

Comparison of ultrafiltration and dissolved air flotation efficiencies in industrial units during the papermaking process

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SUMMARY

The efficiency of an ultrafiltration unit has been studied and compared with a dissolved air flotation system to get water with a suited quality to be reused in the process. The study was done at a paper mill producing light weight coated paper and newsprint paper from 100% recovered paper. Efficiency was analysed by removal of turbidity, cationic demand, total and dissolved chemical oxygen demand, hardness, sulphates and microstickies. Moreover, the performance of the ultrafiltration unit and the membranes were studied deeply, analysing its variability during the filtration process.

As expected, the ultrafiltration gave higher removal efficiencies than the dissolved air flotation cell in parameters like turbidity, cationic demand, dissolved chemical oxygen demand and microstickies. The greatest difference in performance between the units concerned cationic demand and dissolved chemical oxygen demand. Ultrafiltration was influenced by the operating time, decreasing the removal efficiency of the dissolved fraction by 75% and of the colloidal fraction by 30% after 312 of running. Membrane autopsy, carried out to identify the cause of poor membrane performance, showed that the active layer was degraded due to the effect of suspended solids.

Keywords: ultrafiltration, dissolved air flotation, anionic trash, dissolved and colloidal material, closure of water circuits

1. INTRODUCTION

There exist a worldwide trend in paper industries to reduce freshwater consumption for environmental and economical reasons (water stress, freshwater savings and reduction of effluent treatment and disposal costs) (1,2). In modern paper mills, freshwater consumption can vary between 2 and 20 m³ of water per tonne of paper produced, depending on the type of manufactured paper and on the age of the mill (3). However, as the mills close their water systems, a considerable accumulation of contaminants exists, which can affect both the product quality and the efficiency of papermaking operations due to, e.g., deposit formation (4,5). This situation is worse in recycling paper mills (6-9).

Dissolved air flotation (DAF) is considered a traditional treatment to remove suspended solids (fines, fillers, or residual ink) effectively (80 to 98%) due to their colloidal nature.

1 Dissolved and colloidal matter (DCM) higher than 0.2 μm can be also removed from the
2 water if suitable chemicals are added before the clarification unit. However, DCM
3 smaller than 0.2 μm , normally remains within the process water, being necessary the
4 use of advanced internal water treatments (10-16). Various techniques have been
5 developed to remove these contaminants from process waters. The best-known
6 strategies include: membrane filtration, biological treatment under anaerobic or aerobic
7 conditions, enzymatic treatments, use of oxidizing agents and multiple-effect
8 evaporation. Each technology presents a different efficiency removal for each
9 contaminant. Therefore, the idea is to find a technology with the minimum cost that
10 reduces contaminants to a level that can be tolerated within the paper mill, without
11 affecting product quality nor paper machine runnability (17,18).

12
13 Membrane-based processes are physical unit operations and, therefore, present inherent
14 advantages over the chemical and biological processes that are commonly used in
15 wastewater treatment. Ultrafiltration (UF) and reverse osmosis (RO) systems are taking
16 advantage as polishing treatment schemes to remove undesirable components,
17 minimizing water consumption and reducing the concentration of contaminants. The
18 high quality of the permeate allows its reuse within the papermaking process (e.g. paper
19 machine showers), reducing freshwater intake. However, the main drawback of
20 membrane systems is their sensibility to be fouled by suspended solids and, particularly,
21 by DCM, or by precipitating salts, leading, at the end, to a permeate flux decline or to
22 obtain a permeate stream of worse quality (19-24).

23
24 In this paper, the efficiency of an industrial UF unit has been studied in detail and its
25 performance has been compared with a DAF unit. The study was based on traditional
26 analysis: consistency, ash content, turbidity, cationic demand (CD), conductivity, total
27 and dissolved chemical oxygen demand (TCOD and DCOD), hardness, sulphates and
28 microstickies analyses of process waters from different paper productions. The
29 variability of the UF process on the efficiency of this unit and the behaviour of the
30 membranes were also studied.

31 32 **2. DESCRIPTION OF THE TREATMENT UNITS**

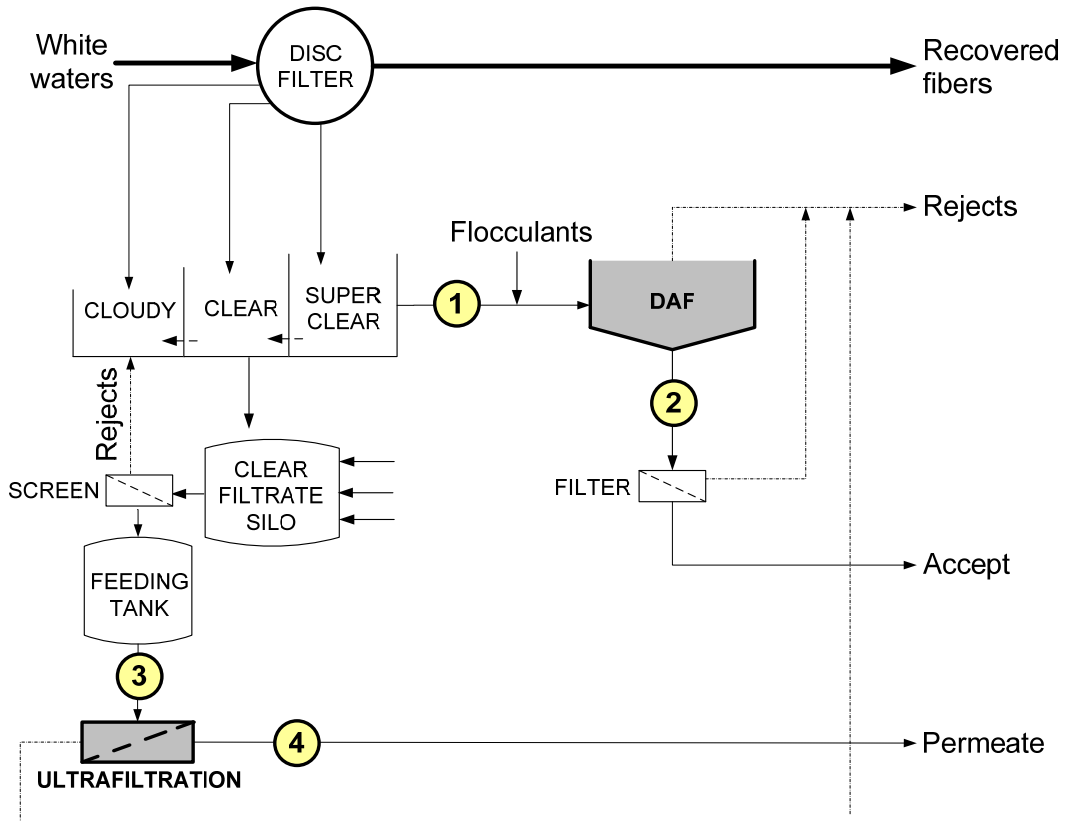
33
34 Water samples were taken from a recycled paper mill using 100% recovered paper as
35 raw material. This paper mill produces light weight coated paper (LWC) and newsprint
36 paper (NP). Figure 1 shows a general flowsheet of the paper mill water loop where the
37 DAF and UF units are integrated.

38 39 **2.1 Ultrafiltration unit**

40
41 The UF unit is placed in the machine circuit to treat the clear filtrate coming from the
42 disc filter. This filtrate is screened through 0.2 mm and stored in the feeding tank
43 before entering the unit. The permeate will be used in the machine showers to clean the
44 forming wire and rolls. For this application the water has to be of very high quality to
45 avoid the clogging of shower holes and to keep the wires as clean as possible to
46 optimize the drainage and the forming of paper sheet.

47
48 The UF unit (CR1010-100, METSO Paper, Finland) consists of a serial of cells or
49 cassettes which are assembled one on top of the other. The membranes sheets, made of
50 regenerated cellulose, are installed on both sides of each cell. Between each cassette

1 there is a rotor, which rotation causes a high turbulence and a cross-flow across the
 2 membranes, keeping the solids and trash in constant movement, reducing the effect of
 3 fouling. The cell has three channels, one for the feed, which comes into the unit from
 4 the bottom; another for the concentrate, collected on the top; and the permeate, which is
 5 taken out at the bottom of the unit. Filtration phenomenon is achieved by maintaining
 6 0.9 bar of transmembrane pressure (TMP).
 7



8
 9 **Fig. 1.** Simplified flow-sheet of the paper mill water loop with the location of the
 10 sampling points.
 11

12 To keep a constant permeate flow, the UF is cleaned chemically when its filtration
 13 capacity decreases 20 to 30% from the previous wash. Besides, although the filtration
 14 capacity does not decrease the mentioned percentages, maintenance cleanings are
 15 needed: a weekly cleaning with alkali and a monthly cleaning with an acid solution.
 16 Washing is started by pre-rinsing the unit with warm water; after this, the detergent
 17 solution is pumped to the UF and is kept in circulation for some time. After the stated
 18 time, the solution is kept inside the unit for a soaking period. Finally, the pump and the
 19 rotors start running again and the cleaning solution is flushed from the filter by clean
 20 warm water. After washing, the UF is ready for filtering.
 21

22 **2.2 Dissolved air flotation unit**
 23

24 The DAF unit (“KROFTA” SUPRACELL, Krofta Engineering Limited, India) is also
 25 placed in the machine circuit, in parallel with the UF, but its objective is to treat a
 26 fraction of the super-clear filtrate after the addition of 3 to 5 mg/L of a cationic
 27 polyacrylamide of medium charge density and ultra-high molecular weight. The water
 28 clarified in the DAF is used for pulp dilutions along the deinking process and at the

1 flotation deinking cells showers to break the foam. Therefore, its quality is not so
2 critical.

3 3. METHODS

4
5
6 As shown in Figure 1, the samplings points selected for the study of the DAF and UF
7 units were the feed streams (1 and 3, respectively) and the accept or permeate streams (2
8 and 4, respectively). A total of five samplings were carried out, collecting the samples
9 in different days and production conditions (Table 1). Both paper qualities were
10 produced under conventional alkaline chemistry during pulping: NaOH (0.6-0.8%),
11 H₂O₂ (0.9-1.1%), Na₂SiO₃ (0.3-0.4%) and soap (0.1-0.2%).
12

13 **Table 1.** Sampling conditions.

Trial	Conditions	Production	Unit	
1	312 hours running since start-up	LWC	DAF	UF
2	120 hours running since start-up	LWC	DAF	UF
3	120 hours running since start-up	LWC	-	UF
4	120 hours running since start-up	NP	DAF	UF

14
15
16 The samples were separated by size fractions before their chemical characterization, as
17 shown in Figure 2. Water samples were filtered in a Büchner funnel with a paper filter
18 of 7 µm (MN 640W, from Macherey-Nagel GmbH & Co) to obtain the colloidal
19 fraction, which was filtered with a syringe filter of 0.45 µm (Millex, from Millipore) to
20 obtain the dissolved fraction. All the parameters were measured twice. Consistency and
21 ash were measured by a gravimetric method, filtering the water through the mentioned
22 paper filter and drying it at 105 °C for 1 hour. The filter, with the dried solids retained
23 on it, was then dried at 525 °C to obtain the ash content. Turbidity was measured with a
24 LP 2000-11 nephelometer supplied by Hanna Instruments, according to ISO 7027:2001.
25 Cationic demand was measured by colloidal titration of the samples with 0.001 N poly-
26 diallyldimethylammonium chloride (PDADMAC). The end-point was detected with a
27 PCD 03 particle charge detector (Mütek Analytic GmbH) used in combination with an
28 automatic titrator, model Compact I (Crison Instruments, S.A). The COD was
29 determined with Merck Chemicals Kit (1.14691.0001) using an Aquamate-
30 spectrophotometer (AQA 091801), and a PF-11 Filterphotometer (Macherey-Nagel
31 GmbH & Co) equipment was used to measure sulphates (Test 0-86) and hardness (Test
32 0-43). Sulphates content is a critical parameter for the paper mill where this study was
33 done because all effluents sent to the Madrid sewerage network can not exceed the level
34 of 1000 mg/L to avoid the corrosion of concrete pipes due to microbial sulfur
35 metabolism (25). During the manufacture of both paper grades, NP and LWC, sulfuric
36 acid was added to the pulp to control pH in the paper machine. This sulfuric acid
37 remains in the process water until it finally appears in the effluent as sulphates.
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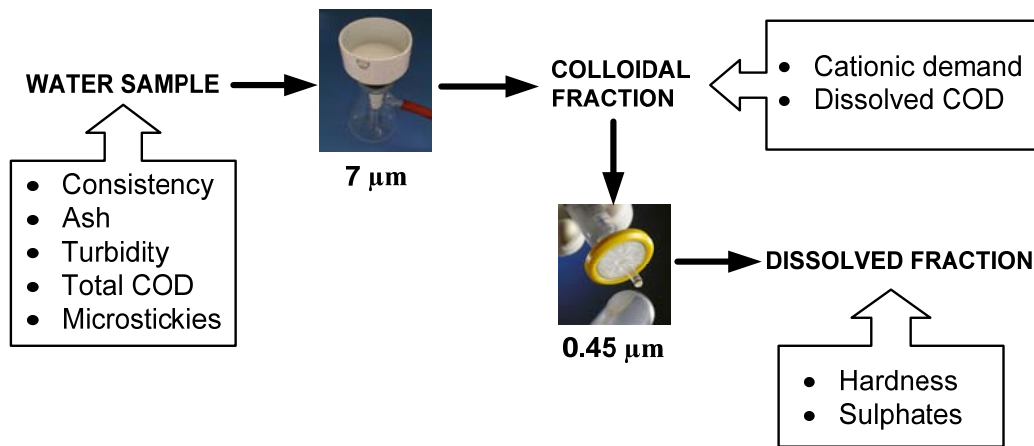


Fig. 2. Parameters measured in different fractions of the sample.

Microstickies were obtained using the deposition tester developed by the University Complutense of Madrid (UCM) and quantified by image analysis (Figure 3). The deposition tester consists of a vertical cylindrical rotor assembly with open ends, collector plates (films) lined with 0.05 mm thick stainless steel films, and an axial flow propeller. The propeller steers the liquid through the rotor assembly which directs the liquid toward the internal collector films which collect deposits by an impact mechanism. Simultaneously, the liquid passes the external plate which collects the deposits by a transference, or dynamic-fluid (flow) mechanism. The tests were carried out three times, using 1800 mL of sample. The stainless steel collectors are subsequently removed and dried before scanning with a commercial computer flatbed scanner (HP Scanjet 6100C) at 600 dpi. The resulting scanned images are analyzed using the image analysis system “Deposit Evaluation Software 1.2” developed also by the UCM Research Group (26, 27). In this paper, the microstickies results are expressed as mm²/L.

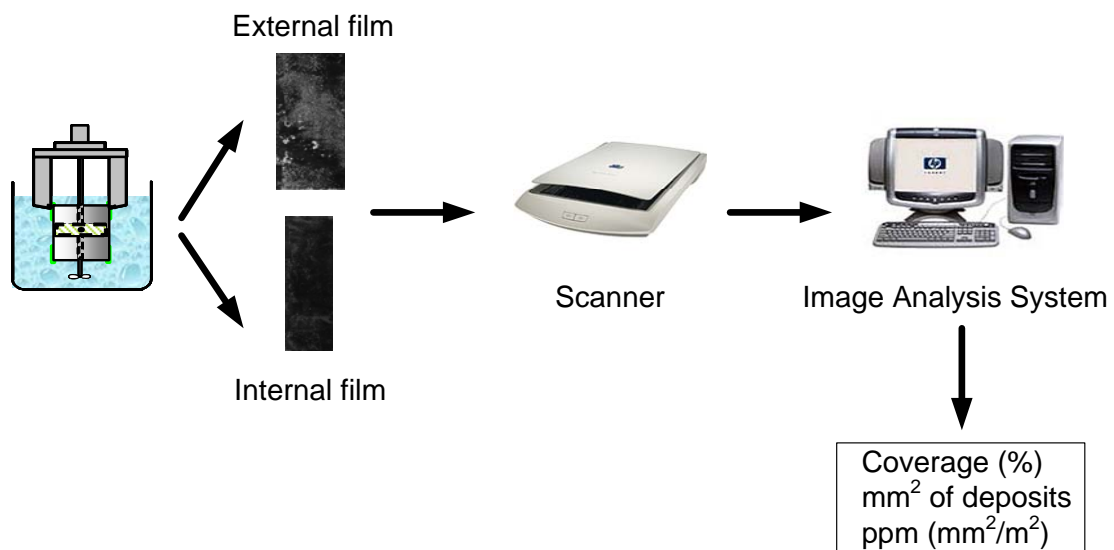


Fig. 3. Procedure followed to analyse microstickies.

1 An autopsy of the used UF membranes was carried out at the end of the trials to identify
 2 the cause of poor membrane performance. Mercury porosimetry technique
 3 (Micromeritics Autopore IV equipment) was used to determine membrane pore size
 4 distribution, and scanning electron microscopy (Philips XL30 microscope) was used to
 5 see the structure of the membrane layer.

6
 7 **4. RESULTS AND DISCUSSION**

8
 9 **4.1 Effect of water chemical composition on the efficiency of DAF and UF units**

10
 11 The first objective was to compare the efficiencies of both units at similar operational
 12 conditions (120 h running since start-up) in both mill environments (LWC and NP),
 13 corresponding to trials 2 and 4 from Table 1.

14
 15 The main parameters of the inlet and the outlet streams from each unit are shown in
 16 Table 2. All the parameters were measured twice (variability lower 5%), but
 17 microstickies, which were measured three times (variability lower 10%), and the values
 18 presented in Table 2 are the average value of all the measurements. Figure 4 represents
 19 the removal efficiencies achieved for each contaminant. The removal efficiencies are
 20 calculated using Equation [1].

21
 22
$$R (\%) = \frac{X_f - X_o}{X_f} \cdot 100 \quad [1]$$

23
 24 Where, *R* represents the removal efficiency (%); *X_f* is the measured parameter in the
 25 feeding stream; and, *X_o* is the measured parameter in the accepted or permeated stream.

26
 27 Waters obtained during NP production have higher suspended solids and inorganic
 28 compounds. However, the colloidal fraction, represented by CD, DCOD and
 29 microstickies are higher in LWC production. These results were also observed by
 30 Miranda et al. in 2009 (4). The raw material used to produce NP and LWC papers had
 31 an approximate newsprint/magazine ratio of 1.3 and 0.9, respectively. As the proportion
 32 of magazines fed to produce LWC paper is higher, there is a higher proportion of
 33 coating binders being released into the process waters during pulping than in NP
 34 production (28). The higher value of hardness in NP production could be a consequence
 35 of the lower pH of pulping in NP (7.5 to 7.6) than in LWC production (7.7 to 7.8),
 36 enhancing the dissolution of calcium carbonate (4). Although total solubility of CaCO₃
 37 is achieved below pH≈4.5, its solubility increases around 50 mg/L by changes on pH of
 38 only 0.5 units below pH=8.0 (29). That is why minimal variations on pH produce
 39 important changes on hardness measurements.

40
 41 **Table 2.** Water characterization depending on the type of paper production.

42

Production	DAF		UF		
	Feed (1)	Accept (2)	Feed (3)	Permeate (4)	
Consistency	LWC	0.04	0.003	0.04	0.001

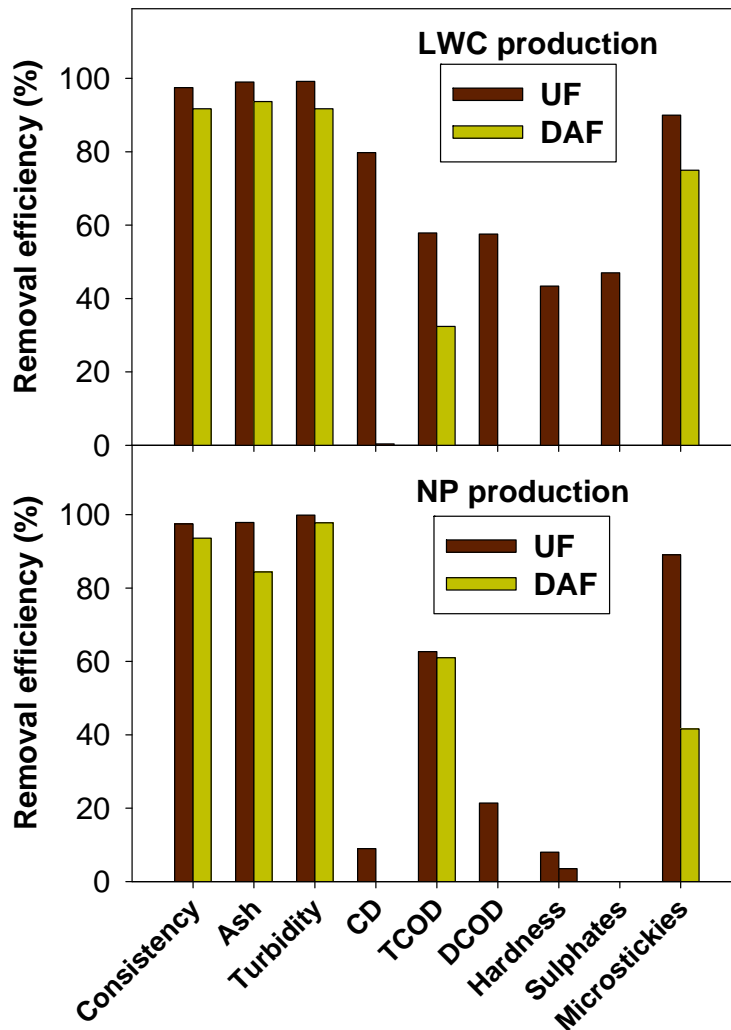
(%)	<i>NP</i>	0.08	0.005	0.04	0.001
Ash (mg/L)	<i>LWC</i>	111	7	196	2
	<i>NP</i>	257	25	280	6
Turbidity (NTU)	<i>LWC</i>	739	62	634	5
	<i>NP</i>	2140	48	1720	1
CD (μ eq/L)	<i>LWC</i>	370	368	247	50
	<i>NP</i>	154	158	155	141
TCOD (mg/L)	<i>LWC</i>	1155	781	657	277
	<i>NP</i>	1625	634	1298	484
DCOD (mg/L)	<i>LWC</i>	712	710	628	266
	<i>NP</i>	572	605	616	484
Hardness (mg/L)	<i>LWC</i>	151	157	131	74
	<i>NP</i>	201	194	217	200
Sulphates (mg/L)	<i>LWC</i>	198	198	386	203
	<i>NP</i>	343	341	346	348
Microstickies (mm ² /L)	<i>LWC</i>	459	115	1311	145
	<i>NP</i>	216	126	855	93

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Normally, the solid content should decrease sequentially within the cloudy, clear and super-clear filtrates. Mäkinen et al. (2003) determined that during NP production the cloudy filtrate should normally contain 230 to 390 mg/L of solids, the clear filtrate approximately 80 to 135 mg/L and the super-clear 34 to 61 mg/L; while in LWC manufacturing the solids content is usually a bit higher: 250-400 mg/L, 85-145 mg/L and 38-65 mg/L, respectively. These values were presented for white waters with 0.8% of consistency (in the current study white water consistencies vary from 0.73% after 120h up to 0.95% after 312h), and the intervals are function of the speed of the disc filter (from 0.5 to 1.5 rpm). The higher values of consistency, ash and turbidity in the super-clear stream obtained in our trial (Table 2), besides of obtaining consistency values higher in NP production than in LWC, reveals that the disc filter was damaged and needed to be repaired. The higher value of TCOD in the super-clear stream is associated with the consistency, the higher the consistency, the higher the TCOD, as more fines and fibres are being oxidized during the analysis.

Figure 4 shows that the UF gave higher removal efficiencies than the DAF unit for parameters such as consistency, ash, turbidity, CD, DCOD and microstickies in both production environments. For NP production, removal efficiencies in TCOD were similar in both units; however, in LWC manufacturing better results were obtained after the UF. Solids removal efficiencies in DAF cells are normally better with increased

1 solids in the feed stream. The greatest difference in performance between the units
 2 concerned CD and DCOD, which were not affected at all by the DAF operation, but
 3 decreased around 10% (NP), 80% (LWC) and 20% (NP), 60% (LWC), respectively,
 4 through the UF unit. According to Brun and Carré (31), the removal efficiency of
 5 colloidal substances in DAF cells, measured in terms of CD, can vary between 10 and
 6 40%, but dissolved and colloidal matter of inorganic and biological nature is hardly
 7 affected. This could mean that the filtrates obtained in the disk filter are mainly formed
 8 by these last substances. Reaching high percentages of CD and DCOD removal is an
 9 important aspect to prevent deposits promoted by stickies.



10 **Fig. 4.** Removal efficiencies in DAF and UF units depending on paper production.
 11
 12

13 **4.2 Effect of water quality on the efficiency of DAF and UF units** 14

15 The second objective of this study was to compare the efficiencies of both units after
 16 different operation times (120 and 312 h of operation since the start-up of the paper
 17 mill) during LWC production, corresponding to trials 1 and 2 in Table 1. Table 3 shows
 18 both the water chemical characterization at the inlet and outlet of both units, and the
 19 percentage increase of each contaminant at the longer operation time (from 120 up to
 20 312 h). The accumulation in time of each contaminant is calculated using the Equation
 21 [2].

1

$$2 \quad \text{Accumulation (\%)} = \frac{X_{f_{312}} - X_{f_{120}}}{X_{f_{120}}} \cdot 100 \quad [2]$$

3

4 Where $X_{f_{312}}$ represents the measured parameter in the feed stream after 312h operation;
5 and $X_{f_{120}}$ means the measured parameter in the feed stream after 120h operation.

6

7 **Table 3.** Water characterization in DAF and UF units depending on running time during
8 LWC production.

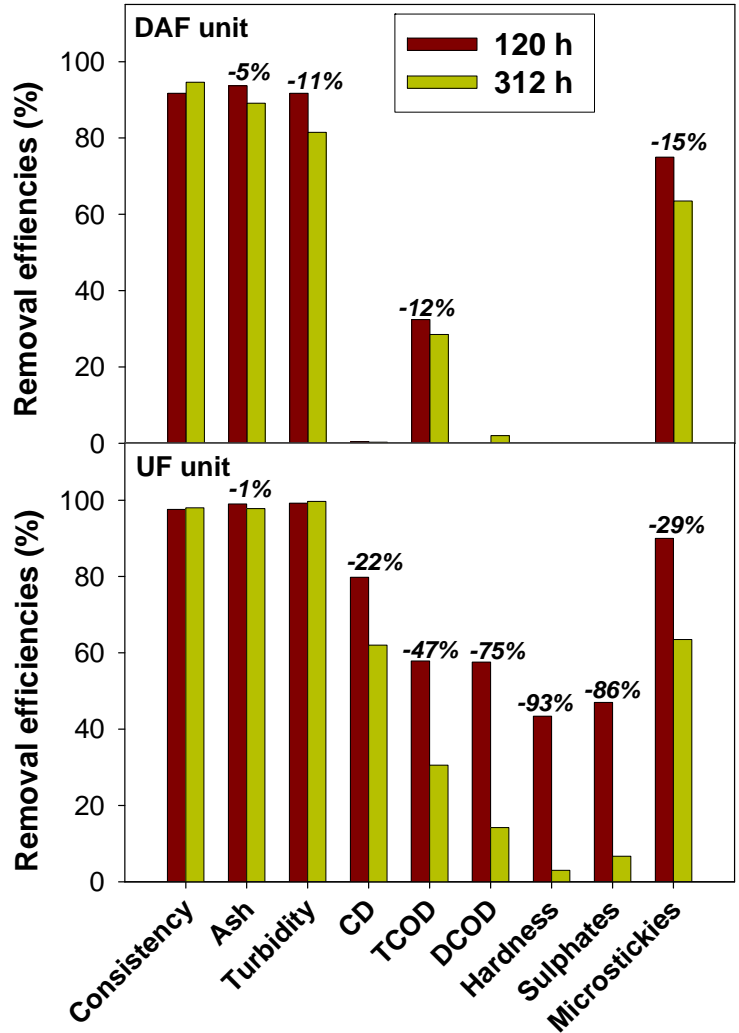
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	DAF				UF		
	Running time	Feed (1)	Accumulation (%)	Accept (2)	Feed (3)	Accumulation (%)	Permeate (4)
Consistency (%)	120 h	0.036	106	0.003	0.041	34	0.001
	312 h	0.074		0.004	0.055		0.001
Ash (mg/L)	120 h	111	74	7	196	38	2
	312 h	193		21	271		6
Turbidity (NTU)	120 h	739	-15	62	634	56	5
	312 h	627		116	987		2
CD ($\mu\text{eq/L}$)	120 h	370	107	368	247	206	50
	312 h	766		764	757		288
TCOD (mg/L)	120 h	1155	70	781	657	167	277
	312 h	1969		1408	1755		1218
DCOD (mg/L)	120 h	712	88	710	628	128	266
	312 h	1339		1312	1434		1231
Hardness (mg/L)	120 h	151	-17	157	131	4	74
	312 h	126		137	136		132
Sulphates (mg/L)	120 h	198	368	198	386	168	203
	312 h	927		957	1035		965
Microstickies (mm^2/L)	120 h	459	14	115	1311	41	145
	312 h	521		190	1846		186

10

11 As expected, the quality of the inlet stream got worse with operation time. Furthermore,
12 considerable variability in the process is observed in some cases. For example,
13 parameters such as CD and sulphates at both, DAF and UF inlet streams, increase over
14 100%.

1 Figure 5 shows the removal efficiencies of both units. After 312 h of operation, DAF
 2 lost 5 to 15% of its efficiency in ash, turbidity, TCOD and microstickies removal, while
 3 CD, DCOD, hardness and sulphates were not removed at all. To the contrary, the
 4 operation time did not affect consistency, ash and turbidity removal efficiencies in the
 5 UF, but it affected in an important manner DCOD, hardness and sulphates removal
 6 efficiencies, which were reduced more than 70%.
 7



8
 9 **Fig. 5.** Removal efficiencies for DAF and UF at different operation times.
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 11

12 **4.3 Study of the UF unit**

13
 14 **4.3.1 Variability of the UF process**

15
 16 The variability of the UF process was assessed by the performance of two samplings
 17 carried out at the same conditions: LWC paper production and 120 h of operation after
 18 the starting-up (trials 2 and 3 in Table 1). Variability of water quality (RSD) was
 19 determined by Equation [3] (32). Table 4 shows the average parameter of water
 20 characterization at the inlet and outlet streams, the percentage of water quality
 21 variability and the removal efficiency of each parameter.
 22

$$\pm RSD(\%) = \frac{X_i - \bar{X}}{\bar{X}} \cdot 100 \quad [3]$$

Where, *RSD* is the variability of water quality (%); X_i represents the measured value; and \bar{X} represents the mean value of the two measurements (three in microstickies) of the parameter being considered.

Table 4. Variabilities of water quality and UF removal efficiencies.

	Average feed (3)	Average permeate (4)	Average efficiency (%)
Consistency (%)	0.039±0.001 (4% RSD)	0.0015±0.0005 (33% RSD)	96.2±1.5 (2% RSD)
Ash (mg/L)	178±18 (10% RSD)	3.5±1.5 (43% RSD)	98.0±1 (1% RSD)
Turbidity (NTU)	398±236 (60% RSD)	4±1.0 (25% RSD)	98.8±0.4 (0.5% RSD)
CD (µeq/L)	296±49 (17% RSD)	91.5±41.5 (45% RSD)	70.7±9.1 (13% RSD)
TCOD (mg/L)	793±136 (17% RSD)	525±248 (47% RSD)	37.4±20.5 (55% RSD)
DCOD (mg/L)	775±147 (19% RSD)	472.5±206.5 (44% RSD)	42.0±15.6 (37% RSD)
Hardness (mg/L)	146±15 (10% RSD)	107±33 (31% RSD)	28.0±15.4 (55% RSD)
Sulphates (mg/L)	229±157 (69% RSD)	135.5±67.5 (50% RSD)	25.7±21.3 (83% RSD)
Microstickies (mm ² /L)	762±549 (72% RSD)	121±24 (20% RSD)	72.5±17.5 (24% RSD)

Most of the parameters (consistency, ash, CD, TCOD, DCOD and hardness) of the feed showed 15% of variability. However, turbidity, sulphates and microstickies resulted in variabilities higher than 60%. These variations depend on the specific quality of the raw materials within the same recycled paper grade. However the variability of the permeate parameters is higher than 20% in all cases.

There is not a correlation between the variability of the feed or the permeate parameters and of the UF efficiency. For example, although turbidity varied 60% respecting its

1 mean value, the efficiency of the UF reflected a variability of 0.5% from the mean.
2 However, hardness variability was 10% and the removal efficiency varied 55%.
3 Therefore, independently of the consistency, ash and turbidity values in the feed stream,
4 the UF achieves removal efficiencies higher than 50%.

5
6 It is known that membranes are built on different layers with a varied pore size
7 distribution (33). In fact, as a result of the mercury porosimetry, the structure of the UF
8 membranes analyzed in this study is based on three differentiate layers: (a) the support
9 layer with an average pore size of 3 μm ; (b) an intermediate layer with an average pore
10 size of 0.4 μm ; and (3) the active layer with pore sizes between 0.1 and 0.005 μm .

11
12 The active layer does not have a fixed cut-off limit for the matter present in water, and
13 this explain why large colloidal and particulate material, represented by consistency and
14 turbidity, is better removed and with a lower variability, than small colloidal and
15 dissolved particles.

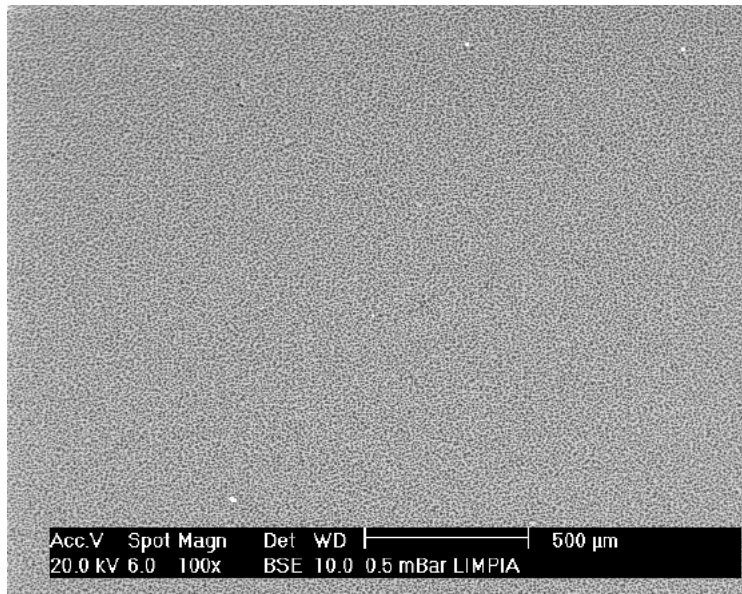
16 17 **4.3.2 Autopsy of the UF membranes**

18
19 After developing all the previous study, two important questions come out: why
20 removal efficiencies in DCM are lower during NP production? and why the operation
21 time affected UF removal efficiencies at short times?

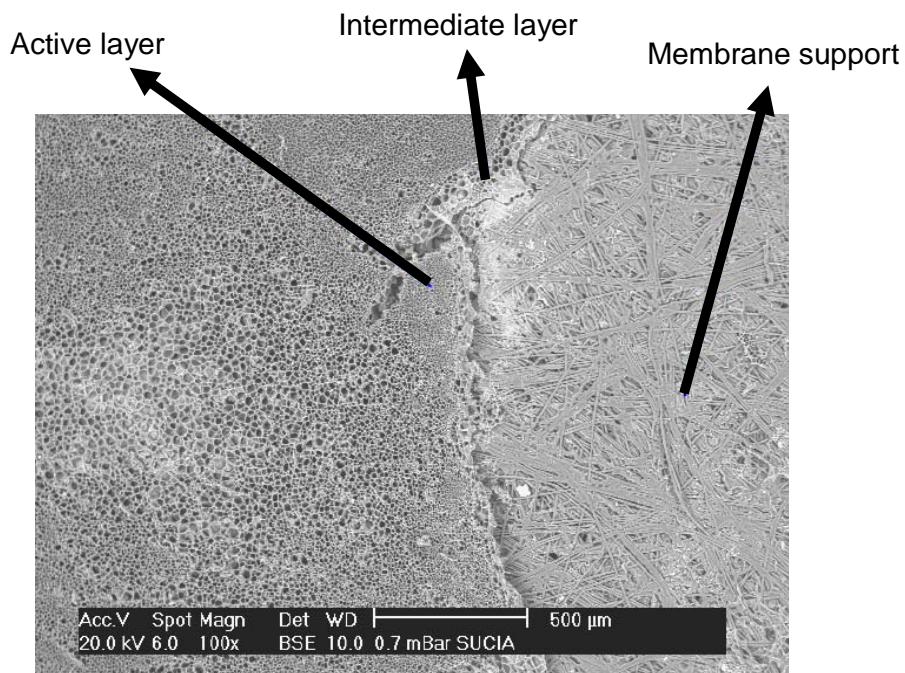
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23 An autopsy of the used membranes was done after finishing the trials. Figure 6 shows
24 two microphotographs of the membrane surface before (Figure 6a) and after (Figure 6b)
25 using it.

26
27 The three different membrane layers mentioned in section 4.3.1 are distinguished in
28 Figure 6b; where it can be concluded that the active layer of the membrane was
29 completely degraded in the areas where the support is visible. This degradation is a
30 consequence of the abrasive effect of the suspended solids (cellulose fibres and fines)
31 present in the clear filtrate stream.

32
33 As the active layer is destroyed, DCM goes easily through the membrane, detecting
34 higher CD and DCOD values in the permeate. The TSS and ash content during NP is
35 higher than in LWC production, so the mentioned erosion is more accused in the first
36 process. As the operating time increases, the membranes pass more time in contact with
37 water so, again, this damage is more marked at higher operation times. This damage on
38 active layer also explains the great variability on the removal efficiencies of CD and
39 DCOD shown in Table 4, as the intermediate and support layers have pore sizes of
40 bigger size.



(a)



(b)

Fig. 6. Electronic microscope photographs of:
(a) fresh membrane; (b) used membrane.

5. CONCLUSIONS

The UF unit presented higher removal efficiencies than the DAF unit for parameters such as ash, turbidity, CD, DCOD and microstickies in all productions studied, independently of inlet water contamination load. DAF unit did not affect CD and

1 DCOD, while UF reduced CD a 10% (NP) 80% (LWC) and DOC_D a 20% (NP) 60%
2 (LWC), respectively.

3
4 The UF was more sensitive to the operation time than the DAF, which kept nearly the
5 same removal efficiencies after 312 h of running. As the operation time increased, the
6 UF gave worse removal efficiencies for dissolved fraction than for the colloidal
7 fraction. The cause of this phenomenon was the erosion of the active layer produced by
8 the suspended solids present in the clear filtrate stream. Therefore more resistant
9 membranes need to be used for this application.

10
11 The variability of UF removal efficiencies depended of the measured parameter; the
12 system had a high efficiency reproducibility for consistency, ash and turbidity (around
13 1%), but parameters as TCOD, hardness or sulphates gave efficiency deviations up to
14 50%, which is related to the specific quality of the raw materials. Further studies will be
15 carried out since this variability may affect key effluent parameters as in the case of the
16 sulphates limit in the Community of Madrid.

17
18 The autopsy of the membranes shows that the active layer is destroyed due to the
19 abrasive effect of the suspended solids (cellulose fibres and fines) present in the streams
20 and to the contact with water at higher operation times. For these reasons, DCM goes
21 easily through the membrane, obtaining higher CD and DCOD values in the permeate.

22 23 **ACKNOWLEDGEMENTS**

24
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