Pitch adsorption on natural and modified talcs

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Abstract

Talc is used traditionally for pitch control in papermaking. The effectiveness of talcs as control agent of dissolved and colloidal pitch depends on its structural and surface characteristics of minerals. Talcs are modified by thermal and surface treatments to obtain different properties e.g specific surface, surface energy, surface charge and ratio lypophilic/hydrophilic surface.

Five commercial talcs have been tested to determine its capacity to adsorb the lypophilic contaminants by experiments of adsorption isotherms. The talcs correspond to two groups of different mineralogical compositions: one with high concentration of talc and some dolomite; and the other, with medium concentrations of talc and chlorite.

Colloidal dispersions of extractives were obtained by extraction of *Eucalyptus globulus* wood at pilot plant scale with acetone, evaporation of the solvent and reextraction with hexane to increase the selectivity of lypophillic compound extraction.

The isotherms of adsorption of the pitch dispersions were carried out at 50ºC on the different talcs. The adsorption took place by a mechanism of colloidal adsorption and the results obtained were adjusted to the Langmuir equation.

Results show that talc addition to bleaching waters or process waters can produce high reductions of colloidal pitch concentrations, at comparatively low doses.
Keywords: Talc, modified talc, pitch, pitch control, wood extractives

Introduction

Wood extractives are compounds from the vegetable metabolism which are present in different proportions depending on the wood species, its genetic characteristics and environmental factors during the growth and seasoning. Lipophilic wood extractives consist of complex mixtures of many different compounds, from low-molecular-mass fatty acids to the high-molecular-mass waxes, steryl esters and triglycerides and the different classes of extractives have different chemical behaviour during and after the pulping. The most of these compounds are removed with black liquors during chemical pulp production, while the proportion in mechanical and thermo-mechanical pulps is higher (1).

Wood extractives may be retained in the pulps as dissolved material or as micelles in dispersion adsorbed onto the pulp, specially, in mechanical pulps.

Wood extractives can be removed with washing waters when they are in dissolved form or in dispersion. However, during bleaching, the oxidant treatment stages and the extraction stages produce change in the pH and in salt concentration (ionic force) which origin the extractive destabilization from the pulps, forming sticky deposits called ñpitchò deposits.

On the other hand, the presence of extractives in washing waters reduces the re-use and recirculation possibilities due to the possible extractive destabilization and pitch formation.

The accumulation of small amounts of wood extractives can result in blockages causing shutdown. These blockages have long been a serious problem in the industry and are responsible for reduced production levels, higher equipment maintenance costs, higher operational costs and increased incidence of quality defects.

Talc as control agent in papermaking

Talc is one of the additives used traditionally for pitch control. Talc is a mineral composed of hydrated magnesium silicate with the chemical formula $Mg_3Si_4O_{10}(OH)_2$. Theoretically, talc contains 31,7% MgO, 63,5% SiO_3 and 4,8% H_2O. Its elementary sheet is composed of a layer of magnesium-oxygen/hydroxyl octahedra or brucite -$Mg(OH)_2$- sandwiched between two layers of silicon-oxygen tetrahedra -SiO_2-. The main or basal surfaces of this elementary sheet do not contain hydroxyl groups or active ions, which explains talc's hydrophobicity and inertness. The size of an individual talc platelet (= a few thousand elementary sheets) can vary from approximately 1 micron to over 100 microns depending on the deposit. It is this individual platelet size that determines a talc's lamellarity. A highly lamellar talc has large individual platelets whereas a compact (microcrystalline) talc's platelets are much smaller. The elementary sheets are stacked on top of one another, like flaky pastry, and because the binding forces (Van der Waal's forces) linking one elementary sheet to its neighbors are very weak, the platelets slide apart at the slightest touch, giving talc its characteristic softness (2, 3, 4, 5, 6).

Talc ores differ according to their mineralogical composition, i.e. the type and proportion of associated minerals present. Although talc is often found with other minerals such as carbonates, the most common related mineral is chlorite. Chlorite is a hydrated magnesium and aluminium silicate with the chemical formula (Mg_{6-x-y} Fe_y Al_x) O_{10} $(OH)_8$. Chlorites are present in varying proportions in several deposits (from 2% to 50%). They are structurally and chemically very similar to talc (talc is a hydrated magnesium silicate and chlorite a hydrated magnesium and aluminium silicate). Each type of chlorite is determined by its aluminium and iron contents. Like talc, chlorites are soft, lamellar and organophilic (having an affinity with organic substances). However, they are a little more reactive than talc and more hydrophilic. Quantitative differences are shown in surface energy, ratio hidrophilic/lipophilic surfaces, charge and zeta potential of their suspensions (3).

Each mineral layer is neutral electrically and adjacent layers are joint by Van der Waal forces, relatively weak forces, without electrostatic interactions.

The talc efficiency as control agent of the dissolved and colloidal pitch depends on the structural and surface characteristics of the minerals, and on the thermal and surface treatments that also determine properties as specific surface, surface energy, charge and ratio hidrophilic/lipophilic surface.

From point of view of dissolved and colloidal control in waters of the pulp and papermaking, the remove of contaminants by talc addition takes place by adsorption of micelles, particles, molecules or ions of these contaminants on talc surfaces. The control efficiency depends on the surfaces properties of talc used and on the physic-chemical nature of the contaminant.

In natural talcs, the specific surface increases with the mineral talc content, with the milling size and with the layer delaminating due to the mechanic action during the milling. Certain grades of talc are treated for certain applications. Their surfaces are modified in order to increase the specific surface by thermal and chemical activation treatments.

In general, talcs are characterized by low values of surface energy which is related to its hidrophobicity and determines the contact angle of the lipophilic contaminant micelles in the aqueous emulsion on talc surfaces.

There is a direct relationship between the capacity of the talcs to retain or passivate these lipophilic contaminants present in pulp and paper waters and its surface energy. In natural talcs, the surface energy decreases and the lipophilic character increases when mineral talc content increases. Inversely, the surface energy increases with the chlorite mineral content in the talc. The surface charge is very important for the retention of the anionic dissolved and colloidal material.

The lipophilic/hydrophobic surfaces ratio is a property also related to the mineralogical composition of talc. Their values are maximum in talc with a high content of mineral talc and decrease with the chlorite content. This property also increases with the delaminating during the milling due to the basal surfaces are hydrophobic and the edges are hydrophilic (7, 8). The lipophilic/hydrophobic surfaces ratio determines its difficulty to be dispersed in water. When the ratio basal/edge surfaces decreases, the proportion of silanol groups, which containing silicon atoms to which hydroxy substituents bond directly, in edges is higher and which interact with the water by hydrogen bridges favouring the talc particle dispersion in polar liquids as water. Although the retention capacity of the lypophilic material by the talc is related to its basal surface, the talc properties for the dissolved and colloidal material control depend on the dispersion capacity of the talc in aqueous medium with the retained material on its surface (3).

Natural talcs are anionic with zeta potentials which vary with the mineralogical composition from -70mV, in talcs with high content in mineral talc, until -55 mV, in talcs with chlorite content about 50%. The talc surfaces can be modified by fixation of cationic compounds, as quaternary ammonium salts, by physic or chemical adsorption. In these cases, the sign of the zeta potential is changed to positive values (from +30mV until +45 mV). These talcs are especially suitable for the anionic trash control and their actuation mechanism is based in the electrostatic retention of the colloidal material, justified by DLVO theory. Simultaneously to this property, the talcs maintain part of retention characteristics of the lypophilic material based on the low surface energy (9). Therefore, two retention mechanisms of detrimental material from pulp suspensions may take place: adsorption mechanism and detackification mechanism. The detackification mechanism occurs firstly throught immobilization of the sticy meaterials (6).

Adsorption mechanism

Colloidal adsorption processes are being studied in areas such as nanotechnology for obtaining coatings with uniform distributions of solids and as biotechnology for the study of the interaction between proteins and membranes. The Random Sequential Adsorption model (RSA) (10) has served as approach to describe the irreversible adsorption of the colloidal particles on solids surfaces, and the diffusinal deposition of colloidal particles whit electrostatic interactions (11).

Monolayer deposition and of self-assembly process, many deposits in nanotechnology are a structured on pre-pattern surface in such a way that each arriving depositing micelle is attached to form a regular pattern (12). More realistically, is the disordered ramdon stochastic deposition.

The fraction of the area covered by particles ɗ is defined as:

ɗ =*n* ´ **û*a*ü**^{2} (1)

where n is defined as the surface density and **û*a*ü** is the second moment of the radius distribution of adsorbed particles. According to this model, the maximum fraction of the area covered by particles is known as ñjamming limitò (**ɗ**$_{jam}$). In the case of spheres or rigid discs monodispersed, **ɗ**$_{jam}$ =0,547, deduced from the simulation Monte Carlo.

RSA models are coincident with the postulated in the Langmuir adsorption model: irreversible adsorption and maximum adsorption surface of the dispersed particles on the adsorbent and blocking the filled surface sites with molecules or particles. Therefore, the maximum adsorbed mass per unit surface is limited by the monolayer thickness, which justifies that this model is used to explain the colloidal adsorption.

Other models, based on "no-sequential kinetics in irreversible colloidal adsorption", can be used to describe the colloidal pitch adsorption (13).

As it has been explain, in the adsorption of light molecules, the maximum adsorbed mass per unit adsorbent mass, is given as the monolayer mass obtained form the surface BET. In the case of macromolecules adsorption or micelles adsorption on microporous solids, the access to inner porous is a limitation to the adsorption.

The surface BET of talc is low comparatively with other adsorbent. The talc has not appreciable micro or meso porosity and the surface area for adsorption is practically the external surface resultant of grinding and cleavage of mineral.

Colloidal adsorption processes can be modelled in a variety of ways. However, many of these are coincident with the simplest and oldest model of Langmuir which takes into account the finite amount of space available on a surface. The Langmuir isotherm displays a linear response to particle (or molecular) concentration in the regime of low coverage and saturation at high surface coverage (14). The Langmuir model requires only the relative rates of adsorption and desorption and the saturation coverage to predict equilibrium coverages (15).

Materials and methods

Characteristics of the studied talcs

In the experimentation carried out, five commercial talcs have been used. The talcs correspond to two groups of different mineralogical compositions: A, with high concentration of talc and some dolomite; and B, with medium concentrations of talc and chlorite.

The A group is formed by a natural talc (A) and anionic (A-T) and cationic (A-K) talcs modified superficially. The B group is formed by a natural anionic talc (B) and a modified cationic talc (B-K). Theses talcs have been characterized by X Ray Diffraction, Scanning Electron Microscopy and Analysis by Dispersive Energies, zeta potential and surface area measurements (table I and II).

Table I. Mineralogical composition of talcs (%)

Mineral	A	A-T	A-K	B	B-K
Talc (1) $Mg_3Si_4O_{10}(OH)_2$	85,4	82,4	94,3	61,7	55,7
Talc (2) $Mg_3Si_4O_{11}nH_2O$	13,2	16,0	-	-	-
Dolomite $CaMg(CO_3)_2$	1,3	1,5	4,2	-	-
Calcite $CaCO_3$	-	-	0,3	-	-
Quarz SiO_2	0,1	1,5	0,3	0,5	0,4
Clinochlore $Mg_5Al(Si_3Al)O_{10}(OH)_8$	-	-	-	37,0	42,1

Ferrous and calcium oxide $Ca_2Fe_7O_{11}$	-	-	-	0,9	1,8

Table II. Physic properties of talcs

Talc	**A**	**A-T**	**A-K**	**B**	**B-K**
Specific area BET (m^2/g)	12	14	12	8,5	8,5
Density (g/cm^3)	2.80	2.78	2.80	2.78	2.78
Hardness (Mohs)	1	1	1	1-2	1-2
Zeta potential (mV)	-69	-69	+45	-55	+30
H_2O adsorbed (%)	15 at 120ºC	<1	1 at 120ºC	>0,5	>0,5
pH (dispersion 10%)	9	8,5	9	9,5	9,5
d_{50} (εm)	4,2	4,5	4,2	3,5	3,5

Preparation and characterization of pitch dispersions

The colloidal dispersions of extractives were obtained by extraction of *Eucalyptus globulus* wood sawdust from a pulp mill in North Spain at pilot plant scale with acetone (30 L), evaporation of the solvent and reextraction with hexane in order to increase the selectivity of lypophillic compound extraction, according to standard SCAN-CN 50:93. After, the solvent was evaporated in a rotary evaporator. Colloidal dispersions were obtained after alkaline hydrolysis with KOH solution and a new extraction of lipophilic compounds with hexane. A concentrated solution of pitch in acetone is obtained by evaporation until a 3000 mg/L concentration. Pitch dispersions are obtained by dilution of this concentrated solution with water.

The analysis of extractives in the aqueous samples was carried out by a chromatograph Varian 3800 GC with a detector FID, coupled with a Varian 8200 Autosampler and with injector for liquids 1079 Universal Capillary Injector. The capillary column has a 15 m length and a 0,53 mm diameter and a film thickness 0,15 μm. The chromatograph was programmed from 100ºC (0,5 min) to 340ºC at a rate of 12ºC/min. The injector was programmed from 100ºC (0,5 min) to 340 ºC at 200ºC/min.

The solvent used for liquid-liquid extraction was methyl-terbutyl-ether (MTBE) containing four internal standards: 1,3-dipalmitoil-2-oleilglycerol ($C_{53}H_{11}O_6$), for the identification and quantification of triglycerides; henicosanoic acid ($C_{21}H_{42}O_2$), for the identification and quantification of organic acids; cholesteryl heptadecanoate ($C_{44}H_{78}O_2$), for the identification and quantification of steryl-esters; and betulinol for the identification and quantification of sterols. Silylation was the used derivatization technique using a combination of BSA (N,O-bis(trimethylsilyl)acetamide) and TMCS (trimethylchlorosilane) as silylating reagents.

Adsorption isotherms

Experiments of adsorption isotherms were carried out to determine the capacity of the talcs to adsorb the lypophilic contaminants. The isotherms of adsorption of the pitch dispersions were carried out at 50ºC on the different talcs. Therefore, a set of adsorption equilibrium essays were performed by adding pitch dispersions at different concentrations to a talc slurry at 1000 mg/L. Initial pitch concentration is given by the mass of pitch added in the volume of pitch dispersion and talc slurry .Talc concentration is equal to 1000 mg/L multiplied by volume of talc slurry/ volume of pitch dispersion plus talc slurry ratio. Once added the pitch to the talc slurry the mix was agitated for 2 hours. After the samples were centrifuged during 15 minutes at 1500 rpm, 10 mL of supernatant were extracted with 10 ml of MTBE. When the phases were separated, 5 mL of organic phase were analyzed by gas chromatography.

Results and discussion

Characterization of extractives

Results of the extractive characterization are shown in table III. The composition of the lypophilic fraction determined by GC is shown in figure 1. The extractive content of the *Eucalyptus globulus* wood used in this experimentation is very low comparing with other same genus species. This justifies the need to use a pilot plant extractor.

Table III.- Composition of *Eucalyptus globulus* extractives

Total extractives (%)	0,75±0,5
Total lypophilic fraction (%)	0,10
Lypophilic fraction on total extractives (%)	13,50

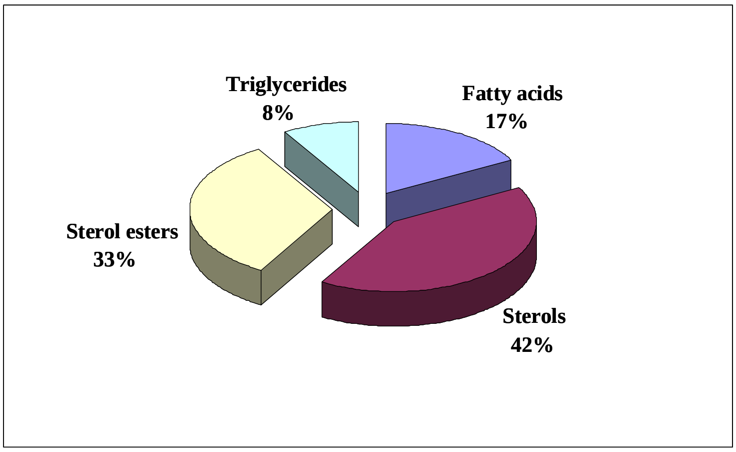

Figure 1.- Composition of lypophilic fraction in the hydrolyzed extract

Adsorption of extractives on talcs

The adsorption of extractives on talc surface is the main mechanism for the fixation and passivation.

The experiments were carried out in neutral and in alkaline conditions, adding KOH 0,5N, to study the effect of the pH on the talc adsorption.

In the equilibrium, extractive concentration is expressed as C_e and the extractive mass adsorbed (mg) per talc mass (g) is expressed as $\Gamma$and calculated as:

$$\Gamma_{ads} = \frac{C_0 - C_e}{Talc(g)} \times V_{total} \qquad (2)$$

Where:

Γ_{ads}: adsorbed mass per adsorbate mass unit of talc (mg/g)
C_0: initial concentration of pitch dispersion (mg/L)
C_e: equilibrium concentration of pitch dispersion (mg/L)
V_{total}: volume of pitch + volume of talc slurry (mL)

The pitch constituents tested has low solubility in water and form micelles. In the chromatographic analysis, there is not a significant variation in the organic material extracted composition before and after adsorption. Then, these compounds are adsorbed in the same proportions, confirming that the adsorption is carried out through dispersed micelles and the dissolved molecular constituents are not adsorbed. If the adsorption were molecular each of the dissolved components would be adsorbed in different proportions. For example, if the sterols were adsorbed at a higher degree than the fatty acids, the relative composition of these components in liquid phase would be different than the initial one. This conclusion also confirms the low solubility of the pitch components and the high proportion of them adsorbed. The adsorption of pitch on talc surface can occur according to figure 2.

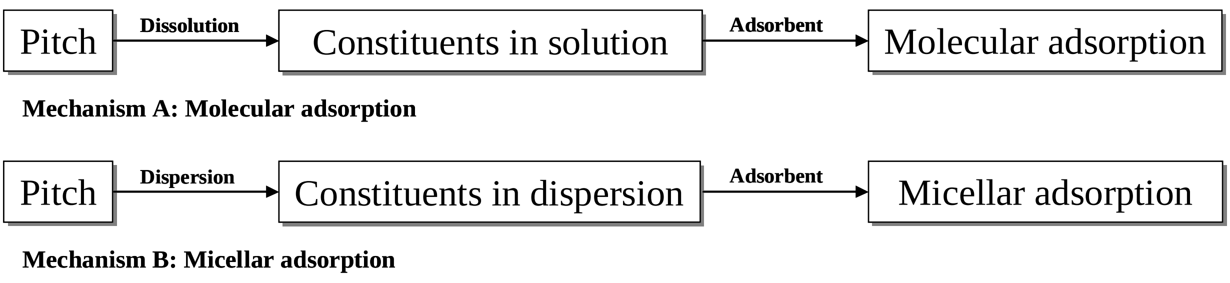

Figure 2.- Adsorption mechanism

In the studied cases in this paper, the expression for the Langmuir adsorption isotherm is:

$$\Gamma_{ads} = \frac{\Gamma_{max} K C_e}{1 + K C_e} \qquad (3)$$

Where:

$\tilde{u}_{ads}$: adsorbed pitch mass per mass unit of talc (mg/g)
$\tilde{u}_{max}$: maximum adsorption (mg/g)
C_e: equilibrium concentration of pitch dispersion (mg/L)
K: Langmuir equilibrium constant $(mg/L)^{-1}$

The figures 3 to 6 show the adsorption isotherm of talcs A and B at pH 7 and pH 9, respectively.

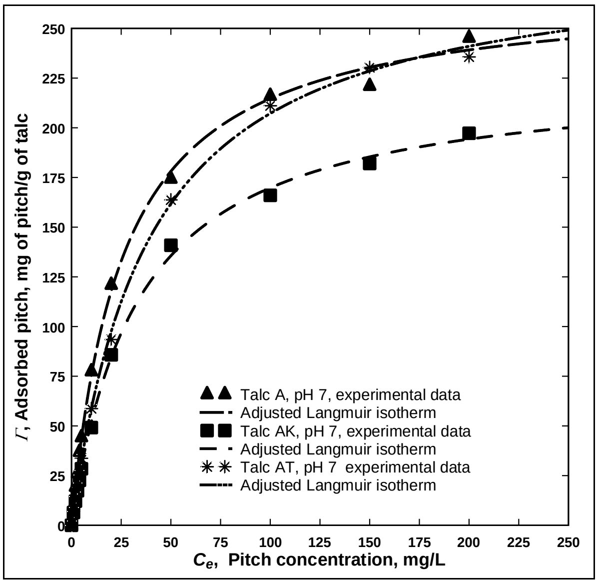

Figure 3. Adsorption isotherms of talcs A at pH 7

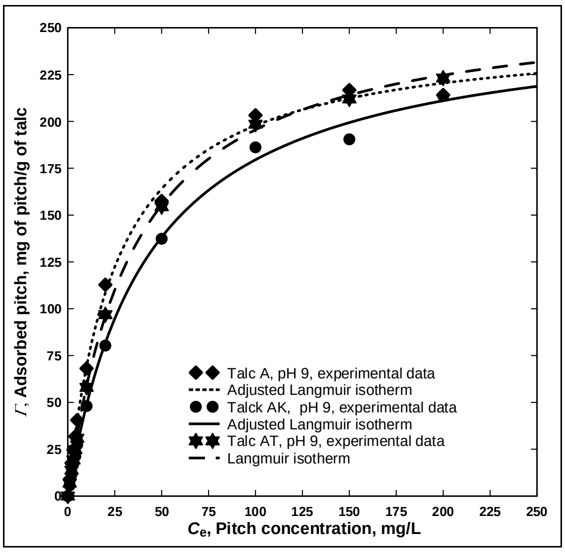

Figure 4. Adsorption isotherms of talcs A at pH 9.

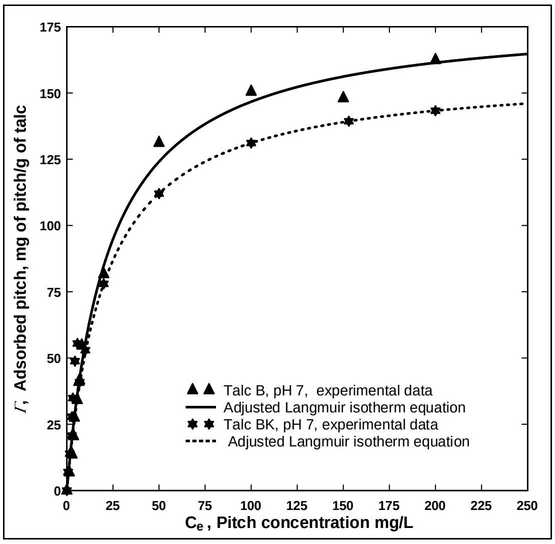

Figure 5. Adsorption isotherms of talcs B at pH 7.

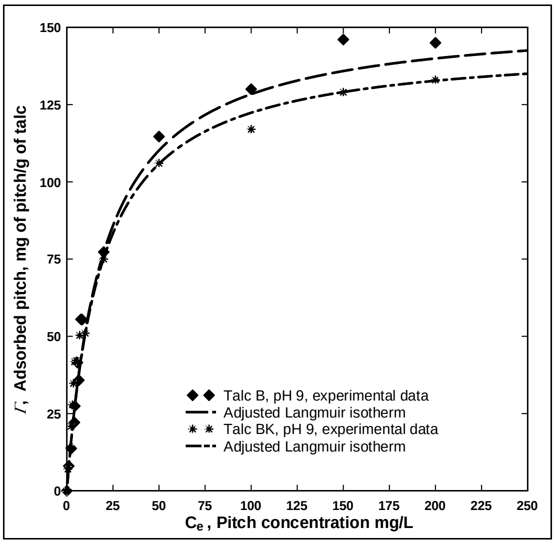

Figure 6. Adsorption isotherms of talcs A at pH 9

pH has low effect in the adsorption due the lipophility of the pitch used in this study, with the only exception of cationic talc AK, having a high talc proportion.

The slopes in origin of the adjusted Langmuir equations, deduced by derivation, are a measurement of the talc adsorption capacity at low concentrations. These slopes show the possibility to get a low final concentration of pitch, with the addition of comparative low mass of talc per cubic meter of treated process water. When the slope of the Langmuir isotherm of a talc is higher, the talc depuration capacity at low pitch concentration of that talc will be higher. Table IV shows the Langmuir equation parameters.

Table IV. Langmuir equation parameters

Talc	pH	ũ max (mg/g)	K $(mg/g)^{-1}$	Slope in origin
A	7	270	$3,88\ 10^{-2}$	10,48
	9	249	$3,86\ 10^{-2}$	9,61
AK	7	227	$2,97\ 10^{-2}$	6,74
	9	256	$2,35\ 10^{-2}$	6,01
AT	7	288	$2,56\ 10^{-2}$	7,38
	9	264	$2,86\ 10^{-2}$	7,54
B	7	179	$4,49\ 10^{-2}$	8,05
	9	154	$5,05\ 10^{-2}$	7,78
BK	7	158	$4,88\ 10^{-2}$	7,71
	9	145	$5,41\ 10^{-2}$	7,84

Figure 7 shows the Langmuir constant for each of the talcs studied at pH 7 and 9.

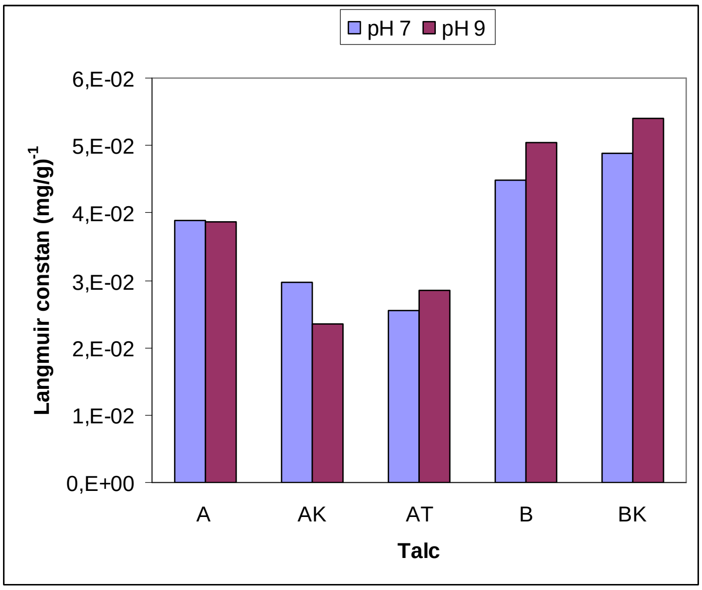

Figure 7 . Langmuir constant, at 50ºC, for different talcs

The property of talc having the greatest influence on their capacity to adsorpt pitch is its mineral composition (lipophilic surface). A group talcs, with a higher talc proportion than those of the group B, have the highest adsorption capacity of the talcs studied.

The maximum adsorption capacity is related to the greatest specific surface what corresponds to the highest proportions of talc (figure 8).

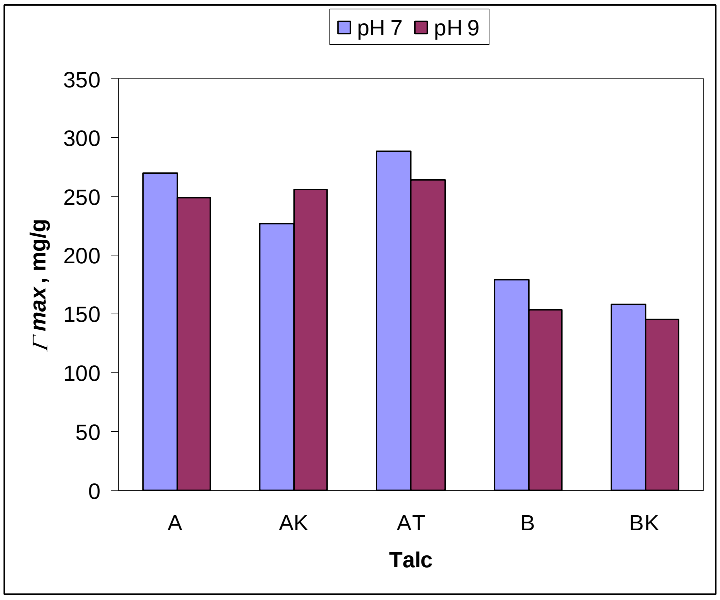

Figure 8. Maximum capacity of adsorption, at 50ºC, for different talcs

The maximum capacity of talc to adsorpt monolayer pitch micelle depositions are related to the lipophilic portion of the BET surface area. The adsorption capacity of pitch in talcs A is related to the amount of talc present in the mineral, having this a greater influence than the cationic or thermal surface treatment applied to the talc.

Talcs B, with a medium talc proportion and higher proportion of chlorite, have less specific surface, and most of this is hydrophilic, (more easily dispersible in water). This asymptotic pitch concentration is higher than pitch concentrations in process water in pulp and paper mills.

In general, talc cationization has a negative effect on pitch adsorption; the reason for this is the competition between the cationiozing agent and the pitch for the talc surface. The polyelectrolytes (with the charge in the ammonium group of the quaternary salt) are adsorbed on talc in one position that could be occupied by pitch micelles, without inducing an increase in the adsorption capacity due the effect of cationic charges on talc surface.

Application to the papermaking

As an example of application, the theoretical talc necessary to reach a 90% depuration of a white water having an initial concentration of extractives of 50 mg/L, has been calculated.

If the temperature and the extractive composition of white water are similar to the isotherm calculated with the experiments, the adsorbed extractive mass in equilibrium with final concentration of 5 mg/L can be calculated replacing this final concentration in the corresponding isotherm for each talc.

The extractive mass to be adsorbed to reach a depuration of 45 g/m^3 is divided by the adsorbed extractives in equilibrium with the final concentration. The talc mass necessary to reach this depuration, expressed as kg/m^3, is calculated from the latter.

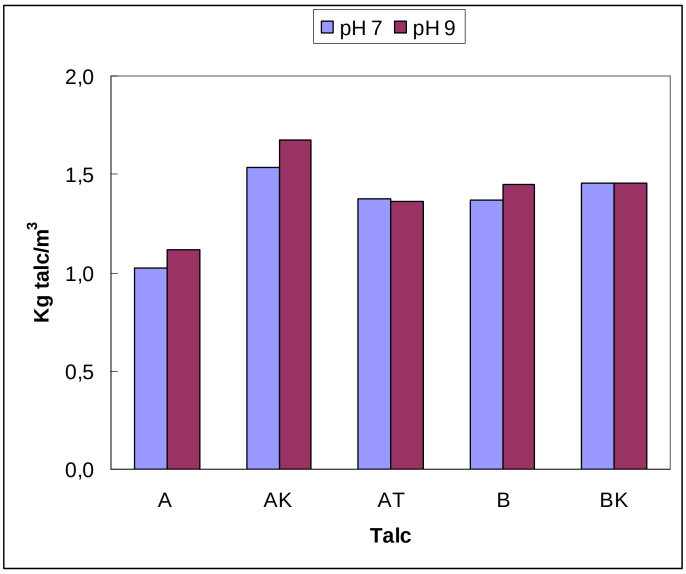

Figure 9. Talc necessary to remove 90% of pitch, in mill process waters with a initial concentration of 50 ppm

The talc dosages necessary to reach a depuration of pitch dispersions of 90% with an initial concentration of 50 mg/L are shown in figure 9. The final concentrations of pitch were decreased to 5 mg/L in all the experiments. Comparing the different groups of talc, talcs A showed the best preformance, being 1 kg/m^3 approximately the mass of talc required to reach the final concentration of pitch indicated above.

The alternative treatments are:

- one adsorption stage followed by a solid-liquid separation stage as filtration or centrifugation. Talc density, is in order of silica sand density 2.65 g/cm^3. Cyclonic separators can be operating whit good separation efficiency.

- to allow the talc to remain in the pulp avoiding its accumulation in the recirculated waters, and a negative effect on the subsequent stages and on the quality of paper.

Conclusions

In the experimental conditions, the pitch adsorption on talcs follows a micellar adsorption model that can be adjusted into a Langmuir equation.

The adsorption constants determined experimentally are related to the specific surface area and nature of the talc employed. The slope in the origin of the Langmuir equation determine the amount of talc necessary to lower the concentration of pitch in pulp mills and paper mills process water depuration.

In general talcs at low dosages can reduce the concentration of extractives contained in water process in papermaking.

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