. Solid characterization: assessment of silica removal mechanisms

3.2.1. FTIR analysis

Fig. 5 shows the FTIR spectra of the solids obtained in the optimization of the operational conditions. Although FTIR analysis is not a quantitative technique, samples were prepared with the same amount of precipitate and KBr to try to observed differences in the composition under the different operational conditions. In all the samples, the same peaks and bands were observed independently of the operational conditions. The O–H vibration produced bands, found out around 3424 and 1635 cm^{-1}, correspond to hydration water or hydroxide groups. At the highest temperatures (35 and 50 °C) and pHs (10.5 and 11.5) it appeared also a peak at 3875 cm^{-1} due to the O–H vibration which appears in the spectra of the antigorite, $Mg(OH)_2$ and MgO. In all the spectra there was a Si–O band at 1013 cm^{-1} that is associated with different silicates such as antigorite, forsterite or enstatite. Two bands were also observed in the low frequency region at 460 and 619 cm^{-1} due to Mg–O vibrations that can be found in compounds such as MgO or antigorite. Carbonate bands were also detected at 1438–1488 and 872 cm^{-1}. This peak in some of the spectra is masked by the band corresponding to silicates.

Fig. 5a shows the FTIR spectra obtained at initial pH = 8.2, 25 °C and different MgO dosages. The Si–O peak (1013 cm^{-1}) is more intense at lower dosages of MgO as at higher dosages there is higher excess of MgO in the solid thus increasing the Mg/Si ratio. It was also observed that the peaks corresponding to carbonates were more significant at the highest MgO dosage. This could be explained as at higher MgO dosages the operational pH is higher and thus the precipitation of carbonates was favoured. On the other hand, the low frequency bands (460 and 619 cm^{-1}), corresponding to Mg–O vibration as expected, were more intense at higher MgO dosages. Fig. 5b shows the FTIR spectra at different initial pHs at constant temperature and dosage (25 °C, 500 mg/L). It could be observed that the precipitation of silicates was favoured at higher pHs as the peak Si–O peak (1013 cm^{-1}) was more intense. Moreover, carbonates precipitation was also favoured at higher pHs. Finally, Fig. 5c shows the spectra at different initial temperatures at constant pH and dosage (pH = 8.2, 250 mg/L). It could be observed that the Si–O peak (1013 cm^{-1}), was slightly more intense at 35 °C than at 50 °C due to the higher solubility of silica at higher temperatures. Carbonate band (1438–1488 cm^{-1}) was more intense at higher temperatures due to the inverse solubility of carbonates in water at higher temperatures.

3.2.2. SEM–EDX analysis

Fig. 6 shows the Mg/Si atomic ratio obtained from the SEM–EDX analysis of several samples of solids obtained in the set of tests carried out for the optimization of the operational conditions. This ratio gives very valuable information about the different silica removal mechanisms, i.e. co-precipitation or adsorption, and the involved species. If silica is removed through the formation of magnesium silicates, although there are many possible magnesium silicates with different stoichometries, the literature indicates that the most common are Mg_2SiO_4 (forsterite, $pK_{ps} = 26.9$), $Mg_3Si_2O_5(OH)_4$ (antigorite, $pK_{ps} = 34.5$) or $MgSiO_3$ (enstatite, $pK_{ps} = 16.9$) [11]. In this case, the ratio Mg/Si would be 2, 1.5 and 1, respectively. However, there are other facts which must be taken into account to analyse the results. First, MgO is a sparingly soluble salt and the unreacted MgO would contribute to increase the Mg/Si in the analyzed solids, especially at the highest dosages, where the excess of MgO is higher. Second, there is also a significant precipitation of $Mg(OH)_2$ at high pHs, which would also increase the

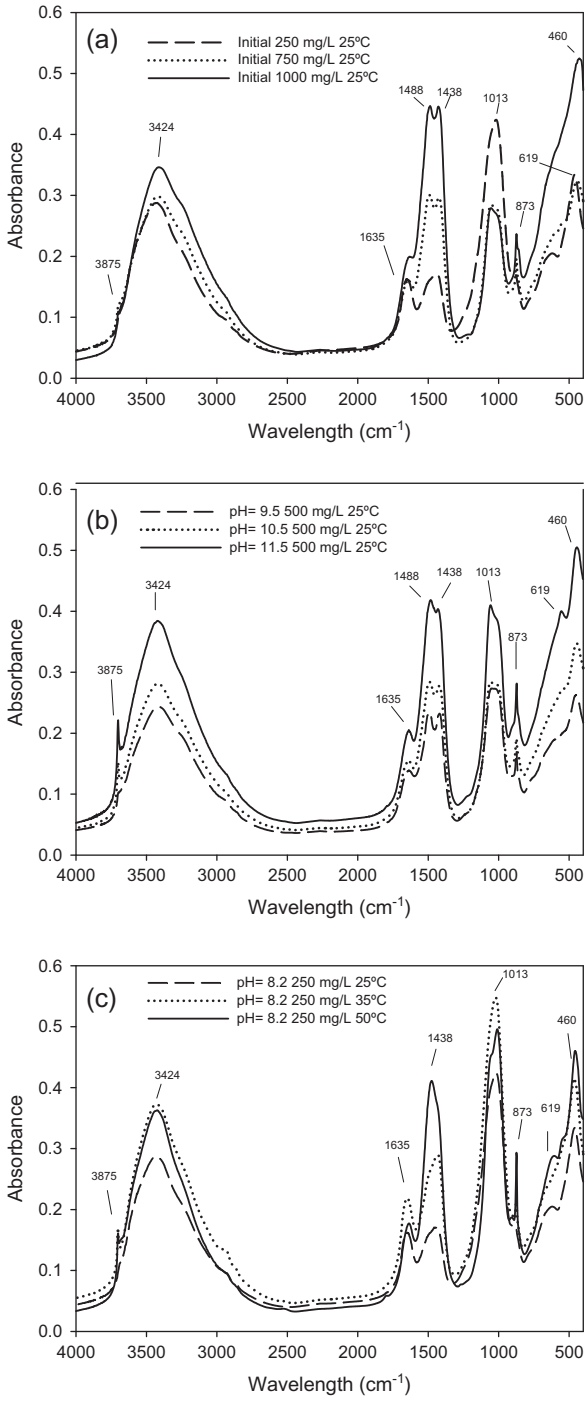

Fig. 5. FTIR spectra of the solids obtained after precipitation at: (a) initial pH = 8.2, 250–1000 mg/L at 25 °C; (b) initial pH = 9.5–11.5, 500 mg/L at 25 °C (c) initial pH = 8.2, 250 mg/L and 25–35–50 °C.

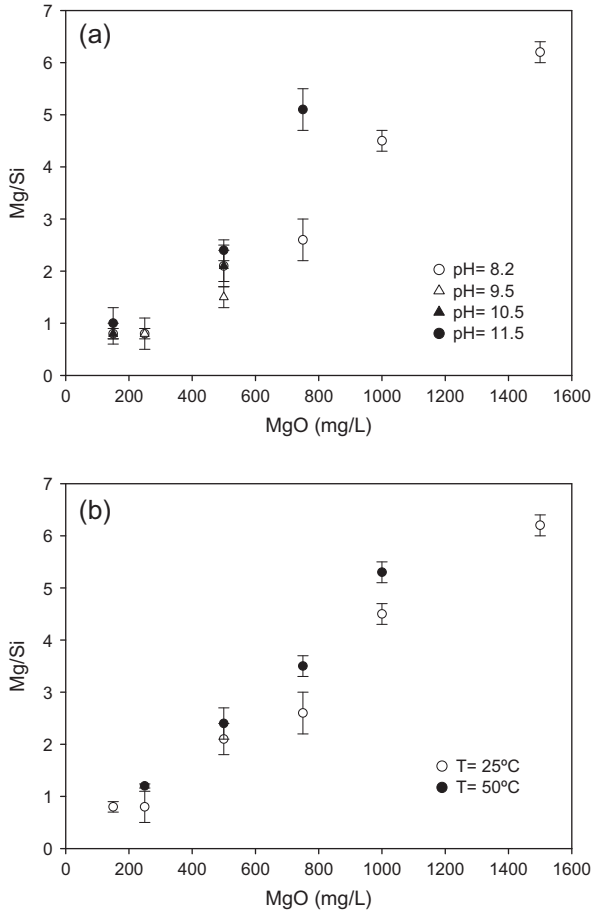

Fig. 6. Mg/Si atomic ratio vs. MgO dosage at: (a) different initial pHs (T = 25 °C) and (b) different temperatures (Initial pH = 8.2).

Mg/Si ratio in the solids formed. This precipitation would become more extensive at pHs around 10.5 as $Mg(OH)_2$ solubility drops steeply as the pH rises above 9.5 and approaches zero a little below 10.5 [19]. Both reacted and unreacted magnesium will be detected in the EDX analysis, the dissolved magnesium corresponding to the equilibrium solubility at each pH and dosage would be the only magnesium not present in the solids formed. Finally, apart from the precipitation of magnesium silicates, adsorption on fresh precipitated $Mg(OH)_2$ is another possible silica removal mechanism which have been reported previously in the literature [12,20].

If adsorption on magnesium hydroxide would be the main mechanism involved, the Mg/Si ratio observed in the solids would be very high, as the magnesium required to remove a certain amount of silica is considerably higher in adsorption than in co-precipitation. In this sense, Chen et al. and Hsu et al. [12,20] reported a molar ratio Mg/Si 22:1 for adsorption on $Mg(OH)_2$, compared to ratios varying from 1 to 2 for the most common magnesium silicates if the main removal mechanism for silica removal is co-precipitation with magnesium. Moreover, Parks and Edwards [11] indicated that co-precipitation of magnesium silicates occurred at initial the molar ratio of Mg: Si less than 6:1. In the present study initial molar Mg/Si ratio was lower than 6 at dosages <1000 mg/L, thus adsorption of silica would only be favorable at MgO dosages >1000 mg/L. Furthermore, even at these high dosages tested Mg/Si molar ratio was always lower than 22 which would indicate that silica was mainly removed by co-precipitation as magnesium silicates and the adsorption on freshly precipitated $Mg(OH)_2$ would be only possible at high dosages.

Fig. 6a shows the effect of MgO dosage in the molar ratio Mg/Si in the solids formed, at different initial pHs at 25 °C. The results obtained at 35 °C and 50 °C were totally equivalent (data not shown). At the lowest dosages (150–250 mg/L of MgO), the ratio Mg/Si was around 1–1.5, independently of the initial pH. This is in agreement with silica removal by co-precipitation of, which could be associated to a mixture of antigorite and forsterite which are more insoluble than enstatite. At these lowest dosages, there is no significant MgO excess compared to the initial silica content of the waters. At higher dosages (>500 mg/L), however, the ratio Mg/Si increased steadily. For example, at 500 mg/L, the ratio Mg/Si was around 2. This was the minimum dosage of MgO at which silica removal obtained were similar for all the initial pHs tested. This higher molar ratio Mg/Si could be due to a significant amount of unreacted MgO, and even a possible adsorption of silica in $Mg(OH)_2$; however, the option of a significant amount of silica adsorbed onto $Mg(OH)_2$ seems not be an important mechanism as the molar ratio Mg/Si is still far from the reference values [12,20]. At 500 mg/L initial molar ratio was around 3, thus according to Parks and Edwards [11] co-precipitation would be favored to adsorption. Finally, there is an option of a significant amount of MgO unreacted. At dosages higher than 500 mg/L, the curves obtained at different initial pHs diverge, ratios obtained at initial pH 8.2 and 9.5 were lower than the ones at pH 10.5 and 11.5. These differences were caused by the operational pH. As it was shown in Fig. 2, at pH = 8.2 and 9.5 the final pH was around 11.0 and at initial pH = 10.5 and 11.5 around final pH around 11.5. Differences in the ratios obtained were due to the equilibrium solubility of MgO (Eq. (1)), at higher pH this equilibrium is shifted to the left and there is less dissolved Mg in the water and therefore more Mg in the solids.

Fig. 6b shows the effect of MgO dosage in the molar ratio Mg/Si in the solids formed at different temperatures (25 °C and 50 °C) at a single pH (initial pH 8.2). As shown in Fig. 6b, the main parameter affecting the Mg/Si molar ratio in thesolids obtained is the dosage of MgO, and the effect of the operating temperature is not much important. Only minor differences can be found between the results obtained at 25 °C and 50 °C. It seems that the Mg/Si ratio is slightly higher at 50 °C than at 25 °C, probably due to the higher solubility of silica in water at higher temperature [21]. Silica solubility increases from 120 mg/L at 25 °C to around 220 mg/L at 50 °C. Although MgO solubility also increases with temperature [22,23], which would decreases the ratio Mg/Si, the increase in silica solubility seems to be more relevant than the increase in MgO solubility, thus resulting a higher Mg/Si ratio.

Fig. 7 shows some of the SEM images obtained of the settled solids under different operational conditions. There are two images for each sample; one at 200× magnification (a, c, e), to have a general vision of the precipitated solid and another one at 1000–3000× magnification (b, d, f), to see in more detail the different morphologies and the presence of some particles with different composition than the aggregates (shown in Table 2). The EDX analysis showed the composition of the solid was mainly Mg, Si and O, corresponding to magnesium silicates, MgO and $Mg(OH)_2$. Although the precipitates obtained were mainly amorphous (Fig. 7a, c and e), white crystals were observed in some precipitates (Fig. 7b, d and f). The EDX analysis showed some solids with high calcium concentration which was associated to $CaCO_3$, which was also detected by FTIR. Calcium carbonate presence was especially observed at low MgO dosages as at higher dosages magnesium precipitates mask calcium carbonate particles. Dissolved calcium levels in the water were not high (33.9 mg/L). In a lower extent crystals of $CaMg(CO_3)_2$ (dolomite) and pure silica were also observed in some samples.

Fig. 8 shows a lineal composition analysis along an amorphous precipitated of those observed in the SEM images. The particle

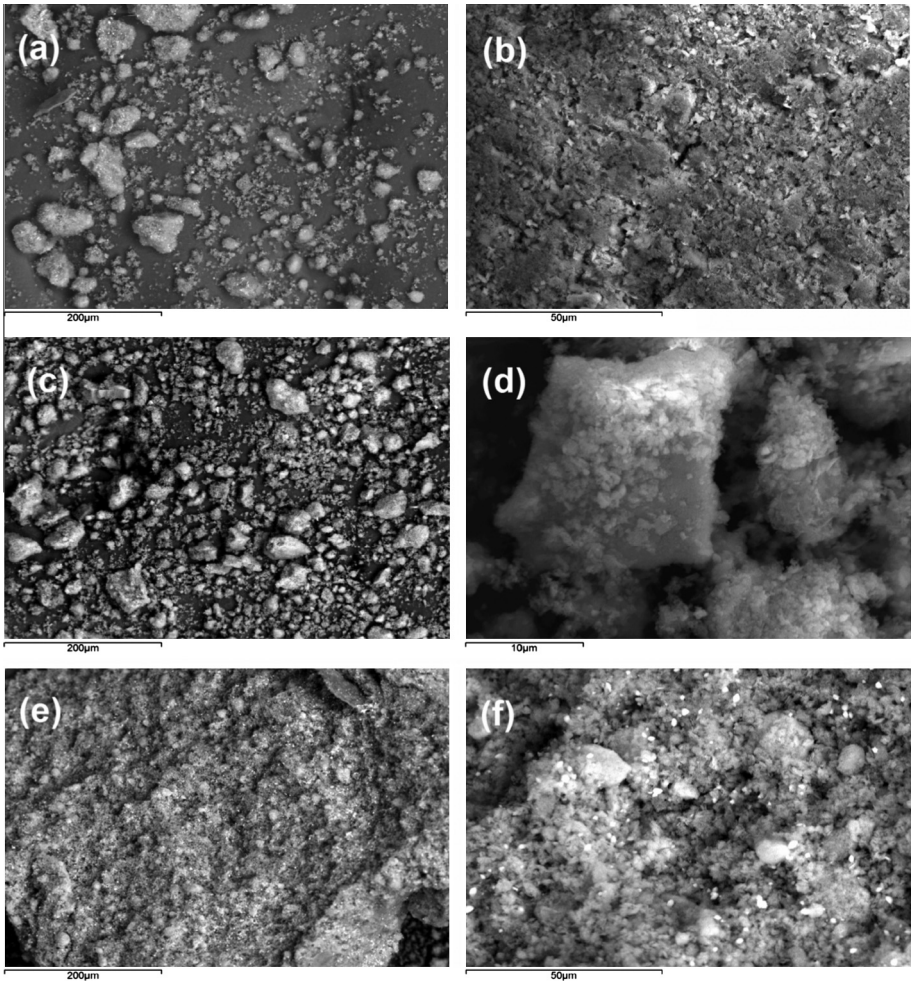

Fig. 7. SEM–EDX images of the typical solids obtained after the treatment at: (a and b) pH = 8.2, 750 mg/L and 25 °C; (c and d) pH = 8.2, 750 mg/L and 50 °C; (e and f) pH = 10.5, 500 mg/L and 25 °C.

Table 2
Average composition of the of the solids obtained after precipitation.

Solid	O (wt.%)	Mg (wt.%)	Si (wt.%)	P (wt.%)	Ca (wt.%)	Mg/Si (mol/mol)
(a,b)	46.6	28.2	15.6	1.0	8.3	2.1
(c,d)	41.3	18.3	24.8	1.4	14.0	0.9
(e,f)	49.3	27.8	13.5	1.0	8.4	2.4

composition was mainly constant except in the white particle of the SEM image, where magnesium signal decreased while calcium signal steeply increase indicating the presence of $CaCO_3$. Silicon and magnesium ratio was maintained constant in the rest of the particle, indicating the precipitated is homogeneous and the silica was not preferably located in the surface as it should occur if silica was removed by adsorption. This again corroborates the main silica removal mechanism is co-precipitation of magnesium silicates.

4. Conclusions

Silica removals higher than 95% were obtained with 500 mg/L of MgO even without pH regulation, minimizing the conductivity increase after the treatment to less than 0.5 mS/cm (final conductivity = 3.0 mS/cm). This is a clear improvement over the previous studies using soluble and pre-acidified soluble magnesium compounds.

Initial pH regulation had no significant effect on silica removal using MgO as magnesium source at high contact times (t = 24 h) or temperatures (T > 35 °C). MgO dissolution increased OH^- concentration and consequently the pH to around pH = 11.5. This increase in pH allows silica ionization and the precipitation of the different magnesium silicates which is translated into high silica removal without an initial pH regulation.

Operational temperature and reaction time have strong effect on silica removal as MgO solubility is limited at temperatures lower than 35 °C. At T < 35 °C silica removal involves three stages, one fast corresponding to the precipitation of magnesium silicates, one slow corresponding to MgO dissolution and another fast stage for the achievement of the equilibrium concentration. At T > 35 °C 80–90% silica removal can be achieved after 2–3 h contact time. At 25 °C and dosages > 500 mg/L silica removals of 80–90% could also been obtained, however, it would be necessary 24 h contact time.

FTIR spectra and SEM–EDX analysis supported the hypothesis of silica removal by the precipitation of magnesium silicates. Mg/Si molar ratio obtained at the lowest MgO dosages (150–250 mg/L) of by SEM–EDX was around 1–1.5, which is in agreement with the precipitation of a mixture of magnesium silicates such as forsterite (Mg_2SiO_4) and antigorite ($Mg_3Si_2O_5(OH)_4$). At higher dosages ($\geqslant$500 mg/L), the ratio Mg/Si increased steadily, due to

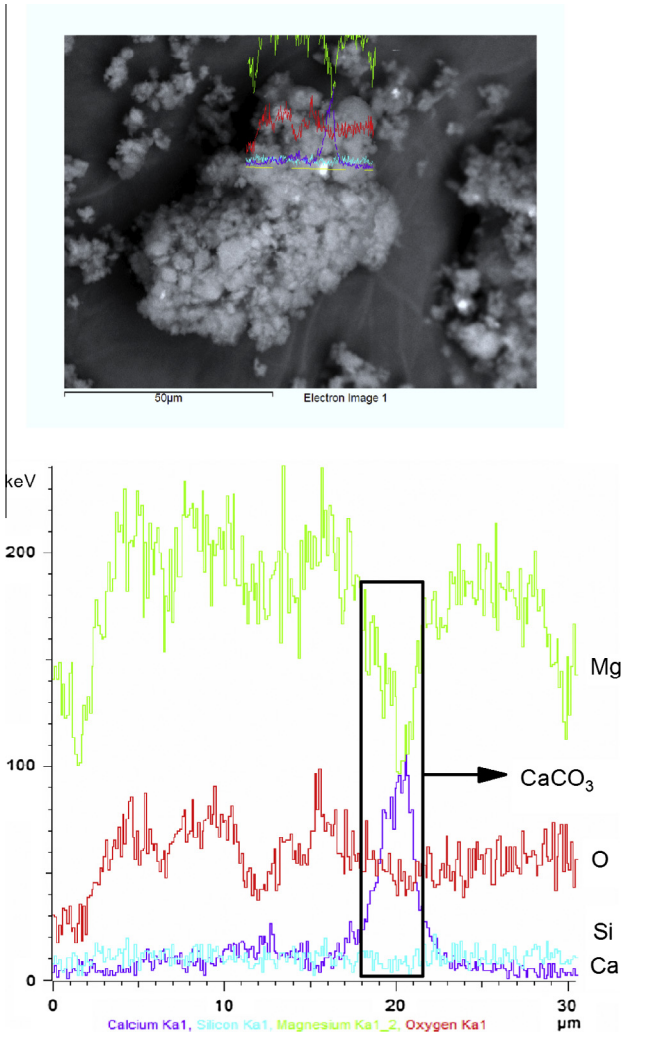

Fig. 8. Lineal analysis composition of a typical precipitate. Note: the magnesium signal is considerably higher to that of silicon due to the high MgO dosage used in this example (5000 mg/L).

the presence of unreacted MgO and also to the precipitation of $Mg(OH)_2$.

Acknowledgments

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