

Influence of pH on the adsorption of dissolved and colloidal substances in a thermo-mechanical pulp filtrate onto talc

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SUMMARY: Talc is often used to control unwanted deposition of resins and wood processing derivatives in the wet end circuit of a paper mill. The effect of pH was studied on the adsorption of dissolved and colloidal substances originating from thermo-mechanical pulp (TMP) onto talc. In this study we investigate, for the first time, the influence of pH on the adsorption of wood resin on talc, dealing with the complex system of real pulp mill water without the presence of fibres, in the pH range of 4–9. It was found that with increasing pH the maximum loading of colloidal substances on the investigated talc grade decreased. The experimental evidence suggests that this was not simply an effect of the changing electrostatic stability of the colloids, but mainly the competition between soluble species and colloidal material. Analysis of the total organics by chemical oxygen demand allowed estimation of the competition of dissolved and colloidal substances for the adsorption onto talc. For the adsorption of the colloidal fraction, characterised by turbidity, a Langmuir adsorption isotherm provided a simplistic characterisation of the process.

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During the production of paper in a paper mill the wood resin is released from the wood during pulping. This wood resin, termed pitch, can detrimentally deposit on the paper and on the paper machine. These deposits mark the paper or can lead to a tear of the paper web involving a loss of output and a reduction in paper quality.

The chemical composition of wood resin is characterised by four classes of lipophilic components, namely fats and fatty acids, steryl esters and sterols, terpenoids, and waxes comprised of fatty alcohols and esters. Colloidal stabilisation of these compounds may occur through the surfactant

action of ligno-sulphonates and polysaccharides (Pelton et al. 1980; Sundberg et al. 1994; Sundberg et al. 1996; Wågberg, Ödberg 1991; Back, Allen 2000). Traditionally, alum ($K_2Al_2(SO_4)_4 \cdot 24 H_2O$) was used to bring the pH in the papermaking process into the acidic domain where colloidal resin coagulates onto fibres. This procedure enabled the colloidal material to be removed harmlessly from the circuit and carried out with the product. Today, increasingly, papermaking pH is either neutral or slightly alkaline, such that the removal of pitch is no longer an automatic corollary of the use of alum. The increase in pH to neutral or slightly alkaline is a growing trend in mechanical papers also, and so the study of pitch removal under these conditions is of increasing importance. Moreover, in the literature (Holmbom, Sundberg 2003) it is stated that mechanical pulps carry over much more dissolved and colloidal matter than chemical pulps and recycled pulps.

Several means are used to fight against pitch deposition. Talc is often used to control the deposition of pitch (Baak, Gill 1971; Parmentier 1973; Parmentier 1979; Dreisbach 1989; Douek, Allen 1991; Lee, Sumimoto 1991; Allen, Douek 1993; Allen et al. 1993). On the one hand talc is known to adsorb the colloidal stable pitch as single pitch droplets, preventing their possible agglomeration (Allen et al. 1993; Guera et al. 2005). On the other hand, talc has been described as a detackifier of already agglomerated pitch, effectively isolating the surface of the sticky pitch agglomerates (Gill 1974; Allen 1977; Allen et al. 1993). However, the literature does not explain satisfactorily the pitch and talc adsorption mechanism.

A part of the answer lies in the amphiphilic nature of talc. The bulk crystal structure of talc is terminated by two different kinds of surfaces usually denoted as basal and edge-face, respectively. Qualitatively, the two different types of surface can be described as being hydrophobic for the basal surface and hydrophilic for the edge surface. However, the terms hydrophobic and hydrophilic describe only the behaviour of a phase towards water. Following the suggestion of Fowkes (1963) the two terms can be written in a more quantitative form dividing the surface energy into an apolar

component and a polar component. Therefore, the surface energy γ^{Tot} of a phase i can be written as,

$$\gamma_i^{\text{Tot}} = \gamma_i^{\text{LW}} + \gamma_i^{\text{AB}} \quad [1]$$

$$\gamma_i^{\text{AB}} = 2\sqrt{\gamma_i^{\text{A}} \cdot \gamma_i^{\text{B}}} \quad [2]$$

in which the designation LW stands for Lifshitz-van der Waals, and summarises London, Keesom and Debye components (van Oss et al. 1988), and the polar component is best described by the Lewis acid-base (AB) theory. Values found in the literature for talc are reported in *Table 1*.

Table 1. Values of the interfacial surface free energy components of talc as reported by Giese et al. (1991).

Mineral	$\gamma^{\text{Tot}} / \text{mJm}^{-2}$	$\gamma^{\text{LW}} / \text{mJm}^{-2}$	$\gamma^{\text{A}} / \text{mJm}^{-2}$	$\gamma^{\text{B}} / \text{mJm}^{-2}$
Talc	36.6	31.5	2.4	2.7

Alternative values are given by Schrader and Yariv (1990), such as a Lifshitz-van der Waals component γ^{LW} of 35.5 mJm^{-2} for talc, and they separate the total surface interaction into a dispersive and non-dispersive component having the ratio 7:3. The remarkably low values for the Lewis acid-base components partly explain the observed hydrophobicity of the mineral in the presence of highly polar water molecules (Giese et al. 1991), but why such surface energies are observed cannot easily be explained by the crystal structure alone. The above mentioned values are reported for samples in ambient atmosphere and are therefore suitable to be considered in an aqueous environment. Values on the other hand for outgassed samples of talc are reported by Douillard et al. (1994) and Malandrini et al. (1997). Higher values for the apolar component γ^{LW} , but also for the polar components γ^{A} and γ^{B} , were measured, concluding, therefore, that outgassed talcs are highly polar compounds, essentially because of their high surface acidity. This is explained by open hexagonal cavities in the ring-like SiO surface structure, where the underlying O-atoms of the brucite layer are accessible for hydrogen bonding. When these active sites are blocked by adsorbed molecules (mainly gas) under ambient conditions, the whole layer is rendered hydrophobic (Michot et al. 1994). Furthermore, in the case of the edge surfaces, on which there is an adsorbed water layer, the acid sites of the Mg^+ sites are rendered inactive (Malandrini et al. 1997). It is, therefore, necessary to resort to an understanding of the nature of hydrophobic interactions. These have been variously described in terms of an adsorbed air layer present when contacted with water, or the generation of a gaseous phase by cavitation. Israelachvili and Pashley (1984) observed a long range interaction between

hydrophobic bodies immersed in water. The physical reasons for this phenomenon are discussed in the literature (Christenson, Claesson 1988; Parker, Claesson 1994; Carambassiss et al. 1998; Ederth et al. 1998). Recently, Kekkonen and Stenius (2001) reflected upon the role of hydrophobic interactions in relation to papermaking and the removal of detrimental organic compounds such as pitch. Wallqvist et al. (2006) measured the hydrophobic interaction with talc platelets using colloidal probe atomic force microscopy. They describe the approach of a hydrophobe toward the surface of talc inducing a force at close range. The force can then be extended on retraction of the probe to long range, suggesting a likely cavitation effect. This observation helps to explain why talc works in pitch control in respect to hydrophobic species, an issue that was not explainable using the DLVO theory based on “classical” charge interactions or surface structure-chemistry relationships alone.

In preceding work, the performance of different talc grades in the adsorption of wood resin constituents, as well as the influence of the available specific surface area of the mineral in the system, was presented (Guera et al. 2005). Furthermore, the closest structural relatives of talc in the family of phyllosilicates, chlorite and pyrophyllite, were tested and compared to the adsorption behaviour of talc (Gantenbein et al. 2009). During this work it emerged that the pH can be strongly influenced by the type of mineral added. Significant pH increase was observed after the addition of chlorite or pyrophyllite.

A large number of publications refer to the influence of the three factors, pH, temperature and calcium ion concentration ($[\text{Ca}^{2+}]$), on the adsorption efficiency of talc, or on pitch deposition (Allen, Filion 1996; Allen, Douek 1993; Douek, Allen 1991; Dreisbach, Michalopoulos 1989; Gustafsson et al. 1952; Hamilton, Lloyd 1984; Hassler 1988; Holmbom, Sundberg 2003; Kekkonen, Stenius 2001; Otero et al. 2000; Sihvonen et al. 1998; Trafford 1988; Otero et al. 2000). Some authors show that the affinity of wood resin constituents for talc is progressively weakened as pH increases (Hughes 1977; Hamilton, Lloyd 1984; Douek, Allen 1991; Allen, Douek 1993; Trafford 1988). These studies, however, were performed using model pitch suspensions, including single compound systems, or contained fibres, on which the pitch was coagulated at low pH.

A recent study investigated the effect of pH on the accumulation of fines and dissolved and colloidal substances in the short circulation water loop in papermaking (Lehmonen et al. 2009). Besides many

other findings, it was found that the effect on the pitch particle count is only moderate over the investigated pH range of 4 to 10, and that above pH 6 fatty acids, but especially resin acids, start to dissolve. This might also influence the adsorption behaviour of the wood resin onto a surface.

The pH mainly influences both the degree of saponification and the electrostatic stability of the colloids. Less deposition might normally be expected with increasing pH as more free acids would be available (Lehmonen et al. 2009), which could act as emulsifiers, but the opposite is observed in reality. The reason is predominantly the presence of Ca^{2+} ions which form, in combination with the free acids, insoluble Ca-soaps with a high tendency for deposition (Otero et al. 2000).

Within this overall context, it was the aim of this study to investigate the effect of pH on the adsorption process of dissolved and colloidal substances onto talc.

Adsorption modelling

A possible way to describe the adsorption properties of wood resin onto talc is the Langmuir (1916) isotherm (Rogan 1994; Hughes 1977). Langmuir described the interaction of single-component dilute gases with surfaces, whereas the current system is much more complicated. The application of the Langmuir isotherm to the current system is therefore merely a method of obtaining parameters by which the adsorption process can be characterised. The Langmuir isotherm relation can be written:

$$\Gamma = \frac{\Gamma_{\max} \cdot K_L \cdot c_{\text{eq}}}{1 + K_L \cdot c_{\text{eq}}} \quad [3]$$

where Γ is the loading of the sorbate on the adsorbent, Γ_{\max} is the maximum loading of the sorbate on the sorbent (reality) or total number of surface sites per mass sorbent (theory) – which is constant for given conditions, K is the Langmuir constant, defining the equilibrium constant of the sorption reaction – i.e. affinity, and c_{eq} is the equilibrium concentration of the sorbate.

The derivation of the Langmuir relation requires assumptions that (i) the sorbent has a limited total number of sorption sites and reaches saturation when they all are occupied, (ii) that the affinity of the sorbate for the sorbent remains constant over the whole concentration range, and (iii), which follows from (ii), that there is only a single layer of adsorption since adsorption of subsequent layers would be at a different affinity. In the present systems, (i) is reasonable, but there is no proof of (ii) and (iii), so the Langmuir coefficients obtained are operationally defined for the systems being studied. Colloidal systems containing adsorbates

and surfactants tend to adsorb in successive phases, and equations explicitly dealing with these successive phases have recently been derived and applied by Samiey and Golestan (2010).

Materials and Methods

Thermomechanical Pulp (TMP)

This study focuses on the colloidal and dissolved pitch fraction of TMP. In this case, the TMP consists of 70% spruce, the rest being composed of fir and a small part of pine.

14.0 kg of the fresh wet pulp (3.6 w/w% solids content) were taken from the “accept” of the screen at a temperature of 90°C before the bleaching step at a paper mill in Switzerland. The mill uses 100% fresh water in their TMP plant. After leaving the TMP for 1 night to cool to room temperature the pulp was wet pressed through a filter of 2 μm pore size (filter paper, circular 602 EH). A sample taken from the 5.0 dm³ of filtrate/liquor thus obtained was examined under a light microscope (Olympus AX-70) to check for the absence of fibrils, which might act to distort otherwise purely colloidal adsorption results. The experiments were performed immediately after filtration. The electrophoretic mobility of the suspension at pH 6.6 was measured with a Zetasizer NS¹, giving a value of $-0.81 \cdot 10^{-8} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$. The total charge was determined by a streaming current detector (SCD) titration (Mütek PCD-02) and was found to be $-0.39 \text{ } \mu\text{Eqg}^{-1}$, and the polyelectrolyte titration (PET) of the pulp filtrate gave $-2.0 \text{ } \mu\text{Eqg}^{-1}$, where 1 Eq (equivalent) is the weight in grams of that substance which would react with or replace one gram of hydrogen. SCD primarily measures the charge on the colloidal fraction whereas PET is an overall charge measure. So a comparison of the two measures shows that there was a substantial amount of anionic polymers in solution. Ion chromatography (Dionex DX 120 Ion-Chromatograph) of the TMP sample showed the following ions in solution present in the TMP filtrate: $\text{SO}_4^{2-} = 0.63 \text{ mM}$, $\text{PO}_4^{3-} = 0.06 \text{ mM}$, $\text{Cl}^- = 0.47 \text{ mM}$, $\text{Na}^+ = 5.30 \text{ mM}$, $\text{K}^+ = 1.18 \text{ mM}$ and $\text{Ca}^{2+} = 1.03 \text{ mM}$.

Talc sample

The talc powder in the present study was analysed both by X-ray fluorescence (XRF) and X-ray diffraction (XRD) from 5-100° 2 θ Bragg diffraction using a Bruker AXS D8 advanced XRD system with $\text{CuK}\alpha$ radiation, automated divergence slits and a linear position-sensitive detector. The tube current

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and voltage were 50 mA and 35 kV, respectively: the step size was $0.02^\circ 2\theta$ and the counting time 0.5 s step^{-1} . The talc grade used was shown to contain the minerals talc, chlorite and magnesite. The presence of these constituents was independently confirmed also by FTIR analysis [Perkin Elmer Spectrum One Spectrometer]. XRF [ARL 9400 Sequential XRF] gave a talc content of $\sim 95\%$. The specific surface area was measured on a Micromeritics Tristar based on the BET (Brunauer et al. 1938) gas adsorption model (Table 2). The weight median equivalent spherical hydrodynamic particle diameter (d_{50}) was measured under sedimentation with a Micromeritics Sedigraph 5120. Additionally, the number median d_{N50} was determined using the Zetasizer, applying the dynamic light scattering technique. The current talc grade has also been used in publications elsewhere (Benecke et al. 2009), being derived from Finntalc PO5, Mondo Minerals Oy, Finland, with subsequent grinding and delamination to generate fineness, high aspect ratio and enhanced specific surface area. These additional processes maximised the hydrophobically acting planar surface of the talc platelets.

Experiments

The TMP was filtered through a $2 \mu\text{m}$ filter, as described previously. The filtrate was split into portions of 2 dm^3 and every portion was adjusted to the corresponding pH by the use of hydrochloric acid (1 M) or sodium hydroxide (1 M) (Table 3). The adjustment of the pH to 4 or 9, respectively, requires the presence of 0.10 mM hydronium or 0.01 mM hydroxide ions. Consequently, the same amount of counter ions are added which correspond to 0.01 mM sodium and 0.10 mM chloride ions. As was described above, these ions have the lowest impact on the total ion balance. The use of sulphuric acid was precluded, in order not to increase the sulphate concentration further. 200 g of each pH-adjusted filtrate were placed in a 250 cm^3 bottle and the required amount of talc was added in slurry form (solids content of chemical-free talc slurry = 10wt%). 0, 1, 2, 4, 5, 10 and 20 g talc (dry) were added per 1 dm^3 TMP filtrate. If required, some deionised water was added in order to have the same dilution. The bottles were air-tight closed and agitated for 2 hours. The suspension was subsequently centrifuged for 15 minutes (Jouan C 312, by IG Instruments) at 2 600 RCF (Relative Centri-

fuge Force). Two phases were collected; an upper aqueous phase and a lower sedimented mineral-containing phase. Furthermore, mineral alone was centrifuged to confirm that the process removed mineral particles from the upper phase. The upper liquid and the lower solid phase obtained after the centrifugation were separated and analysed according to the following procedures.

Table 3 Trial labelling and corresponding pH adjusted with either hydrochloric acid or sodium hydroxide. For trial point pH 7 no additional acid or base was added. Measured turbidity, COD and gravimetric residue of the pH adjusted TMP filtrates.

Trial No./label	Measured pH after adjustment	Turbidity / NTU	Chemical oxygen demand / mg dm^{-3}	Gravimetric residue / g dm^{-3}
pH 4	4.2	496	$4\ 100 \pm 80$	1.46
pH 5	5.0	496	$4\ 100 \pm 80$	1.41
pH 6	5.8	477	$4\ 100 \pm 80$	1.43
pH 7	6.6	451	$4\ 100 \pm 80$	1.45
pH 7.5	7.4	438	$4\ 100 \pm 80$	1.44
pH 8	8.3	409	$4\ 100 \pm 80$	1.45
pH 9	9.1	402	$4\ 100 \pm 80$	1.46

Upper aqueous phase – chemical oxygen demand, turbidity, gravimetry, particle size and electrophoretic mobility

A 100 cm^3 sample of the upper aqueous phase, obtained after centrifugation, was placed into a pre-weighed aluminium beaker and dried in an oven (90°C , 24 hours) to get a total amount of non-volatile residue, by gravimetry, held in the aqueous phase, i.e. that material not adsorbed on talc nor sufficiently agglomerated to be centrifuged into the sediment.

A further 45 cm^3 sample of the upper liquid phase was taken to analyse for turbidity by means of a NOVASINA 155 Model NTM-S (152). Turbidity indicates either that colloidal material remains in the upper liquid phase or that previously extremely fine material has progressed toward colloidal agglomeration.

A yet further 2 cm^3 sample was taken for chemical oxygen demand (COD) analysis, providing a value for the total organic content, irrespective of its state of dispersion or otherwise. The COD analysis expresses the quantity of oxygen necessary for the oxidation of organic materials into CO_2 and was measured using a Lange CSB LCK 014, range 1 000-10 000 mg dm^{-3} , with a LASA 1/Plus cuvette.

Table 2. Properties of the investigated talc grade. Electro-phoretic mobilities were measured in 0.01 M NaCl solution. The d_{50} measured by Sedigraph is weight based whereas the value from the Zetasizer NS measurement is number based.

Description	ssa / m^2g^{-1}	Electrophoretic mobilities / $10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$				d_{50} / μm (Sedigraph 5120)	d_{N50} / μm (Zetasizer)
		pH 4	pH 5	pH 7.5	pH 10		
High specific surface area talc	45	-2.85	-4.25	-3.92	-4.08	0.8	0.4

Particle size was determined on the Zetasizer NS (photon correlation spectroscopy). The samples were directly measured without any further preparation. The electrophoretic mobility was measured on the Zetasizer NS. It was decided not to convert electrophoretic mobilities (EM) into zeta potentials because the model of Smoluchowski and Hückel (Smoluchowski 1921; Hückel 1924) is inappropriate at low ionic strength and for small particles, and the factor required to apply the Henry formula (Henry 1931) is difficult to derive for such a complex system.

Results

Firstly, the turbidity, size and electrophoretic mobility of the TMP filtrate as a function of pH are reported and discussed, and, following that, the adsorption results.

Fig 1 shows the turbidity after the addition of acid or base, marked as “pH titration”. The second set of data, “Ref samples”, was recorded 3 hours after the addition of acid or base. The difference between the two lines may indicate the time dependency of the combination of the various processes occurring, namely the saponification reaction of the fatty acid triglycerides, the subsequent dissolving of the saponified fatty acids and the dissolution of the resin acids.

Fig 2 shows the effect of pH change on the electrophoretic mobility of the pitch particles. As in the turbidity versus pH titration, the electrophoretic mobilities were measured 3 hours after pH adjustment. It can be seen that the lower the pH, the more of the anionic charge carriers (mainly carboxylic groups) on the pitch droplets become protonated. Increasing pH leads to decreasing electrophoretic mobilities of which the strongest decrease is observed between pH 4 and 7.

The particle size of the pitch colloids remains about the same ($d_{N50} = 200 - 250$ nm) for all adjusted pH ranges, as shown in *Fig 3*. The equivalent spherical diameter (ESD) distribution of the talc is also shown, but it must be remembered that the talc platelet diameters are bigger than those shown in the ESD distribution (Jennings, Parslow 1988).

The pH was adjusted before talc addition and was not further buffered during the adsorption experiment. As a result of this the added talc basified the system, as can be seen in *Fig 4*, with the strength of this effect proportional to the distance of the initial pH below pH 9. This underlying basification caused the properties of the pitch particles, such as their EM, to change with increasing talc amount. It also probably changed the surface chemistry of the talk, for example by

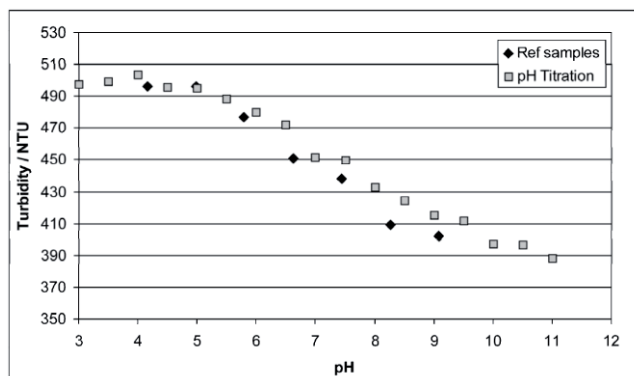


Fig 1. Turbidity of the TMP filtrate as a function of pH. The pH was adjusted by either hydrochloric acid or sodium hydroxide (1 M). The data set labelled with “Ref samples” was recorded 3 hours after the addition of acid or base.

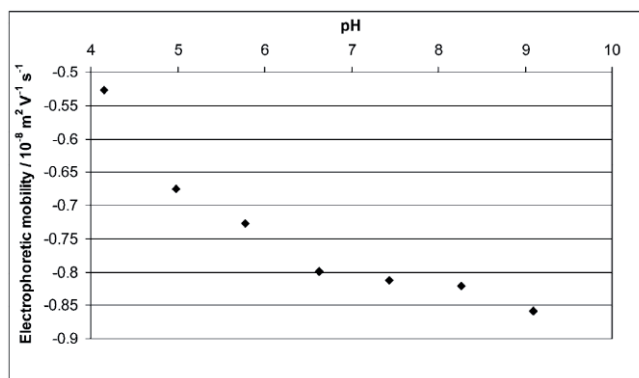


Fig 2. Electrophoretic mobility of the pitch particles as a function of pH. Measurements were performed 3 hours after the addition of the acid (hydrochloric) or base (sodium hydroxide), respectively.

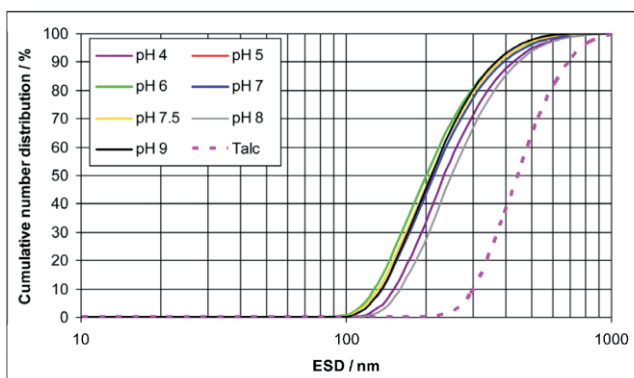


Fig 3. Particle size distribution of the pH adjusted TMP filtrates as well as of the used talc. The distribution curve is number based.

causing a degree of solubilisation of the Mg^{2+} from the ancillary dolomite. In the case of the pH 4 experiments the Mg^{2+} concentration rose from < 0.04 mM to 1.81 mM, whereas at higher pH and lower talc dosage the release of Mg^{2+} was lower. At pH 4, this increased Mg^{2+} can have a number of possible effects: raising conductivity, neutralising any carboxyl groups existing on the pitch or surfactant-acting soaps, and depleting the charge

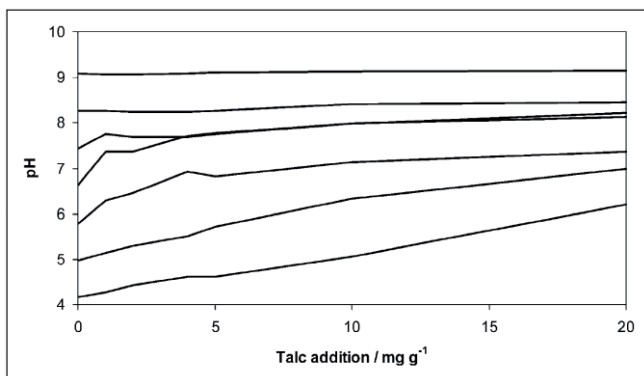


Fig 4. pH of the trials, commencing at a range of pHs from 4.2 to 9.1, as a function of talc dosage.

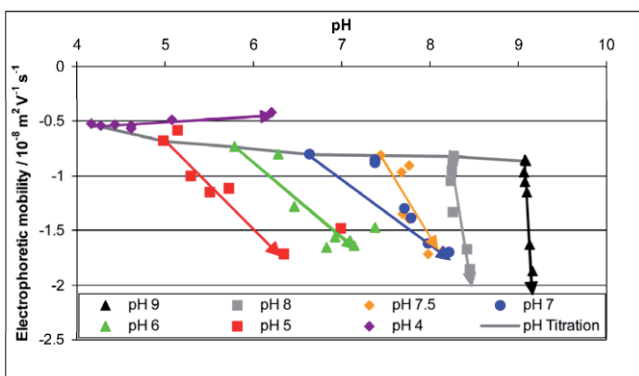


Fig 5. Development of the electrophoretic mobility of the particles in the TMP filtrates as a result of increasing talc addition and of pH. Talc dosage increases in the direction of the arrows.

balance in the talc structure with the resultant introduction of ionic interactions on the talc surface.

Fig 5 shows the EM properties of the non-adsorbed particles. Despite the pH development shown in Fig 4, the non-adsorbed species follow a different trend. The more talc is added, and the more pitch particles get removed, the more negative the EM becomes. A possible reason for that could be the presence of very fine talc particles that were not removed by centrifugation. However, IR analyses of the dried supernatant did not show any talc. Therefore, it can be concluded that EM is that of the remaining colloidal fraction originating from wood resin constituents. It seems either that the material remaining in suspension was even further stabilised, or that the most stable fraction remained in suspension while less stable colloid was adsorbed. The exception is the trial which started at pH 4.

Fig 6 shows the adsorption isotherms for the different pH experiments. The y-axis, Γ , is expressed as removed turbidity by 1 g talc added to 1 dm³ TMP filtrate (Eq 4), whereas the x-axis, c_{eq} , is referring to the equilibrium concentration, or, in this case, the residual turbidity after centrifugation of the talc.

Since

$$\Gamma = \frac{c_0 - c_{eq}}{m_T} \quad [4]$$

where c_0 is the starting concentration in 1 dm³ (turbidity, COD or gravimetry), c_{eq} is the equilibrium concentration in 1 dm³ (turbidity, COD or gravimetry), m_T is the talc dosage in g dm⁻³, then Γ , the operationally defined loading of sorbate on sorbent, can be derived.

It can be seen that the adsorption capacity of talc is increased at lower pH compared with that at higher pH, in agreement with previous work (Hughes 1977). This adsorption behaviour was characterised in terms of the Langmuir constant (K_L), a measure of the affinity between the adsorbate and the adsorbent, and the maximal loading (Γ_{max}) of the adsorbate onto the adsorbent. These coefficients were found by fitting the data to Eq 3 with Tablecurve 2D™ (Non Linear Least Squares NLLS fit), Table 4.

It can be seen from Table 4 that the behaviour at pH 4 is anomalous with respect to behaviour at higher pH, with a relatively high K_L (although with low confidence) and low Γ_{max} . Apart from that, K_L and Γ_{max} decrease monotonically with pH, dropping by around 30% and 50% respectively between pH 5 and 9.

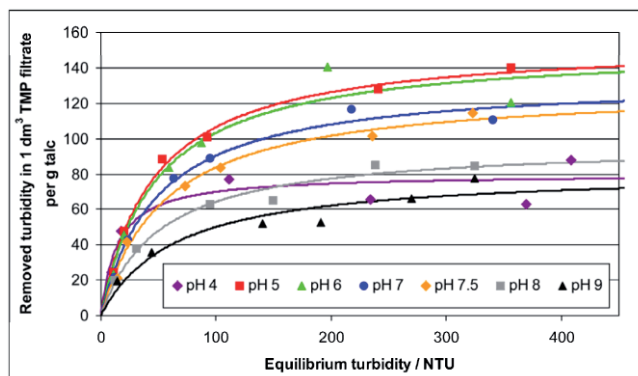


Fig 6. Adsorption isotherm of the trials for turbidity analysis.

Table 4. Summary of the fitting values derived from the turbidity data. The two constants lie all within the confidence interval of 95%, except for K_L at pH 4 and 9 (Given by the t-test with the value of $P > |t|$).

N°	K_L		Γ_{max}		r^2
	Value / NTU ⁻¹	P > t	Value / NTUdm ³ g ⁻¹	P > t	
4	0.069	0.11	80	0.00	0.81
5	0.022	0.00	155	0.00	0.99
6	0.021	0.03	152	0.00	0.95
7	0.021	0.00	134	0.00	0.98
7.5	0.018	0.00	129	0.00	0.99
8	0.019	0.01	97	0.00	0.97
9	0.016	0.09	82	0.00	0.91

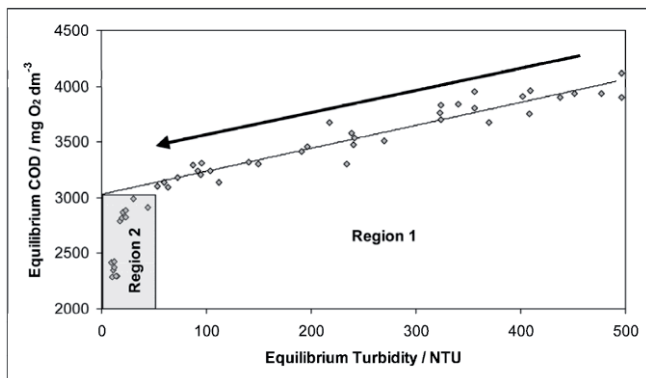


Fig 7. Equilibrium COD of all trials against equilibrium turbidity after adsorption in the supernatant. The arrow shows the direction of increasing talc dosage. The slope of the linear regression line above 50 NTU is $2.07 \text{ mg dm}^{-3} \text{ NTU}^{-1}$, and its intercept at zero turbidity is 3030 mg dm^{-3} .

Whereas turbidity measures the colloidal fraction, chemical oxygen demand (COD) measures all the material, dissolved and colloidal, which is oxidised under the conditions applied. Therefore plotting equilibrium COD against equilibrium turbidity (Fig 7) allows differentiation between the dissolved and suspended species. As can be seen in Fig 7, there is a linear relationship between the two, except at low turbidity at which COD drops markedly. Talc dosage increase from right to left in the figure. So initially and as the talc dose increases, the linear relationship moving from right to left in the figure corresponds to the adsorption of colloidal pitch (region 1). Above a certain talc dosage, corresponding to the region 2 with lower than 50 NTU on the graph, COD drops markedly because now there is sufficient talc and low enough colloidal material for the adsorption of dissolved material, such as carbohydrates, resin acids or lignin.

The linear relationship above 50 NTU in Fig 7 can be extrapolated back to an intercept of $\sim 3030 \text{ mg O}_2 \text{ dm}^{-3}$ at zero turbidity, as shown on the graph. This intercept corresponds to the hypothetical adsorption of all the colloidal species, without any adsorption of dissolved species. By contrast, the COD value for untreated TMP (at the right-hand limit of the graph) containing all the colloidal and dissolved species is around $4100 \text{ mg O}_2 \text{ dm}^{-3}$. Therefore we may conclude that the drop of around $1000 \text{ mg O}_2 \text{ dm}^{-3}$ from 4100 to $3030 \text{ mg O}_2 \text{ dm}^{-3}$ corresponds to the removal of the colloidal fraction. Thus, in terms of turbidity, around 25% ($1000 \text{ mg O}_2 \text{ dm}^{-3}$) of the total organics is colloidal and the other 75% ($3000 \text{ mg O}_2 \text{ dm}^{-3}$) is dissolved. This compares well with earlier data (Gantenbein et al. 2009).

The behaviour of the COD isotherm with pH, Fig 8, is not as clear as the behaviour of the turbidity isotherm with pH, Fig 6.

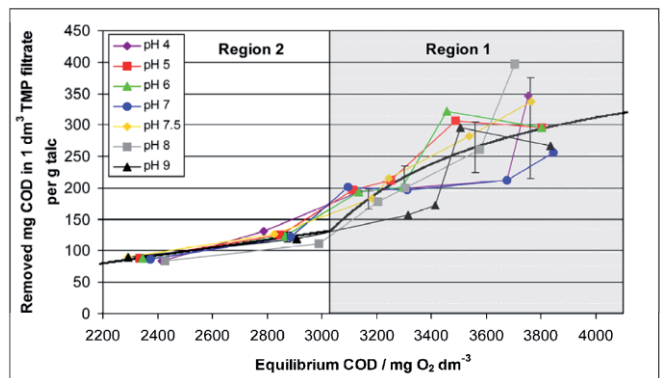


Fig 8. Adsorption isotherm of the trials for the COD analysis. The grey area between 3030 mg dm^{-3} and 4100 mg dm^{-3} represents the region in which colloids are present in the liquid phase. The scatter of the results in this region is due to the uncertainty of the COD analysis, quantified by the vertical error bars. The error bars were calculated based on the error propagation of Eq 4 with the standard deviation of c_0 of 80 mg dm^{-3} (Table 3). The thick line represents a two-stage smoothing curve explained in the text.

The intercept of $3030 \text{ mg O}_2 \text{ dm}^{-3}$ in Fig 7 provides a threshold between what we refer to as regions 1 and 2, Fig 8. In region 2 there is only a very minor fraction of the colloidal particles interacting with the talc, and there is very little dependence of removed COD on pH. In region 1 (shaded), there is significant colloid present. Although in this region there is a general upward trend of removed COD with respect to equilibrium COD, as highlighted by the thick smoothing curve, the effect of pH on this overall trend is apparently fairly random. This scatter is due to the inherent error limits within the COD measurements, the extent of which are shown by the example vertical error bars, and which mask any more subtle trend there is with pH.

The fact that the total amount of organics (COD) is not clearly affected by pH, Fig 8, but that the amount of colloidal material (turbidity) is affected, Fig 6, suggests that the colloidal fraction is in direct competition with dissolved material depending on concentration and pH. In order to make a semi-quantitative characterisation of this effect, we interpret the smoothing curves in the two regions, shown in Fig 8. In region 2, it is most appropriate to fit a straight line through the 14 data points. This regression line has a steepness of 0.062 g^{-1} and an intercept of $-56 \text{ mg dm}^{-3} \text{ g}^{-1}$ ($r^2=0.81$), Fig 8. In region 1, an operational Langmuir isotherm was fitted, eq. 3, with $K_L = 0.0014 \text{ mg dm}^{-3}$ and $\Gamma_{\text{max}} = 314 \text{ mg dm}^{-3} \text{ g}^{-1}$ ($r^2=0.47$).

Fig 9 shows a linear correlation between equilibrium gravimetric analysis (total mass) and equilibrium COD (mass of organic). The intercept of the linear regression line at zero remaining COD, corresponding to the amount of material not

involved in the adsorption, is 1.16 g dm^{-3} , whereas its maximum value in *Fig 9* is around 3.0 g dm^{-3} . It can be shown that only organic material is involved in the adsorption process. Therefore the residual 1.16 g dm^{-3} is other inorganic material not taking part in adsorption. Around 40% (i.e. $1.16 / 3.0$) of the mill water filtrate is thus of inorganic nature, whereas the rest (60%) is organic, of which 25% ($1\ 000 / 4\ 100$ as above) is the colloidal fraction.

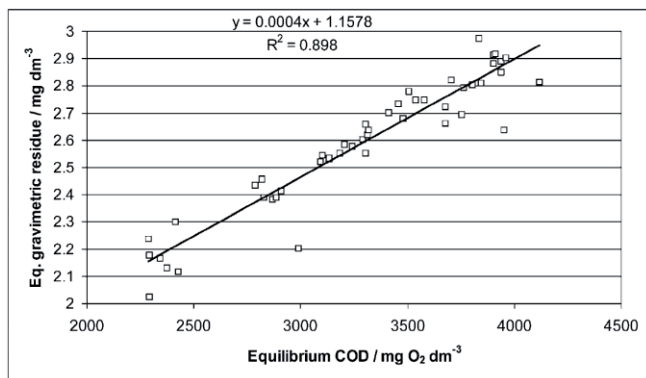


Fig 9. Equilibrium gravimetry versus equilibrium COD: enabling the COD to represent mass of organic remaining after adsorption.

Based on the linear correlation of COD with turbidity (*Fig 7*) in the region of $\text{COD} > 3\ 030 \text{ mg O}_2 \text{ dm}^{-3}$ and the linear correlation of COD with gravimetry (*Fig 9*), it is possible to calibrate turbidity and COD data for absolute mass. The question of the impact of dissolved species can be answered by subtracting the total mass of organic material given by COD from the mass of colloidal organic material given by turbidity as presented in *Eq 5*.

$$\Gamma(c_{\text{eq}})_{\text{Dissolved}} = \Gamma(c_{\text{eq}})_{\text{Total}} - \Gamma(c_{\text{eq}})_{\text{Colloidal}} \quad [5]$$

The COD isotherm representing the total organic material was transformed to total organic mass by multiplying the equilibrium concentration c_{eq} and the loading Γ with the steepness found for the linear regression line in *Fig 9* (0.0004 g mg^{-1}). For the turbidity isotherm, the Langmuir constant K_L and the maximum loading Γ_{max} expressed earlier were converted in a first step into COD values, using the correlation in *Fig 7*. In order to do so K_L was divided by the steepness of the linear regression in *Fig 7* ($2.07 \text{ mg dm}^{-3} \text{ NTU}^{-1}$), and Γ_{max} was multiplied by the same value. It must be remembered that turbidity recorded a value of zero when COD retained at the extrapolated value of $3\ 030 \text{ mg dm}^{-3}$. That implies that we subtract $3\ 030 \text{ mg dm}^{-3}$ from the equilibrium colloidal fraction concentration leading to *Eq. 6*.

$$\Gamma_{\text{Colloidal}} = \frac{\Gamma_{\text{max}} \cdot K_L (c_{\text{eq}} - 3\ 030 \text{ mg dm}^{-3})}{1 + K_L (c_{\text{eq}} - 3\ 030 \text{ mg dm}^{-3})} \quad [6]$$

The variables (Γ , c_{eq}) of *Eq 6* can then be converted from COD to colloidal mass by multiplication using the correlation steepness of the linear regression, linking mass and COD, in *Fig 9* (0.0004 g mg^{-1}) as already described above for the transformation of COD into mass. The starting point for the colloidal isotherm is at the specific value of 1.21 g dm^{-3} . This is due to the intercept in *Fig 7* of $3\ 030 \text{ mg dm}^{-3}$ at 0 NTU and transformation with the steepness of $0.0004 \text{ mg dm}^{-3} \text{ g}^{-1}$ in *Fig 9* (*Fig 10* - *Fig 12*). Thus, in summary, the total organic measured by COD is converted into total organic mass, and the organic colloid fraction is converted in 2 steps from turbidity into mass.

The result of this approach is presented in *Figs 10*, *11* and *12*, which refer to pH 5, 7 and 9 respectively. In each figure, the black line is the mass based adsorption isotherm derived from COD, and the blue line is the mass based adsorption isotherm derived from turbidity. The red line, which is the difference between these two isotherms, is the mass based adsorption isotherm for the dissolved organic species. For pH 5 (*Fig 10*), the values for loading of the dissolved material appear to go below zero, whereas the loading of colloidal material goes above the total loading, but this is an artefact of the errors within the adsorption isotherms, especially observed for the COD analysis.

Discussion

In order to explain the processes occurring, we split the adsorption process into three phases, as shown in *Fig 11*. Phase I occurs in region 1, and phase III in region 2, with phase II on the borderline of the two regions. The schematic drawing in *Fig 13* explains the adsorption process in each of these phases, and hence the reason for the trends in *Fig 10* to *Fig 12*. The starting point for each experiment is the TMP filtrate without any talc. Phase I begins on the addition of a low amount of talc. The ratio of colloidal and dissolved species to talc is high, and reduces as more talc is added. In phase I colloidal and dissolved materials compete for the talc surface. By the addition of more talc more and more colloidal and dissolved materials get adsorbed. Due to the limited availability of the colloids, most of them have been adsorbed, the system enters phase II. The ratio of dissolved material to available talc is now increasing and more and more of the talc surface gets covered with dissolved material. At $c_{\text{eq}} = 1.21 \text{ mg dm}^{-3}$, the border line to phase III, all colloidal particles are removed. At the end of phase II, the entire colloidal fraction has been adsorbed.

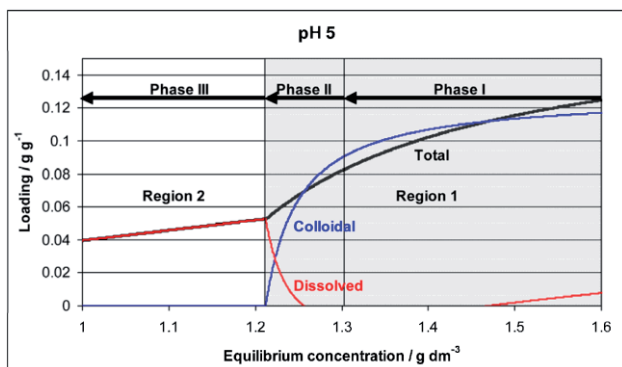


Fig 10. Adsorption isotherm at pH 5 for the dissolved and colloidal fractions (black), adsorption isotherm for the colloidal fraction only (blue) and adsorption isotherm for the dissolved fraction only (red). All isotherms in figs 10 to 12 are mass based. The direction of the arrows indicates the increasing talc dosage, which reduces the equilibrium concentration. The phases are described in the Discussion section.

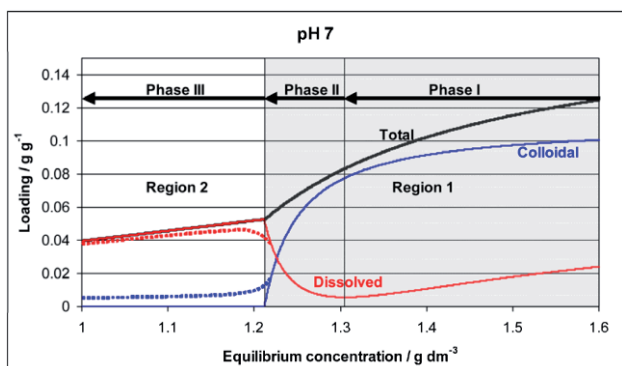


Fig 11. Adsorption isotherm at pH 7 for the dissolved and colloidal fractions (black), adsorption isotherm for the colloidal fraction only (blue) and adsorption isotherm for the dissolved fraction only (red). The dotted lines indicate the loading of colloidal and dissolved material on talc below the equilibrium concentration of 1.21 g dm⁻³.

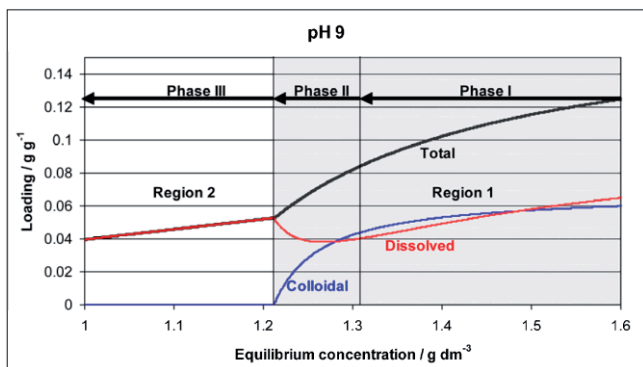


Fig 12. Adsorption isotherm at pH 9 for the dissolved and colloidal fractions (black), adsorption isotherm for the colloidal fraction only (blue) and adsorption isotherm for the dissolved fraction only (red).

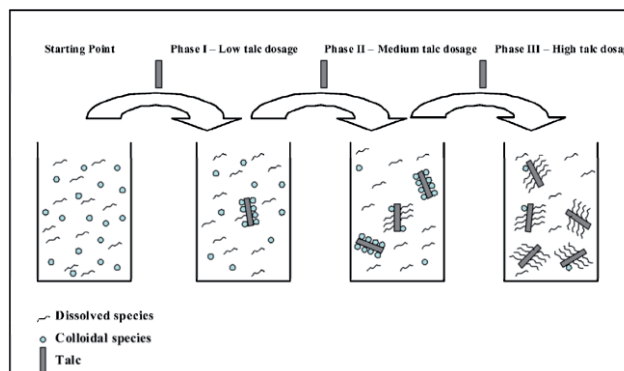


Fig 13. Schematic drawing of the adsorption process. Starting point refers to the untreated TMP filtrate. Talc dosage is increased from left to right whereas the equilibrium concentration decreases from left to right.

Therefore, adding more talc has the effect of providing adsorption surfaces for the dissolved fraction only, a state which we refer to as phase III.

In practice, as shown by *Eq 4*, and more precisely by Samiey and Golestan (2010), the adsorption stages cannot be entirely separate and successive. A more realistic plot is therefore shown by the dotted linear line in *Fig 11*, the route described implies that even when the colloid concentration is = 0 mg dm⁻³ the talc loading includes a certain fraction of colloids, which is linearly decreasing the more talc is added. This intercept is presented in *Fig 11* by the dotted linear line with unknown steepness.

The adsorption of colloidal and dissolved species is controlled by the two equilibria shown in *Fig 14*, where K_{Coll} is the colloid adsorption constant (*Fig 14*) and K_{Diss} is the constant for the adsorption of the dissolved fraction. While the two equilibria do not directly compete with each other, they are in competition for the same adsorption sites on the talc.

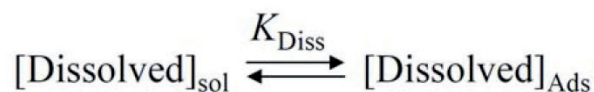
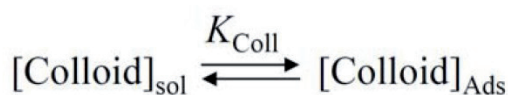


Fig 14. Adsorption equilibria for the adsorption of colloidal and dissolved species.

Changing the adsorption constants is directly related to changing affinities that might be caused by a) change of talc surface properties, b) change of colloid surface properties or c) change of properties of the dissolved species. Furthermore, the equilibria shown in *Fig 14* are also affected by the concentrations of the dissolved species. As discussed previously, a change in talc surface properties (effect a)) only occurs at pH < 5. Electrophoretic mobilities of talc remain on a comparable level between pH 5 and 9. It is also

known that the properties of talc are not significantly changed by pH (Biza 1997; Biza 2001; Parmentier 1979). The change of the colloid surface properties was detected by the electrophoretic mobility measurements presented in *Fig 2*. Because the EM decreases with increasing pH the colloidal stability by electrostatic interaction is increasing as pH rises. Willför et al. (2000) proposed a reduced electrostatic stability for wood resin droplets from peroxide-bleached TMP at pH 5 compared to pH 8. However, wood resin droplets of unbleached TMP, as investigated in this study, are known to be electrostatically and sterically stabilised (Sundberg et al. 1996) and thus effect b) of changed colloidal stability is expected to be rather minor.

Concerning the concentration of the different species it was shown earlier that turbidity decreases with increasing pH whereas COD remains constant (*Table 3, Fig 1*). Additionally to that the particle size measurements (*Fig 3*) showed no significant change in particle size with different pH values. The decreased concentration of colloidal particles and the increasing solubility of resin and fatty acids with rising pH (Lehmonen et al. 2009) further favour the adsorption of dissolved material in the higher pH ranges due to the changed concentration ratio of the colloidal and dissolved material.

The main effect was seen on the capacity (loading) of the talc but not so much on the affinity of it towards wood resin components. This is another argument suggesting that certain soluble species are covering the surface of talc preferentially at higher pH. It was described earlier that talc has also moderate to strong affinity for components such as carbohydrates, lignin, defoamers, and fatty and resin acids, which might act to suppress the attraction to pitch (Willför et al. 2000; Mosbye et al. 2003; Allen et al. 1993; Rogan 1994). Molecular compounds like fatty and resin acids likely being released at higher pH by saponification and by increased solubility are expected to form molecular mono layers on the talc surface (Rogan 1994). Thus, already very low amounts of these compounds may cover a significant area of the talc surface. Today's continuing trend towards alkaline papermaking is further reinforcing such effects. While the adsorption capacity and surface property of talc are rather stable within the studied range of pH, the chemistry of the papermaking environment changes and with it the capacity of talc to control wood pitch problems is reduced.

The exception is the behaviour at pH 4. This is against the described effect of pH in the literature (Hughes 1977). However, as discussed previously, impurities present in talc, like dolomite, are strongly affected by pH, and especially at low pH

magnesium is observed to be dissolved. Furthermore, Hughes (Hughes 1977) used model pitch which was purely colloidal and did not contain dissolved material. Other studies (Allen, Douek 1993) observed a reduced amount of pitch particles at pH < 3, but this was in the presence of fibrous material on which the pitch heterocoagulated, and so cannot explain what happened during the current trial. Another argument could be that below a certain pH a fraction of the system strongly competes with the colloidal fraction. Allen and Douek (Douek, Allen 1991) found that lignin strongly suppresses the adsorption of tall oil especially with decreasing pH. Unfortunately, the investigated pH range reported only covered pH 8 – 12.

Such effects will not occur at the natural or higher pH, nor be expected from the structure of pure talc. It is to be expected, therefore, that the mechanism of adsorption will change at reduced pH. Further work will be undertaken to study this effect, including introduction of Mg²⁺ at ambient pH.

Conclusions

The effect of pH was studied on the adsorption onto talc of dissolved and colloidal substances originating from TMP. It is the first study that deals with the complex system of real pulp mill water without the presence of fibres in the pH range of 4 – 9, and is of particular relevance as papermaking pH continues to trend upwards to neutral and higher.

For the colloidal fraction measured by turbidity, it was possible to apply an operational Langmuir adsorption isotherm. It was seen that with increasing pH, the maximum loading and affinity of colloidal material for talc decreased. Analysis of the total organic material by COD did not show a particular change in the affinity. The impact of increasing soluble species on the adsorption of colloidal material with increasing pH was shown by calculating the total mass of dissolved organics as the difference between the total organic mass and the mass of colloidal organics alone. Thus, it is postulated that the release of dissolved molecular compounds at higher pH, such as fatty or resin acids with a high affinity towards the talc surface, causes a competition with the colloidal fraction and hence reduces the adsorbed amount of colloids on talc.

In today's trend towards neutral or alkaline paper production, there needs to be careful consideration of pH sensitive effects and the consequential adjustment of the pitch control strategy.

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