

REMOVAL OF LIPOPHILIC EXTRACTIVES AND MANGANESE IONS FROM SPRUCE TMP WATERS IN A CUSTOMIZED FLOTATION CELL

Dariusz Zasadowski,* Erik Hedenström, Håkan Edlund, and Magnus Norgren

The influence of a chelating surfactant, different foaming agents, cationic polyelectrolytes, pH value, and temperature on the purification efficiency of process waters from a mechanical pulp mill has been studied by flotation in a 1 L customized unit. Turbidity measurements and gas chromatography (GC) were carried out to determine the removal and characteristics of dissolved and colloidal substances (DisCo). The manganese ion content in the process waters before flotation and the metal chelate removal capacity by flotation were determined by Inductively Coupled Plasma (ICP) and Atomic Absorption Spectrometry (AAS) measurements. It was found that a 99% removal of complex bound manganese ions and a 94% decrease in turbidity of the TMP water produced at the laboratory can be achieved in a single-stage flotation with a chelating surfactant and a foaming agent. Furthermore, a 91% decrease in turbidity, the removal of up to 96% of resin and fatty acids, and 93% of triglycerides from TMP water can be obtained after application of a foaming agent.

Keywords: Flotation; Extractives; Foaming agents; Chelating surfactant; Purification; Internal cleaning stage

Contact information: Fibre Science and Communication Network (FSCN), Mid Sweden University, SE-851 70 Sundsvall, Sweden; *Corresponding author: dariusz.zasadowski@miun.se

INTRODUCTION

Dissolved and colloidal (DisCo) substances are released into the process water during the production of thermomechanical pulp when the wood structure is opened up (Back and Allen 2000; Lindström *et al.* 1977; Sundberg *et al.* 1993; Tanase *et al.* 2009). The DisCo substances have a tendency to accumulate in the process water due to the closure of the water systems in paper mills. The presence of these components in the process water may negatively affect the papermaking processes and the final product properties.

The dissolved and colloidal substances consist of both lipophilic and hydrophilic compounds (Sundberg *et al.* 2000). The lipophilic extractives are also called pitch. It is well known that disturbances of the production process, such as pitch deposits (Vähäsalo and Holmbom 2006) on the paper machine, interferences with cationic process chemicals (Shevchenko and Duggirala 2009), and reduced efficiency in the biological effluent treatment plant (Wang *et al.* 1995; Zhang and Sain 2002) are all results of such lipophilic extractives. Disturbances of the final product, such as impaired strength and optical properties and the presence of dirt and holes, may occur because of the presence of the

lipophilic extractives (Back and Allen 2000; Holmbom and Sundberg 2003; Kokkonen *et al.* 2004; Lindström *et al.* 1977; Otero *et al.* 2000; Sjöström 1993; Sjöström and Alén 1998). The lipophilic extractives can be found in the production process in the form of colloidal droplets in water and can be adsorbed on the fibre surface and encapsulated in the fibres. Additionally, the results of Johnsen and Stenius (2007) show that only about 30% of the pitch may be retained in the paper. This means that the residual non-adsorbed components may increase the toxicity of the effluent and may increase the risk of uncontrolled pitch aggregation and other disturbances (Basta *et al.* 2004; Holmbom and Sundberg 2003; Johnsen and Stenius 2007). The hydrophilic extractives are said to beneficially affect the production process by sterical stabilization of pitch; *e.g.* hemicelluloses give a protective layer, decreasing risks of uncontrolled pitch depositions (Kokko *et al.* 2004; Sundberg *et al.* 1996). A part of fines and fibres material is also released into the process water during production of thermomechanical pulp, having significant influence on paper properties (Mosbye and Moe 2002).

With the development of new bleaching techniques, disturbances have been noticed coming from metal ions bound to acidic groups in the fibre walls. The main task of introducing chelating agents to the process is to form metal ion chelates, especially chelates of transition metal ions, such as manganese, copper, and iron, which negatively affect the bleaching efficiency by the decomposition of the bleaching chemicals. The process based on hydrogen peroxide (H_2O_2) is most widely used for both chemical and mechanical pulp due to its versatility. When decomposition of H_2O_2 takes place, the consumption of H_2O_2 increases, and the optical properties of the final product may be impaired. The transition metal ions promote the rapid transformation of H_2O_2 to hydroxyl radicals that lead to an increase in manufacturing costs (Kujala *et al.* 2004; Norkus *et al.* 2006). Besides the pulp and paper industry, chelating agents are commonly used in the production of textiles, rubbers, polymers, and in soil-washing processes. They can also be found in soaps, cosmetics, detergents, and photographic process baths.

The ability of chelates to form with high resistance to degradation is often necessary for the stability of various technical processes (The Dow Chemical Company 1974). Thus, the issue of using chelating is expected to create both strong chelates and low impact on the environment. Substances that are released and added during the pulping process are not easily biodegradable (Nörtemann 2005; Sillanpää 1996). Removal of colloidal substances from the process with help from new methods that decrease harmful effects both on paper properties and on the environment is of great importance (Pirkanniemi *et al.* 2007; World Health Organization 2008). The application of the well-known flotation technique as an internal cleaning process may be an interesting approach. The flotation process has already been applied in the area of mining for over 80 years. In general, flotation is based on the control of the surface hydrophobicity/ hydrophilicity of dispersed materials in the water, which has made it possible to rapidly transfer the technology to the paper industry, specifically for deinking of waste paper and white water purification (Saarimaa *et al.* 2006; Woodward 1986). There have been few publications describing flotation as an internal cleaning stage in purifying process waters. Miranda *et al.* (2008 and 2009) describe the application of the dissolved air flotation to purify the process water from paper mill producing newsprint from 100% recovered paper, where lipophilic extractives are aggregated with the help of

cationic polyelectrolytes and are then removed in the flotation process. Negro *et al.* (2005) show that the aggregation of the lipophilic extractives with a cationic polyelectrolyte and dissolved air flotation (DAF) can be used successfully in the purification of eucalyptus process water as well. Controlling the pitch by additions of cationic polyelectrolytes may introduce limitations in the further utilization of the removed material due to the fact that polyelectrolyte adsorption is, in general, irreversible (Holmberg *et al.* 2002).

In this study, a new approach using inducted air flotation (IAF) without a cationic polyelectrolyte addition for the removal of pitch and metal ions from mechanical pulp mill process waters, is presented. The inducted air flotation of different process waters is facilitated by the addition of a chelating surfactant (Högberg *et al.* 2011, 2012) and different foaming agents. The influence of the pH value and the temperature on the flotation efficiency has been investigated.

EXPERIMENTAL

Materials

Foaming agents

The following foaming agents were used: zwitterionic N,N-dimethyl dodecylamine-N-oxide (*i.e.* DDAO, Sigma-Aldrich), cationic dodecyltrimethylammoniumchloride (*i.e.* DoTAC, Fluka), and anionic sodium dodecyl sulfate (*i.e.* SDS, Calbiochem).

Cationic polyelectrolytes

The following cationic polymers were used: polyacrylamide (*i.e.* Fennopol K1384; Kemira; charge density 0.2 meq/g; molecular weight $9 \cdot 10^6$ g/mol), polydiallyldimethylammonium chloride (*i.e.* Fennofix 40; Kemira; charge density 2.6 to 2.9 meq/g; molecular weight $5 \cdot 10^4$ g/mol), and poly-(D)glucosamine (*i.e.* Chitosan; Sigma-Aldrich; viscosity of 1% in 1% acetic acid 200 to 800 cP; degree of deacetylation 75 to 80%; molecular weight 1.9 to $3.1 \cdot 10^5$ g/mol).

Complexing agents

The following complexing agents were used: 4-dodecyl-3,6,9-tri(carboxymethyl)-3,6,9-triazaundecane diacid (*i.e.* 4-C12-DTPA, Mid Sweden University) and diethylenetriamine-pentaacetic acid (*i.e.* DTPA, Fluka).

TMP water

The samples of the TMP water were taken from the wire press section before the bleaching tower at SCA Graphic Sundsvall, Ortvikens mill, Sweden. The pulp consistency after the wire press was 35%. TMP water is called O-water in this study. Table 1 presents initial process parameters and chemical characteristics of waters studied.

Water from unbleached TMP

The laboratory water was prepared using a method developed by Holmbom and Örså (1994). Unbleached TMP was diluted with distilled water to 1% consistency and agitated (100 to 150 rpm) at 60 °C for 4 h. The final pH was around 5.5. The suspension was centrifuged at 500 g, and the supernatant containing the dissolved and colloidal substances was separated by decantation and stored in a refrigerator at 10 °C. The water in this study is called L-water. Table 1 presents initial process parameters and chemical characteristics of waters studied.

Table 1. Turbidity (NTU), Total Concentration of Extractives (mg/L), and Major Group Extractive Concentrations (mg/L) of Waters Studied

Analysis	TMP water "O-water"	Laboratory water "L-water"
pH	5.0	5.5
Turbidity (NTU)	2400	204
Total concentration of extractives (mg/L)	738	84
Fatty and Resin acids (mg/L)	73	5.2
Lignans (mg/L)	10	1.9
Sterols (mg/L)	11	0.8
Steryl esters (mg/L)	88	4.9
Triglycerides (mg/L)	137	6
Carbohydrates (mg/L)	1780	330
Mn ²⁺ (ppm)	11.2	1.4

Methods*Flotation of process waters*

O-water and L-water were tested in the 1 L induced air flotation cell, and a description of the flotation cell is presented in Högberg *et al.* (2012). Different amounts of the investigated foaming agents were added. The flotation of L-water was continued until the formation of stable foam ended. This purpose of this was to maximize the removal of foaming agents and avoid potential foaming risks during application of the method in the pulp and paper industry. The flotation time was found to correlate with the amount of added foaming agent and varied between 35 min for the lowest additions and 70 min for the highest addition. For the O-water, the flotation was continued to the end of the foam-forming process, as well. The flotation times for O-water ranged from 40 min at 80 ppm of DoTAC up to 240 min at 400 ppm of the foaming agent concentration.

Analyses*Carbohydrates*

The carbohydrate content was determined using the Orcinol method based on a colour reaction of carbohydrates with 0.2% orcinol reagent solution in concentrated sulphuric acid. A water sample (5 mL) after addition of 10 mL of orcinol reagent was heated for 25 min in a water bath. The solution was cooled down to room temperature

and analyzed according to SCA-F W 15:77 on a Varian 100 Bio UV-Vis spectrophotometer at 540 nm of wavelength.

Lipophilic extractives

The total concentration of extractives was determined gravimetrically, according to the SCA-F W 35:97 method based on a solid-phase extraction (SPE) that was preceded by addition of methanol to a concentration of 15% in the water sample and pH adjustment to pH 2. Before extraction, a SPE disc (3M Empore, SDB-XC, 47 mm, Scantec Lab) was washed with 10 mL of MTBE, 10 mL of methanol, and 10 mL of distilled water. During the extraction, small amounts of water samples were added so that the flow did not exceed 2 mL/min. After the extraction, the SPE disc was washed with 2 portions of 10 mL of 40% methanol and vacuum dried for 30. The disc was eluted with 3 portions of 10 mL of MTBE. The received solution was vacuum-dried at 40 °C for 3 h and weighed.

The main groups of lipophilic extractives were investigated by gas chromatography (GC) analysis using an Agilent 6980 instrument according to the SCA-F G15:95 method, that is similar to a method presented in Holmbom and Örså (1994). The water samples were extracted with methyl tert-butyl ether (MTBE) and silylated with bis-(trimethylsilyl)-trifluoro-acetamide (BSTFA) and trimethylchlorosilane (TMCS) before analysis. The temperature of the injector during the injection was programmed to a range of 53 °C to 343 °C at a rate of 16 °C/min. The detector temperature was held at 350 °C. The column was a 5 m/0.53 mm i.d. wide-bore capillary column (DB-1) with a film thickness of 0.15 µm.

Turbidity

The turbidity measurement was used as an indirect measurement of the content of lipophilic extractives due to a good linear correlation between them (Johnsen 2007; Sundberg *et al.* 1993; Sundberg *et al.* 1996). The turbidity was analyzed using a HACH RATIO/XR 43900 turbidimeter. TMP water contained fibres and fines that significantly influenced the turbidity measurements. The measurements of the water before and after flotation were carried out after 1 h of sedimentation.

Images of foam fractions

Two droplets of each water sample were placed on a microscope slide (76 x 26 mm Geschnitten) and covered by a microscope glass cover slip (18 x 18 mm Chance Proper). The images of the foam fractions after flotation with DoTAC and cationic polyelectrolyte were taken with the help of a Leica DMRX light microscope and DFC 320 Camera equipped with the software LAC V3.8.

Residual foaming agent

The residual foaming agent content in the water samples after flotation experiments was determined by mass spectrometry measurements on an electrospray ionization mass spectrometry (ESI-MS) Quattro II instrument equipped with the software Masslynx™ 4.0. The following (instrument) parameters were used during measurements: source temperature 60 °C, drying gas flow 250 L/h, nebulising gas flow 10 L/h, capillary

voltage 4.5 kV, HV Lens 0.5 kV, and sample cone voltage 30 V. The fibres and fines from the water samples were removed by filtration through a MILLEX[®]-GS filter of 0.22 µm. The methanol was added to a concentration of 50% in the water samples; 3 standard solutions of DoTAC were prepared consisting of concentrations 1.1 ppm, 2.2 ppm, and 5.5 ppm. The coefficient of determination of the chart equation was $R^2=0.9968$. The water samples were measured in ES+ mode and a strong signal at m/z 228.1 was obtained.

Metal ion contents

A water sample of 10 mL was refluxed for 5 minutes with 2.5 mL of concentrated nitric acid and 2 mL of 30% hydrogen peroxide in order to digest the fibre fraction. The solution was filtered through a Munktell 00H paper filter and adjusted to 25 mL. The metal ion contents in waters before and after flotation were analyzed according to SCAN standard method CM 38:96 on a Varian ICP-OES 720 inductively coupled plasma spectrometer (ICP) and atomic absorption spectrometry (AAS).

RESULTS AND DISCUSSION

Effect of Different Foaming Agents in Combination with a Chelating Agent and a Chelating Surfactant, pH Value, and Temperature on the Flotation Efficiency of L-water

The comparison of flotation trials of 4-C12-DTPA and DTPA with various foaming agents is shown in Table 2. The combinations of 4-C12-DTPA with DDAO and DoTAC gave the highest removal of the Mn^{2+} from L-water. At 160 ppm, the reduction of Mn^{2+} for 4-C12-DTPA with a combination of DDAO and DoTAC was 81.5% and 65.8%, respectively. The application of DTPA in combination with DDAO and DoTAC resulted in the reduction of Mn^{2+} at the level of 19.4% and 17.9%. When looking further at the decrease in the turbidity of the process water at 160 ppm, it was found that DoTAC gave the highest reduction of the lipophilic extractives, which was up to 57.1% and up to 46.5% for 4-C12-DTPA and DTPA, respectively. A decrease in turbidity of up to 94% and the Mn^{2+} concentration of up to 99% for the combination of 4-C12-DTPA with DoTAC at 320 ppm was obtained. The combination DTPA/DoTAC at the same concentration gave a decrease in turbidity of 85.4% and a reduction of Mn^{2+} ions with 34.6%. The combination of 4-C12-DTPA/DoTAC gave better results than the combination of DTPA/DoTAC with regard to the reduction of both the turbidity and the content of Mn^{2+} in the L-water. It is correlated to the adsorption at air-water interfaces of the chelating surfactant, which results in the efficient foam formation ability compared to the usual DTPA (Högberg *et al.* 2011, 2012).

Table 3 shows the results from the investigation of the influence of temperature and pH value on both the removal of Mn^{2+} ions and the decrease of turbidity in L-water, respectively. The investigation into the influence of temperature and pH value was carried out for combinations of 4-C12-DTPA and DTPA with 160 ppm of DoTAC in the 1-L flotation cell.

Table 2. Removal of Mn²⁺/4-C12-DTPA and Mn²⁺/DTPA Chelates (%), Decrease in the Turbidity (%), and the Amount of the Foam Fractions (wt%) during Flotation with the L-water at Different Foaming Agent Additions at pH 5.5 and 20 °C

Complexing agent	Mass (ppm)	DDAO			SDS			DoTAC		
		Mn ²⁺ (%)	Turb. (%)	Foam F. (wt%)	Mn ²⁺ (%)	Turb. (%)	Foam F. (wt%)	Mn ²⁺ (%)	Turb. (%)	Foam F. (wt%)
4-C12-DTPA	8	48	13	1	7	5	1	6	20	1
	16	53	13	1	13	13	1	22	37	1
	40	69	15	4	28	23	8	37	46	1
	80	74	19	3	29	28	14	42	48	3
	160	82	19	4	31	34	22	66	57	6
	320							100	95	9
DTPA	8	0	19	0	4	18	1	10	17	0
	16	0	22	0	8	20	1	7	26	0
	40	7	30	3	12	25	1	6	29	0
	80	11	21	9	16	28	8	7	36	1
	160	19	31	7	20	32	10	18	46	2
	320							35	85	5

It can be noted that with the increase in temperature, the removal efficiency of Mn^{2+} and the removal efficiency of the lipophilic extractives increases for both 4-C12-DTPA and DTPA. A 73.4% removal of Mn^{2+} ions and a 93.3% decrease in turbidity can be obtained using a combination of 160 ppm of DoTAC with 4-C12-DTPA. The increase in temperature gave a 37% removal of Mn^{2+} ions and an 82% decrease in the turbidity when using a combination of 160 ppm of DoTAC with DTPA.

Investigations into the influence of pH value on pitch droplet behaviour becomes more complex since it is known that pitch droplets have a two-layered structure with triglycerides and sterylcesters located in the core of the droplets and fatty and resin acids located in an outer layer.

Sundberg *et al.* (2009) and Strand *et al.* (2011) showed that the pH value has a significant influence on the phase distribution of fatty and resin acids in water solution. The lower the pH value, the higher the content of fatty and resin acids in the colloidal phase. The transition of resin and fatty acid to colloidal phase and water phase took place very fast at radical pH changes.

The removal efficiency of lipophilic extractives increased with the decrease of pH value and with the increase of temperature, as shown in Table 3. The flotation process was most efficient at pH 3 with regard to the decrease in turbidity. At this pH, a part of the acidic groups of the resin and fatty acids located in the outer layer of the pitch droplet is dissociated; this facilitates the attachment of the DoTAC molecules to the pitch droplets, and the partly dissociated resin and fatty acids are anchored by the tails in the pitch droplets. At pH 5, the dissociation degree of the acidic groups is most likely higher than at pH 3, which gives more attachment places for DoTAC. This means that a greater number of DoTAC molecules adsorb onto each pitch droplet, which may result in a decrease of flotation efficiency at the same DoTAC concentration compared to pH 3. At pH 8, resin and fatty acids are probably both released, resulting in the decrease in the amount of sites to which DoTAC can be attached; this lowers the removal of the lipophilic extractives from the O-water. At the same time, a high amount of the foam fraction was observed due to that released from the outer layer of pitch droplet resin and fatty acid into the water. The resin and fatty acids are natural foaming agents. A reason why DoTAC is more efficient in the removal of lipophilic extractives than other foaming agents is correlated to the chemical character of DoTAC. DoTAC is a cationic foaming agent that is most likely adsorbed on negatively charged double-layered pitch droplets and creates stronger interactions than both DDAO, which is a zwitterionic foaming agent, and SDS, which is an anionic foaming agent (Nelson 2003). The removal of the manganese ions increases as the pH value increases due to an increased dissociation degree of functional groups in the complexing agents, providing more potential attachment sites for Mn^{2+} . The stability constants increase with increasing alkalinity in the pH range investigated (The Dow Chemical Company 1974). At pH 8, a 98% and a 54% removal of Mn^{2+} ions can be received for 4-C12-DTPA and DTPA, respectively.

Table 3. Removal of Mn^{2+} /4-C12-DTPA (%) and Mn^{2+} /DTPA Chelates (%), Decrease in Turbidity (%), and the Amount of Foam Fractions (wt%) during Flotation with L-water at Different Temperatures and pH Values at DoTAC Concentration 160 ppm and pH 5

Temp. (°C)	pH	4-C12-DTPA/DoTAC			DTPA/DoTAC		
		Mn^{2+} (%)	Turb. (%)	Foam F. (wt%)	Mn^{2+} (%)	Turb. (%)	Foam F. (wt%)
20	3	44	97	5	7	97	5
20	5	66	57	6	18	46	2
20	8	98	58	11	54	44	10
50	5	73	94	6	37	82	3

Effect of DoTAC, pH Value, and Temperature on the Flotation Efficiency of O-water

When it was established that DoTAC influenced the removal efficiency of both Mn^{2+} and lipophilic extractives from L-water, a similar study was carried out with O-water. It is important to mention that there is a substantial difference in chemical composition between L-water and O-water, where the O-water has higher concentrations of lipophilic extractives and already contains DTPA. No trials with 4-C12-DTPA were carried out in this study.

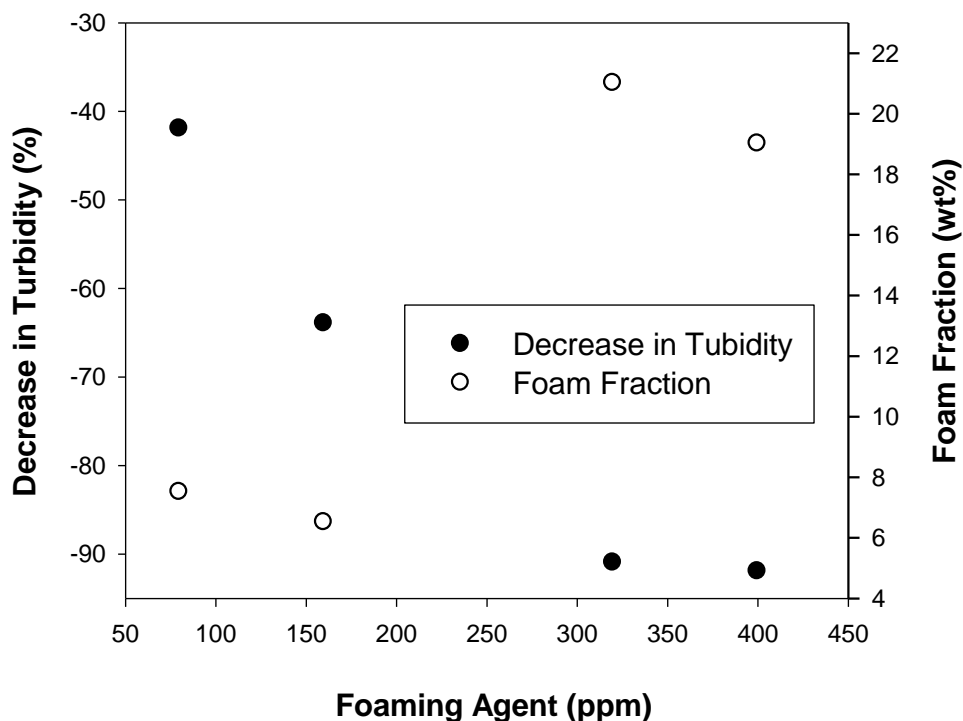


Fig. 1. Decrease in turbidity (%) and amount of foam fraction (wt%) in O-water as a function of different DoTAC concentrations after flotation at pH 5 and 21 °C

Figure 1 shows that a 91% decrease in the turbidity of O-water could be obtained at a DoTAC concentration of 320 ppm. The amount of the foam fraction within 20% indicates a high amount of water. Further increase of DoTAC did not result in significant changes in the results.

The effect of pH on the decrease in turbidity and foam fraction was investigated, and results are shown in Fig. 2.

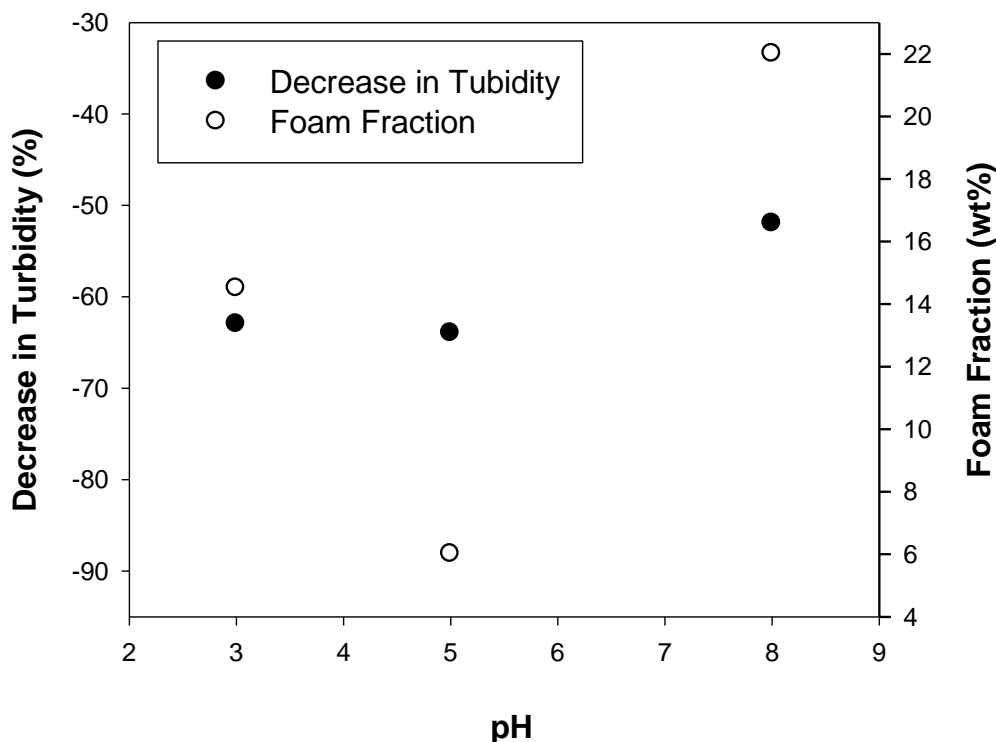


Fig. 2. Decrease in turbidity (%) and amount of foam fraction (wt%) in O-water as a function of different pH values at DoTAC concentration 160 ppm after flotation at 21 °C

Figure 2 confirms that pH value had a significant effect on the amount of the foam fraction and on the decrease in turbidity as in the case of L-water trials. There is a difference at pH 3, where a lesser decrease in turbidity was obtained compared to L-water. This most likely indicates that the number of potential attachment sites in the form of the pitch charges disappears, and that DoTAC head groups may therefore interact easier with water. Additionally, it is difficult to compare these two types of water. O-water is a complex process water matrix containing various components released during the mechanical treatment of the pulp, in addition to chemicals added during the production process.

It was observed that a change in temperature did not significantly affect a change in turbidity or the amount of foam fraction during flotation of O-water. The trials were performed at pH 5 with a DoTAC concentration of 160 ppm. The turbidity of the O-water fell slightly from 64% to 53% with an increase in temperature from 21 °C to 50 °C. The amount of the foam fraction decreased from 6% to 5.2% after the temperature was

increased. The presence of the particles in the process water produces an additional stabilizing effect on the foam formation.

The change in DoTAC concentration, pH value, and temperature did not result in a change of Mn^{2+} ions concentration, which is correlated to low affinity of DTPA to air bubbles produced during flotation.

A Comparison Between the Efficiency of Cationic Foaming Agent (DoTAC) and Cationic Polyelectrolytes

Applying cationic polyelectrolytes as fixing agents is the most common way of pitch control in paper manufacturing. The pitch droplets are removed from the process on the final product surface (Wågberg and Ödberg 1991). Basta *et al.* (2004) report that the combination of cationic polyelectrolytes and flotation is an efficient way of removing the pitch from the process water as an approach of the internal cleaning process (Miranda *et al.* 2008). Colloidal substances can be removed efficiently by aggregation and dissolved air flotation (DAF) from peroxide-bleach TMP water as well. (Saarimaa *et al.* 2006). Based on this argument, an initial comparison between the effects of adding different cationic polyelectrolytes and DoTAC was performed, and results are presented in this section. The flotation trial was preceded by a polyelectrolyte dose determination. The aggregation trials of the O-water were carried out using various cationic polyelectrolytes. The water samples of 50 mL were heated to 60 °C in glass beakers; cationic polyelectrolytes (50 ppm to 300 ppm) were added, while stirring. The dose that gave the highest decrease in turbidity was used in the subsequent flotation trial. Figure 3 shows the results from the determinations of the polyelectrolyte doses.

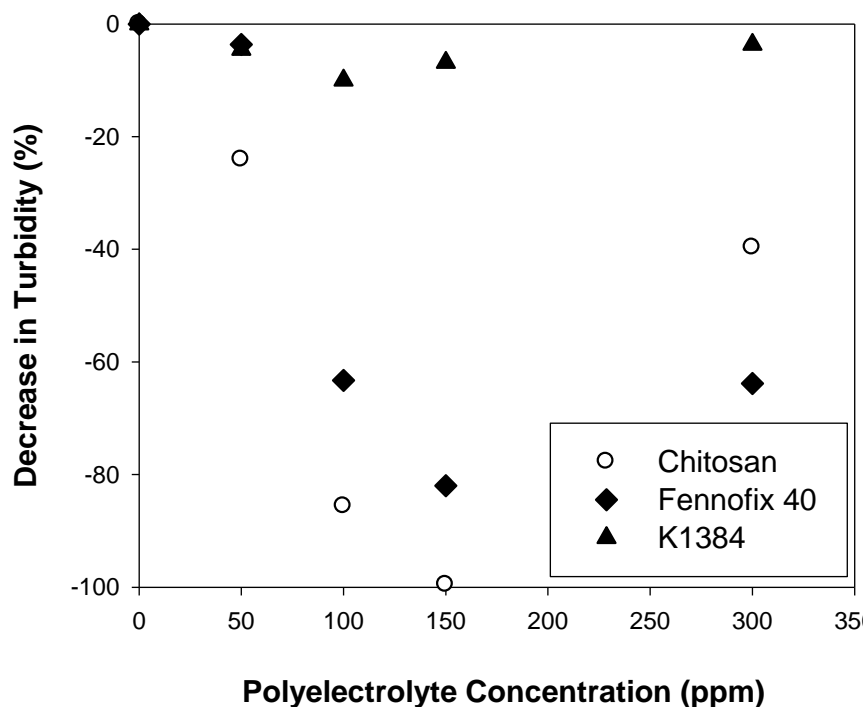


Fig. 3. Decrease in turbidity (%) of O-water as a function of different cationic polyelectrolytes additions at pH 5 and 60 °C

The most substantial decrease in turbidity was obtained at 150 ppm for chitosan, a non-conventional polyelectrolyte in this context, which was used in the subsequent flotation experiments. After addition of chitosan, both the lipophilic extractives and the fibre fraction were successfully aggregated, and flocs of various sizes were obtained. In order to remove the aggregates from TMP water by flotation, an additional foaming agent must be introduced. This is necessary so that the largest flocs do not sediment, and they stay in the flotation unit, which may decrease the chemical efficiency of the flotation process and increase costs of the chemicals. After the aggregation of the lipophilic extractives with chitosan, SDS, an anionic foaming agent, was added in a concentration of 40 ppm to the TMP water.

Table 4 shows the results of the decrease in turbidity, the total concentration of the extractives, and the concentration of major groups of extractives in O-water before and after flotation with the addition of chitosan and with DoTAC. As expected, the cationic polyelectrolyte gave the largest decrease in turbidity and in the total concentration of the lipophilic extractives. Over 99% of triglycerides, 97% of steryl esters, 94% of resin and fatty acids, and 65% of lignans could be removed in the one-stage flotation process after the addition of chitosan. Over 93% of triglycerides, steryl esters, and resin and fatty acids could be removed after the addition of DoTAC.

Table 4. Decrease in Turbidity (%), Decrease of Both Total Concentration of Extractives (mg/L), and Major Groups Extractives Concentrations (mg/L) in O-Water Before and After Flotation at Different Purification Conditions

Analysis	O-water alone	Chitosan/SDS 150 ppm / 40 ppm	DoTAC 320 ppm
Decrease in turbidity (%)	-	99	91
Total concentration of extractives(mg/L)	738	103	149
Fatty and Resin acids (mg/L)	73.1	2.9	2.8
Lignans (mg/L)	10	3.5	9.3
Sterols (mg/L)	11.8	2.2	3.2
Steryl esters (mg/L)	88.2	2.4	7.6
Triglycerides (mg/L)	137	0.1	7.7

It should be noted that only 43% of the total concentration of extractives were accounted for in the group determination by GC, as shown in Table 4. This is in agreement with results obtained in laboratories participating in the “COST E41 Joint Analysis Effort” (Willför *et al.* 2006)

Boonyasuwat *et al.* (2003) described a procedure for the removal of cationic and anionic surfactants by multistage foam fractionators. It has been shown that a cationic surfactant (cetylpyridinium chloride) is easier to recover from water than an anionic surfactant (sodium dodecylsulfate). In addition, it was more rapid in more turbulent conditions. A 75% decrease in the initial foaming agent concentration was obtained at 6000 L/h airflow, and the foam wetness was 69 g/L. A 0.8% of initial 320 ppm of DoTAC was detected in the water after the finished flotation. This indicates that both

detrimental substances and added chemicals could be successfully removed from the O-water.

A difference in the behavior of the cationic polyelectrolyte and DoTAC was observed, and pictures of the foam fractions are shown in Figs. 4 and 5.



Fig. 4. Light microscope image of a foam fraction after flotation of TMP water with 150 ppm chitosan and 40 ppm SDS

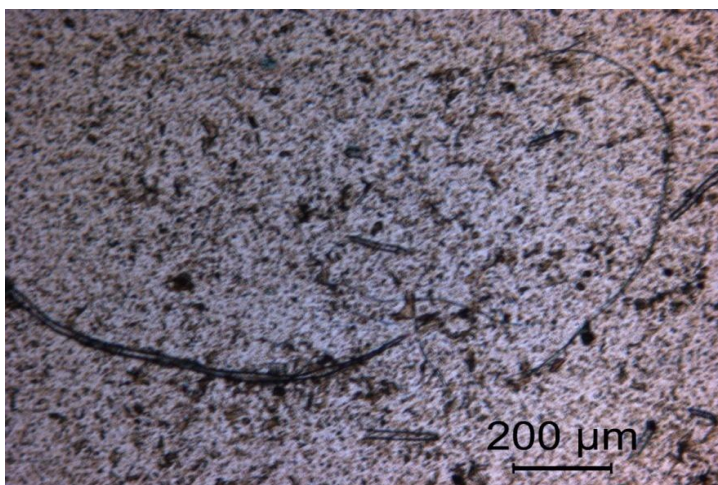


Fig. 5. Light microscope image of a foam fraction after flotation of TMP water with 320 ppm DoTAC

It can be noted that the cationic polyelectrolyte chitosan has the ability to form large and compact flocs, which facilitates the removal of the disturbing substances from the TMP water. However, the interactions with the lipophilic extractives and fibres are irreversible. These irreversible interactions are formed due to a bridging flocculation when a single chain of the polyelectrolyte is attached to several pitch droplets and fibres. In this way, the application of the separated material from TMP water by flotation with the chitosan application can be limited. In the case of the cationic foaming agent, the molecules can only be adsorbed by the individual pitch droplets and fibres, changing their surface properties, so that the lipophilic extractives are easily removed from the process waters by flotation. Figure 5 indicates that due to neutralization of the charges of pitch

droplets, small aggregates of the lipophilic substances and the cationic foaming agent micelles on the pitch droplets and fiber surfaces and in the water may appear (Holmberg *et al.* 2002). The function of DoTAC in the flotation of O-water is probably similar to the function of calcium ions in deinking flotation (Rutland and Pugh 1997). The calcium ions work as collectors after the introduction of negative charges to ink particles by the addition of fatty acid soaps. They neutralize the ink charges, which facilitate the formation of ink aggregates; this in turn increases the flotation efficiency. The pitch droplets in TMP water are negatively charged by anchored fatty acid resin and fatty acid. In Fig. 6, suggested mechanisms of the DoTAC-pitch interactions are presented, together with the mechanisms earlier suggested for cationic polyelectrolytes.

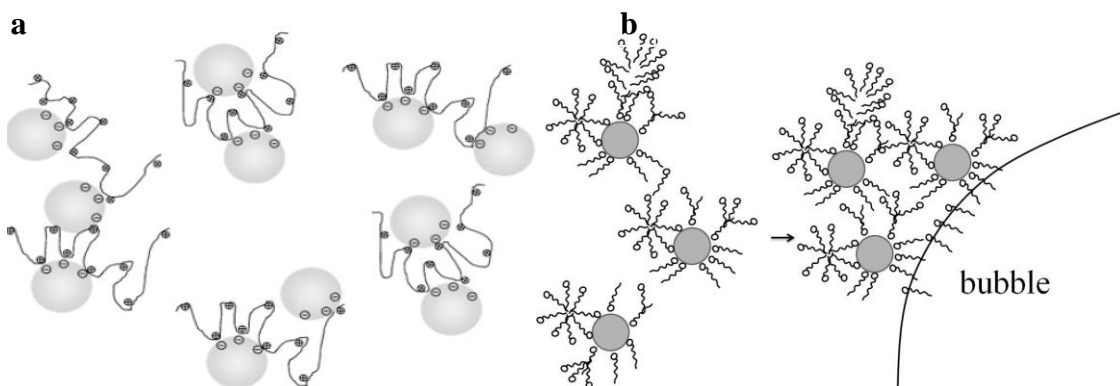


Fig. 6 a) Suggested scheme of the bridging flocculation mechanism between pitch droplets and cationic polyelectrolytes (Miranda *et al.* 2008) and, **b)** between a cationic foaming agent and pitch during flotation

CONCLUSIONS

1. The lipophilic extractives were removed efficiently and selectively from TMP process waters by applying induced air flotation and a cationic foaming agent.
2. Mn^{2+} ions were removed efficiently from process waters by applying a chelating surfactant.
3. The concentration of the residual cationic foaming agent after tests were carried out in waters was low.
4. pH and temperature influence the amount of water in the foam fraction.
5. Initial parameters of tested water have significant influence on the removal of lipophilic extractives and Mn^{2+} .

ACKNOWLEDGMENTS

Financial support from the Bo Rydin Foundation for Scientific Research, the Administrative Board of the County of Västernorrland, and the EU Structural Funds, Objective 2, is acknowledged.

REFERENCES CITED

- Back, E., and Allen, L. H. (2000). *Pitch Control, Wood Resin and Deresination*, TAPPI Press, Atlanta.
- Basta, A. H., Zhan, H., He, B., Wang, X., Zao, G., and Chen, J. (2004). "Cleaning efficiency of process water in newsprint mill," *Prog. Paper Recycling* 13(3), 13-22.
- Boonyasuwat, S., Chavadej, S., Malakul, P., and Scamehorn, F. J. (2003). "Anionic and cationic surfactant recovery from water using a multistage foam fractionators," *Chemical Engineering J.* 93, 241-251.
- Högberg, I., Zasadowski, D., Karlsson, A., Wikman, B., Andersson, F., Hedenström, E., Edlund, H., and Norgren, M. (2012). "Brightness development of a hydrogen peroxide bleached Spruce TMP. Comparisons of pretreatments with DTPA and a separable chelating surfactant," *Nordic Pulp Paper Res. J.*, in press.
- Högberg, I., Andersson, F., Hedenström, E., Norgren, M., and Edlund, H. (2011). "The interaction parameter in binary surfactant mixtures of a chelating surfactant and a foaming agent," *Progress in Colloid and Polymer Science* 138, 17-20.
- Holmberg, K., Jönsson, B., Kronberg, B., and Lindman, B. (2002). *Surfactants and Polymers in Aqueous Solution*, John Wiley & Sons, Ltd, London.
- Holmbom, B. and Örså, F. (1994). "A convenient method for the determination of wood extractives in papermaking process waters and effluents," *J. Pulp Paper Science*, 20(12). J361.
- Holmbom, B., and Sundberg, A. (2003). "Dissolved and colloidal substances accumulating in papermaking process waters," *Wochenblatt fur Papierfabrikation* 21, 1305-1311.
- Johnsen I. (2007). "The impact of dissolved hemicelluloses on adsorption of wood resin to TMP fines," Doctoral Thesis, Norwegian University of Science and Technology, Trondheim, Norway.
- Johnsen, I. A., and Stenius, P. (2007). "Effects of selective wood resin adsorption on paper properties," *Nordic Pulp Paper Res. J.* 22(4), 452-460.
- Kokko, S., Niimäki, J., Zabihian, M., and Sundberg, A. (2004). "Effects of white water treatment on the paper properties of mechanical pulp – A laboratory study," *Nordic Pulp Paper Res. J.* 19(3), 386-396.
- Kokkonen, P., Fardim, P., and Holmbom, B. (2004). "Surface distribution of extractives on TMP handsheets analyzed by ESCA, ATR-IR, ToF-SIMS and ESEM," *Nordic Pulp Paper Res. J.* 19(3), 318-324.
- Kujala, M., Sillanpää, M., and Rämö, J. (2004). "A method to leach manganese and some other metal cations from pulp matrix to aqueous phase for the subsequent ICP-AES analysis: A potential tool for controlling the metal profile in a pulp bleaching process," *J. Cleaner Production* 12, 707-712.
- Lindström, T., Söremark, C., and Westman, L. (1977). "The influence on paper strength of dissolved and colloidal substances in the white water," *Svensk Papperstidning* 11: 341-345.

- Miranda, R., Blanco, A., Fuente, E., and Negro, C. (2008). "Separation of contaminants from deinking process water by dissolved air flotation: Effect of flocculant charge density," *Separation Science and Technology* 43, 3732-3754.
- Miranda, R., Negro, C., and Blanco, A. (2009). "Internal treatment of process waters in paper production by dissolved air flotation with newly developed chemicals. 1. Laboratory Tests," *Industrial & Engineering Chemistry Research* 48, 2199-2205.
- Mosbye, J., and Moe, S. (2002). "The charge and chemical composition of fines in mechanical pulp," *Nordic Pulp Paper Res. J.* 17(3), 352-356.
- Negro, C., Blanco, A., Saarimaa, V., and Tijero, J. (2005). "Optimization of pitch removal by dissolved air flotation in a eucalyptus kraft mill," *Separation Science and Technology* 40(5), 1129-1143.
- Nelson, R. (2003). "Dispersing powder in liquids, Part 3," *Educ. Reso. for Part. Tech.*
- Norkus, E., Vaiciuniene, J., and Vuorinenb, T. (2006). "Removal of transition metals from alkaline suspensions of cellulose pulp using CDTA as chelating agent," *Carbohydrate Polymers* 66, 316-320.
- Nörtemann, B. (2005). "Biodegradation of chelating agents: EDTA, DTPA, PDTA, NTA, and EDDS," *Biogeochemistry of Chelating Agents*, Chap. 8, 910, 150-170.
- Otero, D., Sundberg, K., Blanco, A., and Holmbom, B. (2000). "Effects of wood polysaccharides on pitch deposition," *Nordic Pulp Paper Res. J.* 15(5), 607-613.
- Pirkanniemi, K., Metsärinne, S., and Sillanpää, M. (2007). "Degradation of EDTA and novel complexing agents in pulp and paper mill process and waste waters by Fenton's reagent," *J. Hazardous Material* 147, 556-561.
- Rutland, M., and Pugh, R. J. (1997). "Calcium soaps in flotation deinking; Fundamental studies using surface force and coagulation techniques," *Colloids and Surfaces.* 125, 33-46.
- Saarimaa, V., Sundberg, A., Holmbom, B., Blanco, A., Negro, C., and Fuente, E. (2006). "Purification of peroxide-bleached TMP water by dissolved air flotation," *Tappi J.* 5(5), 15-21.
- Shevchenko, S., and Duggirala, S. (2009). "Deposit management for the bleach plant," *Tappi Pulping & Environmental Conf.*, October 11-14, Memphis, Tennessee.
- Sillaanpää, M. (1996). "Complexing agents in waste water effluents of six Finnish pulp and paper mills," *Chemosphere* 33(2), 293-302.
- Sjöström, E. (1993). *Wood Chemistry: Fundamentals and Application*, Academic Press, USA.
- Sjöström, E., and Alén, R. (1998). *Analytical Methods in Wood Chemistry, Pulping, and Papermaking*, Springer, Berlin.
- Strand, A., Sundberg, A., Vähäsalo, L., and Holmbom, B. (2011). "Influence of pitch composition and wood substances on the phase distribution of resin and fatty acids at different pH," *J. of Dispersion Science and Technology* 32(5), 702-709.
- Sundberg, A., Ekman, R., Holmbom, B., Sundberg, K., and Thornton, J. (1993). "Interactions between dissolved and colloidal substances and a cationic fixing agent in mechanical pulp suspensions," *Nordic Pulp Paper Res. J.* 1(1), 226-231.
- Sundberg, A., Holmbom, B., Willför, S., and Pranovich, A. (2000). "Weakening of paper strength by wood resin," *Nordic Pulp Paper Res. J.* 15(1), 46-53.

- Sundberg, A., Strand, A., Vähäsalo, L., and Holmbom, B. (2009). "Phase distribution of resin and fatty acids in colloidal pitch emulsions at different pH-levels," *J. of Dispersion Science and Technology* 30(6), 912-919.
- Sundberg, K., Thornton, J., Holmbom, B., and Ekman, R. (1996). "Effects of wood polysaccharides on the stability of colloidal wood resin," *J. Pulp Paper Science* 22(7), 226-230.
- Tanase, M., Stenius, P., Johansson, L., Hill, J., and Sandberg, C. (2009). "Mass balance of extractives around impressafiner in mill and pilot scale," *Proceedings of IMPC*, May 31- June 4, Sundsvall, Sweden.
- The Dow Chemical Company. (1974). "Versene: Chelating agents," Technical note.
- Vähäsalo, L., and Holmbom, B. (2006). "White pitch deposition and styrene-butadiene-rubber binder content in paper mill process waters," *Appita J.* 59(3), 213-217.
- Wågberg, L., and Ödberg, L. (1991). "The action of cationic polyelectrolytes used for the fixation of dissolved and colloidal substances," *Nordic Pulp Paper Res. J.* 6(3), 127-135.
- Wang, Z., Chen, T., Gao, Y., Breuil, C., and Hiratsuka, Y. (1995). "Biological degradation of resin acids in wood chips by wood-inhabiting fungi," *Applied and Environmental Microbiology* 61, 222-225.
- Willför, S., Hemming, J., and Leppänen, A.S. (2006). "Analysis of extractives in different pulps – Methods development, evaluation, and recommendations," Report B1, Åbo Akademi University.
- Woodward, T. W. (1986). "Appropriate chemical additives are keys to improved deinking operations," *Pulp and Paper* 11, 59-63.
- World Health Organization. Guidelines for Drinking-water Quality, Geneva 2008
- Zhang, X., and Sain, M. (2002). "Isolation and identification of toxic chemicals in wood bark and its correlation to pulp mill effluent," *Tappi Environmental Conf. 2002*, Montreal, Canada.

Article submitted: January 11, 2012; Peer review completed: February 26, 2012; Revised version received: March 30, 2012, Accepted: April 18, 2012; Published: April 25, 2012