

Coagulation of wood extractives in chemical pulp bleaching filtrate by cationic polyelectrolytes

T. Leiviskä*, J. Rämö

Water Research and Environmental Engineering Laboratory, University of Oulu,
P.O. Box 4300, FIN-90014 University of Oulu, Finland

Received 7 June 2007; received in revised form 27 August 2007; accepted 29 August 2007
Available online 1 September 2007

Abstract

The purpose of this research was to investigate the effectiveness of short-chain cationic polyelectrolytes of different molecular weights and charge densities in reducing turbidity and selectively removing toxic wood extractives from chemical birch pulp filtrate. The effects of chemical type, dosage and temperature were of interest. An effective performance was achieved with a copolymer of acrylamide and methacrylate of medium molecular weight and medium charge density at 72 °C and pH 5–6. The dosage range optimum for reducing the turbidity was 102–142 mg/L. Up to 92% of the wood extractives was selectively removed.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Coagulation; Cationic polyelectrolyte; Wood extractive; Bleaching filtrate

1. Introduction

Wood extractives such as resin acids, unsaturated fatty acids, and sterols make a considerable contribution to aquatic toxicity even at very low concentration [1]. Toxic effects of a common resin acid, dehydroabietic acid (DHAA), on rainbow trout have been observed at a level of 20 µg/L [2], even though DHAA is the least toxic of the common resin acids, to *Daphnia magna* [3]. Reproduction and growth of fish are reportedly disrupted by sterols at exposure levels of 10 and 20 µg/L [4].

Most of the wood extractives in pulp mills can be removed by activated sludge treatment [5]. The extractives are degraded, transformed into other compounds, or adsorbed to biosludge [6]. The rest of the wood extractives in the effluent will find their way to receiving water systems and adjacent sediments. A resin acid concentration as high as 1470 µg/g (dry weight) has been observed in sedimenting particles in samples obtained from a lake receiving bleached kraft mill effluent [7]. Furthermore, there is no guarantee that biological treatment will always work properly. Toxicity breakthroughs may occasionally occur. The

pulp industry should therefore not only aim at permitted and desirable levels of wood extractives discharge but continuously work to diminish emissions.

Besides affecting aquatic toxicity, wood extractives cause problems within the mill, including pitch deposits on process equipment, and sometimes in low quality pulp. The increasing need for recirculation of water in pulp mills only accentuates the problem. Kraft mills approach pitch control in several ways. Seasoning of the wood leads to a decrease in the extractives of woods (e.g. birch, aspen and certain tropical hardwoods) with a high ratio of unsaponifiables to saponifiables in their wood extractives [8]. Another approach in the case of hardwood pulp is to add tall oil (consisting mainly of resin acids and fatty acids) to the wood digestion process to improve pulp deresination. Hardwoods themselves do not contain resin acids. Some mills benefit considerably from a rapid alternation of species in the digestion process. Thus, the removal of extractives from birch is improved by digesting birch just one day at a time, after pine cooking, so that the alkaline cooking liquor of pine helps in removing hardwood extractives. Pitch dispersants may be added to improve deresination in the washing stage, and retention aids to fix extractives in the pulp.

An advantageous approach in every way would be to reduce the amount of extractives in circulating waters by an internal water treatment. This would have a positive impact

* Corresponding author. Tel.: +358 40 5544531; fax: +358 8 5534507.

E-mail addresses: tiina.leiviska@oulu.fi (T. Leiviskä), jaakko.ramo@oulu.fi (J. Rämö).

Nomenclature

AOX	adsorbable organic halogen (mg/L)
COD	chemical oxygen demand (mg/L)
D	a chlorine dioxide stage
DOC	dissolved organic carbon (mg/L)
eq/L	equivalent/litre
E	an alkaline extraction stage
ECF	elemental chlorine free
G	gas chromatography
O	an oxygen stage
Paa	a peracetic acid stage
S/m	siemens/meter
TOC	total organic carbon (mg/L)
UV	ultraviolet
W	washing
XQ	a chelation stage

on pulp quality as well as on effluent toxicity. Readsorption of extractives on to fibers would diminish, while the organic matter removed could be used as fuel.

Methods that have been studied for internal water treatment in kraft pulp mills include evaporation [9], membrane processes [10–13], ion-exchange [14,15], adsorption [14], and coagulation–flocculation [14,16–19]. Most studies dealing with the coagulation–flocculation of organic material from kraft pulp bleaching filtrates or waste water have evaluated the success of purification by measuring color reduction [14,20–25], ultraviolet (UV) absorbance [23], turbidity [20,24,26], or parameters such as total organic carbon (TOC) [14,21], dissolved organic carbon (DOC) [23], chemical oxygen demand (COD) [17,23,25,26], adsorbable organic halogen (AOX) [22,23], and chlorinated phenolics [22]. Measurement of residual wood extractives has seldom been reported. In pilot plant and full-scale studies at chemical and mechanical pulp mills, Rampotas [16] demonstrated the deresination of filtrates by flocculation with polyethylene oxide. Removal of more than 90% of wood extractives was achieved, along with high removal efficiencies of non-process metals. In kraft mills, this kind of kidney system might be installed near the oxygen stage. The deresination, i.e. the decrease in lipophilic extractives, of pulp in bleaching occurs mainly at the oxygen or extraction stages [27,28].

We investigated the effect of four cationic polyelectrolytes on the removal of extractives from chemical pulp process water. Cationic polyelectrolytes, which contain a large number of positively charged groups, have been found useful in wastewater treatment processes [29] as well as in other industrial applications. The sludge formation is less than with inorganic coagulants and the sludge is more suitable as fuel owing to the lower content of inorganics and thus ash. Before industrial use of organic coagulants, their toxicity and biodegradability would need to be carefully investigated since microbial toxicity has been observed at least for anionic polymers [30]. In addition to being non-toxic and biodegradable, the polyelectrolytes need to be selective so that beneficial

compounds, such as carbohydrates, are retained in the process.

Filtrate from the oxygen stage was selected for study. Not only did it contain huge amounts of wood extractives, but also other organic substances including carbohydrates were well represented. The investigations were performed at high temperature because chemical pulp process waters are typically very warm. It is widely assumed that the use of cationic polyelectrolytes in conditions of the oxygen stage filtrate would encounter insuperable problems because of the high pH but also the high conductivity and temperature. Reducing the pH is thus a prerequisite for an effective coagulation–flocculation treatment. One feasible approach in the mill would be to use acidic waste fractions for this purpose. Besides the internal treatment discussed above, the purification of filtrate from the wood extractives could also be performed as a pretreatment before biological wastewater treatment. Thus, pH adjustment is also necessary for adequate microbial growth in biological treatment. It may be industrially relevant to perform the pH adjustment already in the process. Our main aim in this work was to determine whether a successful, selective removal of wood extractives can be achieved at moderate pH level (5.5) with use of differently charged cationic polyelectrolytes.

2. Experimental

2.1. Sampling

In a search for an appropriate sample, bleaching filtrates from two Finnish kraft pulp mills undertaking elemental chlorine-free (ECF) bleaching of birch (*Betula verrucosa*) were sampled, and the samples were analyzed to determine the amounts of wood extractives. Representative values are included in Table 1.

The sequence of Mill A consists of the oxygen stages O₁ and O₂, i.e. oxygen delignification, and displacement bleaching. The bleaching comprises a chlorine dioxide stage (D₀) followed by two alkaline extraction stages (E₀ and E₁) and washing (W), with the E₀ stage fortified with oxygen; a second chlorine dioxide stage (D₂); and finally a peracetic acid stage (Paa). The bleaching filtrates are extensively recycled. The volume of the discharged bleach plant effluent is approximately 13.5 m³/t of pulp. Inorganic and organic substances are thus highly concentrated in the filtrates. In particular, a high concentration of calcium leads to the deposition of calcium oxalate and calcium carbonate in some places.

The sequence of Mill B consists of oxygen delignification, an enzyme treatment and a chelation stage (XQ), oxygen stage reinforced with hydrogen peroxide (Op/O), a chlorine dioxide stage (D₁), E_p stage fortified with hydrogen peroxide, a second chlorine dioxide stage (D₂), and a peracetic acid stage. The volume of the discharged bleach plant effluent is approximately 23 m³/t of pulp.

The filtrates sampled from the oxygen stage wash press contained huge amounts of wood extractives. The presence of resin acids (not found in birch itself) can be explained by the alternate pulping of birch and pine at the mills, and the use of tall oil to improve pulp deresination. The O₂ filtrate (charge quantity

Table 1
Amounts of wood extractives and lignans (mg/L) in process waters from ECF birch pulp bleaching in two different Finnish pulp mills

Bleaching stage	Fatty acids	Resin acids	Sitosterols	Steryl esters	Triglycerides	Lignans	Total ^a
MILL A							
O ₂	259	107	2	8	1	18	377
D ₀	4	<1	<1	<1	<1	<1	4
E ₀	2	4	<1	<1	<1	<1	6
E ₁	3	3	<1	<1	<1	<1	6
W	4	4	<1	<1	<1	<1	8
D ₂ ^b	6	1	<1	<1	<1	<1	7
MILL B							
O ₂ ^b	190	56	23	6	<1	4	275
XQ	6	<1	<1	<1	<1	2	6
Op/O	37	9	<1	1	<1	4	47
D ₁	1	<1	<1	<1	<1	<1	1
E _P	8	8	<1	<1	<1	2	16
D ₂	<1	<1	<1	<1	<1	<1	<1

^a Lignans are not included.

^b Samples were not taken on the same day as the others.

–10 000 µeq/L, conductivity 905 mS/m, and pH 10.6 at 25 °C) from Mill A was selected for coagulation studies.

2.2. Chemicals

Short-chain cationic polyelectrolytes, namely epichlorohydrindimethylamine copolymer (PAE), polydiallyldimethylammonium chloride (Poly-DADMAC), and two cationic copolymers formed of methacrylates and acrylamides with different charge densities (C-PAM1 and C-PAM2), were obtained from Kemira Oyj, Finland (Table 2). Fresh 0.1% and 1% solutions were prepared daily. Dosages throughout the study are quoted as effective polyelectrolyte dosages, not as a product. Hydrochloric acid (VWR Prolabo BDH) was used to lower the pH of the samples.

2.3. Coagulation experiments

Coagulation experiments were performed in jar tests using a 600 mL beaker. The O₂ filtrate (280 mL) was added to a beaker with 20 mL (reference sample) or less of Milli-Q water. The amount of Milli-Q water depended on the amount of polyelectrolyte solution. The final sample volume was 300 mL. The mixture was warmed in a water bath, which was placed on a platform with five magnetic stir positions. The sample pH was adjusted to 5.5 with 1 mol/L hydrochloric acid. Then the polyelectrolyte solution was added, and the sample was rapidly mixed (200 rpm) for 1 min and slowly mixed (40 rpm) for 9 min. After centrifugation (1950 rpm for 15 min), the supernatant was

Table 2
Properties of the tested polyelectrolytes

Polyelectrolyte	Molecular weight (g/mol)	Charge density (meq/L)
PAE	20 000	+7–8
Poly-DADMAC	100 000	+6.2
C-PAM1	200 000	+4.2
C-PAM2	200 000	+1.2

sampled for analysis. Until analysis, samples were stored under refrigeration (turbidity, charge quantity, zeta potential) or in a freezer (TOC, organic substances).

Reference samples at different temperatures (18, 57 and 80 °C) were prepared by applying the same method but without addition of polyelectrolyte and with a different heating system: the water was warmed to the desired temperature, and then kept at that temperature with a magnetic stirrer/hot plate. The reference sample volume was also slightly greater (360 mL filtrate + 20 mL Milli-Q water = 380 mL).

2.4. Analytical techniques

Charge quantity (eq/L) was measured with a Müttek Particle Charge Detector PCD 03 pH (Müttek Analytic, Herrsching, Germany). Zeta potential measurements were made with the Coulter DELSA 440SX (Beckman Coulter, Miami, FL, USA), which relies on Doppler electrophoretic light scattering (ELS). The analytical techniques have been described in detail previously [31].

TOC was measured with a Shimadzu TOC 5000A analyzer (Shimadzu Corporation, Kyoto, Japan), where combustion is followed by non-dispersive infrared gas analysis. Wood extractives (fatty acids, resin acids, sitosterols, steryl esters, triglycerides) and lignans were determined by extraction with methyl *tert*-butyl ether (MTBE), followed by silylation and gas chromatography (GC) analysis (Perkin Elmer GC autosystem XL, Shelton, CT, USA) [32]. Carbohydrates were determined by sample freeze-drying and methanolysis [33,34]. Methanolysis is used to degrade hemicelluloses into their monomeric units of methyl glycosides. After silylation, monomers were analyzed by GC. The amount of lignin was determined from the water phase after MTBE extraction by UV measurement, at 280 nm (UV–visible recording spectrophotometer UV-240, Shimadzu Corporation), and using an absorptivity value of 19.8 L/(g cm) [35]. Turbidity was measured with a Hach Ratio XR (Hach Company, Loveland, OH, USA) by ISO method 7027 [36], and pH was determined

with a Radiometer PHM82 (Radiometer, Copenhagen, Denmark) according to SFS 3021 [37].

3. Results and discussion

The performance of polyelectrolytes is mainly governed by pH, impurities in the water, and temperature. Among these, the prevailing pH probably has the major influence on functionality. Not only the polyelectrolyte charge but the solubility of the target compounds depends on pH. At high pH levels, wood extractives are mainly dissolved in such a way that their removal by coagulation with cationic polyelectrolytes is difficult if not impossible. Certain multivalent metal ions have proved useful in precipitating resin acids out of solution under alkaline conditions [38]. Another way to reduce solubility of wood extractives is reduce the pH. In this study, the experiments with polyelectrolytes were carried with pH reduced to 5.5 and at 72 °C.

Fig. 1 shows the residual turbidity obtained with different dosages of the cationic polyelectrolytes. Only C-PAM1 significantly lowered the turbidity. For C-PAM1, the optimum dosage range was fairly narrow, 102–142 mg/L, and the lowest turbidity value, 60 NTU, was recorded at a dosage of 142 mg/L. The initial increase in turbidity at low dosage levels is probably due to the precipitation of dissolved wood polymers as small nonsettleable particles [39]. Charge quantity (Fig. 2) gradually decreased with increased dosage of C-PAM1, but only slightly. Within the optimum C-PAM1 dosage range, the zeta potential (Fig. 3) was clearly neutralized but still negative (−6 mV with 142 mg/L C-PAM1). Also with higher dosages the zeta potential remained negative.

In terms of turbidity reduction, the other polyelectrolytes did not work in the studied dosage range and 72 °C (Fig. 1). The addition of flocculant (certain long-chain organic polymer) together with short-chain polyelectrolyte might improve the formation of settleable floc. The supernatants from C-PAM2 experiments (>100 mg/L) were nevertheless strongly postprecipitated after 1-day storage under refrigeration, and the

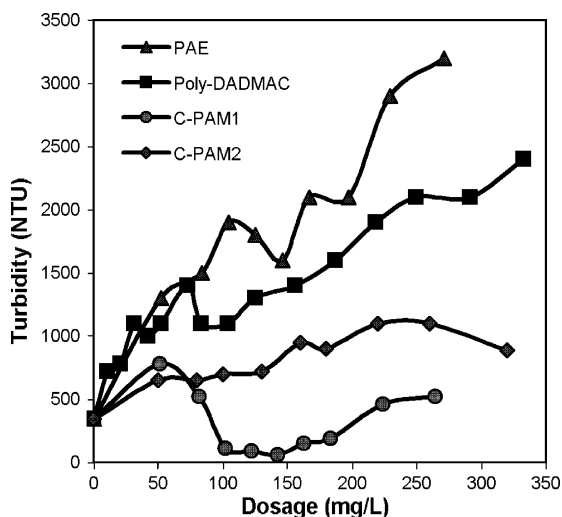


Fig. 1. Effect of polyelectrolyte dosage on residual turbidity in the coagulation of oxygen-bleached process water at 72 °C and pH 5.5.

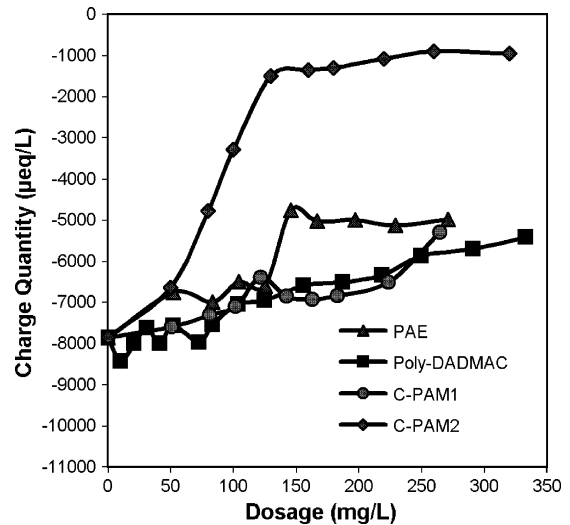


Fig. 2. Effect of polyelectrolyte dosage on charge quantity in the coagulation of oxygen-bleached process water at 72 °C and pH 5.5.

precipitate settled well resulting in a bright solution. In addition, C-PAM2 had the strongest influence of all polyelectrolytes on zeta potential (Fig. 3) and charge quantity (Fig. 2). The dosage of C-PAM2 needed to obtain zero zeta potential and plateau zeta potential was the same, 100 mg/L. From its strong influence on charge quantity, C-PAM2 can be concluded to be highly specific in terms of flocculating with carbohydrates. In sum, C-PAM2 appears to be an effective neutralizer of surface charge under the conditions investigated, but lower temperatures, as well as more time, are needed for agglomeration to occur.

The original oxygen-bleached filtrate was brown in color, mainly due to the high amount of lignin-derived material. The reductions of lignin with the tested cationic polyelectrolytes were 40% with 125 mg/L PAE, 21% with 125 mg/L Poly-DADMAC, 17% with 142 mg/L C-PAM1, and 2% with 130 mg/L C-PAM2 (data not shown).

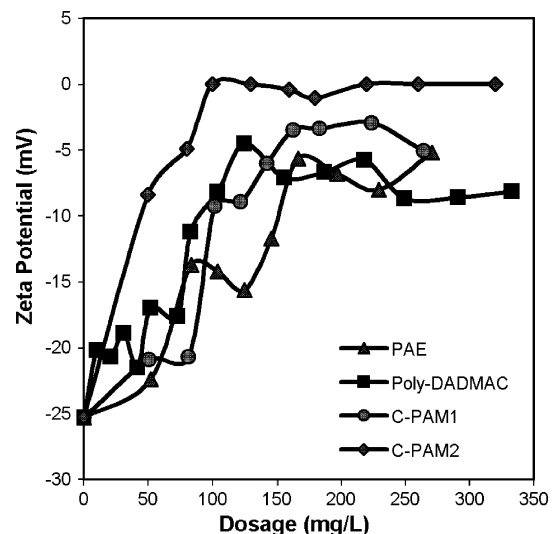


Fig. 3. Effect of polyelectrolyte dosage on zeta potential in the coagulation of oxygen-bleached process water at 72 °C and pH 5.5.

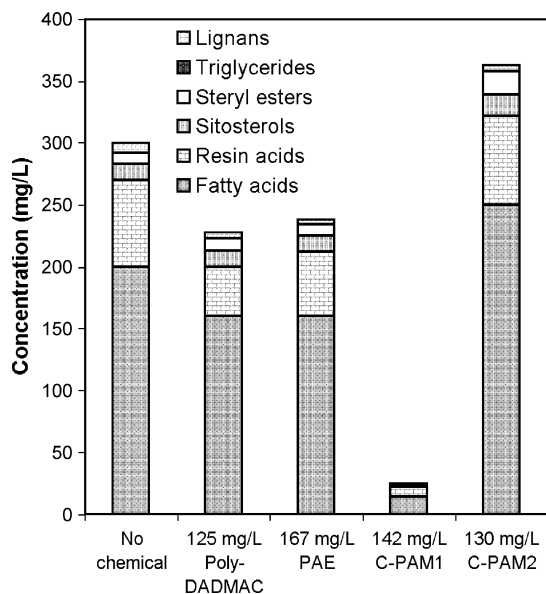


Fig. 4. Residual wood extractives and lignans after coagulation with cationic polyelectrolytes at 72 °C and pH 5.5.

As shown in Fig. 4, at the optimum dosage of C-PAM1 for turbidity reduction (142 mg/L), up to 92% of the wood extractives was removed. Note: since the ability of the other polyelectrolytes to remove turbidity was poor, comparable samples for detailed analysis of wood extractives were selected according to the achieved reductions in zeta potential and TOC. Relative to the concentration in the reference sample, Poly-DADMAC (125 mg/L) and PAE (167 mg/L) removed only 24% and 20% of the extractives, respectively. The concentration of extractives was actually higher with addition of C-PAM2 (130 mg/L): the supernatant contained 50 mg/L (25%) more fatty acids and 10 mg/L (11%) more steryl esters than the reference sample prepared at the same temperature.

The effect of temperature, studied with reference samples (pH 5.5) at 18, 57, and 80 °C, was found to be similar to the effect of C-PAM2. The concentration of TOC increased with temperature (data not shown): from 2100 mg/L (18 °C) to 2300 mg/L (80 °C). More precisely, and as shown in Fig. 5, the concentration of carbohydrates increased significantly particularly the amount of xylose, but also the amounts of arabinose, rhamnose, and galacturonic acid. The opposite trend, to a lesser extent, was observed for mannose, glucose, and 4-*O*-methyl-glucuronic acid. Furthermore, as presented in Fig. 6, the concentrations of some extractives increased with temperature. The reference sample prepared at 80 °C (pH 5.5) contained 14% more fatty acids and 20% more resin acids than the reference sample prepared at 18 °C (pH 5.5).

In addition to pH and the presence of multivalent metal ions, the water solubility of extractives depends on temperature and ionic strength [40]. Differences in the components themselves (e.g. chain length, unsaturated/saturated) also contribute to the solubility. Probably a part of the carbohydrates were agglomerated with the wood extractives during the refrigerated storage of the O₂ filtrate before the coagulation experiments. In the case of the reference sample prepared at 18 °C, the agglomerates may

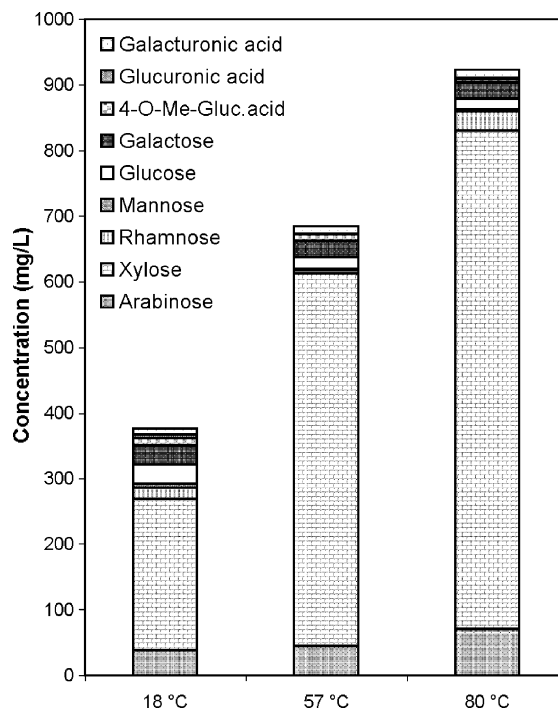


Fig. 5. Residual carbohydrates in the reference samples (no chemical added) prepared at different temperatures and pH 5.5.

have been removed at the centrifugation stage or else they could not be analyzed. At higher temperatures most of the agglomerates may have decomposed. Those agglomerates that were not significantly affected by temperature might have been decomposed upon addition of C-PAM2, so explaining the higher value of extractives that was observed.

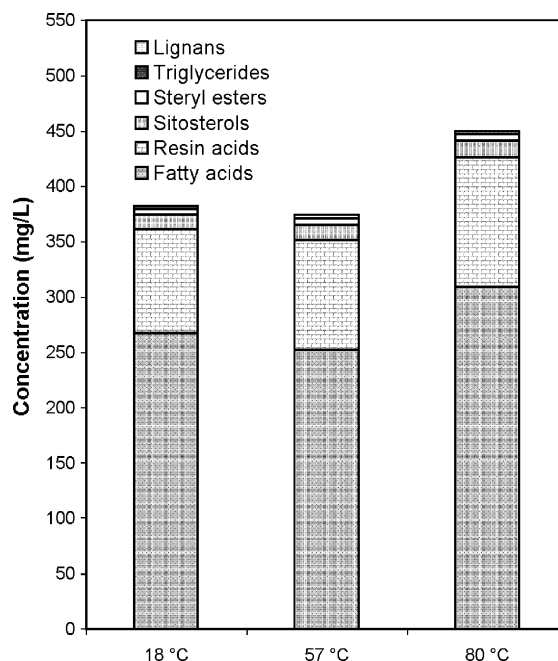


Fig. 6. Residual wood extractives and lignans in the reference samples (no chemical added) prepared at different temperatures and pH 5.5.

The conformation of a polyelectrolyte is strongly dependent on the electrolyte concentration. Normally polyelectrolytes assume an expanded conformation so that repulsion between groups with equal charge is minimized [38]. The repulsion decreases as the ionic strength of the solution increases until at higher electrolyte concentration, the conformation of a polyelectrolyte changes from an expanded to a collapsed, coil-like conformation. The filtrate used in this study was of very high conductivity so the polyelectrolytes formed a tight coil in solution.

Greenwood and Kendall [41] demonstrated with Poly-DADMAC-based polyelectrolytes that the optimum concentration for flocculation was strongly affected by ionic strength and weakly affected by polyelectrolyte molecular weight. The amounts of polyelectrolyte adsorbed onto alumina particles were much less at 50 mmol/L than at 10 mmol/L electrolyte concentration. The final plateau value of the zeta potential decreased as the salt concentration increased due to screening of the polyelectrolyte and particle charges by the electrolyte. The flocculation mechanism was concluded to be electrostatic patching.

Short-chain cationic polyelectrolytes with high charge density such as PAE and Poly-DADMAC are well suited for patch flocculation, where oppositely charged patches of a particle are attracted to each other. At very high electrolyte concentration, the cationic polymer may desorb from the particles, leading to lower aggregation [38].

Patching may also be the main aggregation mechanism for C-PAM1 and C-PAM2 owing to the short-chain structure. However, the interaction between these polyelectrolytes and surfaces is weaker than for PAE and Poly-DADMAC due to the lower charge densities, and they may not be adsorbed as a flat conformation on the surface but instead form loops and tails, even short ones, able to attach to other particles (bridge flocculation). Compared with PAE and Poly-DADMAC, moreover, the chain lengths of C-PAM1 and C-PAM2 are slightly longer (Table 2). The bridging may be enhanced by a total electrolyte concentration sufficient to suppress the thickness of the diffuse layer and shorten the mean distance between particles. Conversely, high ionic strength may impair the ability to form bridges due to the coil conformation [38]. No charge reversal took place with high dosage of C-PAM1. The zeta potential remained negative (Fig. 3), probably due to screening of the charges by the electrolyte. It has been shown [42] that, at low polyelectrolyte concentration, bridging between particles occurs with a moderately charged cationic copolymer of acrylamide and 2(methacryloxy)ethyltrimethyl ammonium chloride.

The charge density of the polyelectrolyte also affects the floc structure: the flocs formed with highly charged polyelectrolytes are more open and thus less shear resistant than those formed with polyelectrolytes of lower charge [28]. Temperature, in turn, affects floc stability. Probably the lower temperature during storage allowed aggregation to occur with C-PAM2. One explanation for stable floc formation at lower temperature could be decrease in the collision frequency due to Brownian (thermal) motion [38], which controls the collision frequency for small particles (<1 µm).

Not only electrolyte concentration but also temperature affects the conformation of polyelectrolyte. An earlier study has shown that the temperature effect is more pronounced for non-ionic polyethylene oxide (PEO) than for anionic polyacrylamide (PAM) [43]. At high temperature, a coil conformation with fewer loops and tails is preferred. In the case of Poly-DADMAC and PAE postprecipitation during refrigerated storage did not occur. From the findings of this study, it is difficult to say whether the high electrolyte concentration was the reason for the poor aggregation with PAE and Poly-DADMAC. The degradation of these polyelectrolytes due to the high temperature is also possible.

4. Conclusions

The performance of cationic polyelectrolytes is dependent on many parameters, including electrolyte concentration, temperature, pH, and the dosage and charge density of added polyelectrolyte. This study provided deeper understanding of the behaviour of differently charged polyelectrolytes at high temperature and high electrolyte concentration. With birch pulp filtrate taken from the oxygen bleaching stage, effective performance was obtained with a copolymer of acrylamide and methacrylate of medium molecular weight and medium charge density at 72 °C and pH 5–6. The optimum dosage range based on the reduction of turbidity was 102–142 mg/L. Up to 92% of the extractives was selectively removed. Besides internal treatment, cationic polyelectrolytes could be used in an external treatment, supplemental to biological treatment, to lower the amount of detrimental wood extractives and their access to the water system.

Acknowledgments

This research was funded by Kemira Oyj, the Kemira Research Foundation, and the Walter Ahlström Foundation. We gratefully acknowledge the enthusiastic support of Ilkka Laakso and Esa Ruonala (both from Stora Enso Oyj.), Heikki Palonen, Kati Matula, Tiina Sarja, Veli-Matti Vuorenpalo and Mari Zabihian (all from Kemira Oyj.).

References

- [1] E.L. Back, L.H. Allen, Pitch Control, Wood Resin and Deresination, Tappi Press, Atlanta, 2000.
- [2] A. Oikari, B.-E. Lönn, M. Castrén, T. Nakari, B. Snickars-Nikinmaa, H. Bister, E. Virtanen, Toxicological effects of dehydroabietic acid (DHAA) on the trout, *Salmo gairdneri richardson*, in fresh water, *Water Res.* 17 (1983) 81–89.
- [3] G. Peng, J.C. Roberts, Solubility and toxicity of resin acids, *Water Res.* 34 (2000) 2779–2785.
- [4] K.-J. Lehtinen, K. Mattsson, J. Tana, C. Engström, O. Lerche, J. Hemming, Effects of wood-related sterols on the reproduction, egg survival, and offspring of brown trout (*Salmo trutta lacustris* L.), *Ecotoxicol. Environ. Saf.* 42 (1999) 40–49.
- [5] A. Kostamo, J.V.K. Kukkonen, Removal of resin acids and sterols from pulp mill effluents by activated sludge treatment, *Water Res.* 37 (2003) 2813–2820.
- [6] A. Kostamo, B. Holmbom, J.V.K. Kukkonen, Fate of wood extractives in wastewater treatment plants at kraft pulp mills and mechanical pulp mills, *Water Res.* 38 (2004) 972–982.

- [7] H. Leppänen, J.V.K. Kukkonen, A.O.J. Oikari, Concentration of retene and resin acids in sedimenting particles collected from a bleached kraft mill effluent receiving lake, *Water Res.* 34 (2000) 1604–1610.
- [8] L.H. Allen, Pitch control in pulp mills, in: E.L. Back, L.H. Allen (Eds.), *Pitch Control, Wood Resin and Deresination*, Tappi Press, Atlanta, 2000, pp. 265–287.
- [9] O. Dahl, Evaporation of Acidic Effluent from Kraft Pulp Bleaching, Reuse of the Condensate and Further Processing of the Concentrate, PhD Thesis, University of Oulu, Oulu, 1999.
- [10] M.J. Rosa, M.N. de Pinho, The role of ultrafiltration and nanofiltration on the minimisation of the environmental impact of bleached pulp effluents, *J. Membr. Sci.* 102 (1995) 155–161.
- [11] F. Fälth, A.-S. Jönsson, R. Wimmerstedt, Ultrafiltration of effluents from chlorine-free, kraft pulp bleach plants, *Desalination* 133 (2001) 155–165.
- [12] C.R. Tavares, M. Vieira, J.C.C. Petrus, E.C. Bortoletto, F. Ceravollo, Ultrafiltration/complexation process for metal removal from pulp and paper industry wastewater, *Desalination* 144 (2002) 261–265.
- [13] S. Cortiñas, S. Luque, J.R. Álvarez, J. Canaval, J. Romero, Microfiltration of kraft black liquors for the removal of colloidal suspended matter (pitch), *Desalination* 147 (2002) 49–54.
- [14] W.R. Knocke, D. Bhinge, E. Sullivan, G.D. Boardman, Treatment of pulp and paper mill wastewaters for potential water reuse, *Proc. Purdue Univ. Industrial Waste Conf.* (1986) 421–429.
- [15] C.J. Brown, M. Sheedy, M. Paleologou, R. Thompson, Ion-exchange technologies for the minimum effluent kraft mill, *Pulp Paper Can.* 100 (1999) 31–36.
- [16] C. Rampotas, Kidney technology in kraft mills, *Paper Eqmpt. Mater. Intl.* (1999) 928–929.
- [17] G. Lombardo, S. Nivelon, J.L. Piscicchio, H. Suty, Recycling of ECF bleaching plant effluents cleaned by coagulation/flocculation, *Proc. TAPPI Pulping Conf. 2* (1997) 1131–1139.
- [18] R. Järvinen, R. Saunamäki, O. Välttilä, Removal of non-process elements from bleach plant filtrates, *Paperi ja Puu* 76 (1994) 571–572.
- [19] O. Välttilä, S. Jaarmo, R. Järvinen, Removal of silica from bleach plant filtrates, *Proc. Tappi Minimum Effluent Symp.* (1996) 309–315.
- [20] J.L. Garcia-Hares, C.F. Forster, Treating bleaching effluent for suspended solids and Color, *Tappi J.* 72 (1989) 199–206.
- [21] H. Ganjidoust, K. Tatsumi, T. Yamagishi, R.N. Gholian, Effect of synthetic and natural coagulant on lignin removal from pulp and paper wastewater, *Water Sci. Technol.* 35 (1997) 291–296.
- [22] D.A. Barton, E. Drake, T.J. Hall, T. Bousquet, Physicochemical treatment of bleach plant filtrates and final effluents for the reduction of chlorinated organic compounds, *Proc. Tappi Environ. Conf.* (1992) 821–830.
- [23] S. Beulker, M. Jekel, Precipitation and coagulation of organic substances in bleachery effluents of pulp mills, *Water Sci. Technol.* 27 (1993) 193–199.
- [24] Y.M. Chernoberezhskii, A.B. Dyagileva, I.A. Barisheva, Wastewaters treatment of sulphate, sulphite pulp and paper mills by coagulation, *Proc. Intl. Symp. Wood and Pulping Chem.* 3 (1995) 213–218.
- [25] A.T. Hodgson, A.J. Hitzroth, P.D. Premdas, P.V. Hodson, S.J.B. Duff, Effect of tertiary coagulation and flocculation treatment on effluent quality from a bleached kraft mill, *Tappi J.* 81 (1998) 166–172.
- [26] S.S. Wong, T.T. Teng, A.L. Ahmad, A. Zuhairi, G. Najafpour, Treatment of pulp and paper mill wastewater by polyacrylamide (PAM) in polymer induced flocculation, *J. Hazard. Mat.* B135 (2006) 378–388.
- [27] B. Holmbom, Resin reactions and deresination in bleaching, in: E.L. Back, L.H. Allen (Eds.), *Pitch Control, Wood Resin and Deresination*, Tappi Press, Atlanta, 2000, pp. 231–244.
- [28] E. Bergelin, B. Holmbom, Deresination of birch kraft pulp in bleaching, *J. Pulp Paper Sci.* 29 (2003) 29–34.
- [29] L. Eriksson, M.A.G. Dahlgren, B. Alm, P.M. Claesson, The role of polyelectrolyte in wastewater treatment: the fundamental background, *Kemia-Kemi* 22 (1995) 145–150.
- [30] M. Guida, M. Mattei, G. Melluso, G. Pagano, S. Meric, *Daphnia magna* and *Selenastrum capricornutum* in evaluating the toxicity of alum and polymer used in coagulation–flocculation, *Fresenius Environ. Bull.* 13 (2004) 1244–1247.
- [31] T. Leiviskä, J. Rämö, M. Sillanpää, V.-M. Vuorenvalo, Multimodal zeta potential distributions in chemical pulp bleaching filtrates, *J. Pulp Paper Sci.* 31 (2005) 167–174.
- [32] F. Örså, B. Holmbom, A convenient method for determination of wood extractives in papermaking waters and effluents, *J. Pulp Paper Sci.* 20 (1994) 361–366.
- [33] C. Eckerman, R. Ekman, The Analysis of Carbohydrates in Water Phase from Mechanical Pulp Suspensions (In Swedish), Åbo Akademi, Åbo, 1990.
- [34] A. Sundberg, K. Sundberg, C. Lilland, B. Holmbom, Determination of hemicelluloses and pectins in wood and pulp fibres by acid methanolysis and gas chromatography, *Nordic Pulp Paper Res. J.* 11 (1996) 216–219, 226.
- [35] I. Lahdelma, The Determination of Absorptivity Constant for Lignin Isolated from Wood Processing Industry Process Waters, (In Finnish), MSc Thesis, University of Jyväskylä, Jyväskylä, 2002.
- [36] W. Quality, Determination of Turbidity SFS-EN ISO 7027, Finnish Standards Association SFS, Helsinki, 2000.
- [37] Determination of pH-Value of Water SFS. 3021, Finnish Standards Association SFS, Helsinki, 1979.
- [38] D. Eklund, T. Lindström, *Paper Chemistry: an Introduction*, DT Paper Science Publications, Kauniainen, 1991.
- [39] L. Wågberg, L. Ödberg, The action of cationic polyelectrolytes used for the fixation of dissolved and colloidal substances, *Nordic Pulp Paper Res. J.* 6 (1991) 127–135.
- [40] E.L. Back, Resin in suspensions and mechanisms of its deposition, in: E.L. Back, L.H. Allen (Eds.), *Pitch Control, Wood Resin and Deresination*, Tappi Press, Atlanta, 2000, pp. 151–183.
- [41] R. Greenwood, K. Kendall, Effect of ionic strength on the adsorption of cationic polyelectrolytes onto alumina studied using electroacoustic measurements, *Powder Tech.* 113 (2000) 148–157.
- [42] K.E. Bremmell, G.J. Jameson, S. Biggs, Polyelectrolyte adsorption at the solid/liquid interface: interaction forces and stability, *Colloid Surf.* 139 (1998) 199–211.
- [43] P. Mpofu, J. Addai-Mensah, J. Ralston, Temperature influence of non-ionic polyethylene oxide and anionic polyacrylamide and dewatering behaviour of kaolinite dispersions, *J. Colloid Interface Sci.* 271 (2004) 145–156.