Purification of peroxide-bleached TMP water by dissolved air flotation

VILLE SAARIMAA, ANNA SUNDBERG, BJARNE HOLMBOM, ANGELES BLANCO, CARLOS NEGRO, AND ELENA FUENTE

ABSTRACT: Papermakers are continuously searching for better ways to overcome the problems related to accumulation of pitch and polygalacturonic acids (pectins) in process waters. Dissolved air flotation is a technique that could be used as an internal cleaning stage to remove these substances. This study investigated removal of pitch and galacturonic acids from peroxide-bleached, fiber-free thermomechanical pulp (TMP) water by dissolved air flotation (DAF). Both inorganic coagulants and organic flocculants were applied to aggregate the detrimental substances before flotation. The smallest chemical doses that caused aggregation were determined before DAF experiments by turbidity measurements. We also used focused beam reflectance measurement (FBRM) to assess aggregation. Up to 90% of pitch could be removed by DAF at pH 5, determined by gas chromatography and turbidity assessment. At pH 8, the anionic charge of detrimental material increased, accompanied by increased consumption of cationic chemicals. In addition, resin acids dissolve at pH 8, impairing their removal. Aggregation and flotation should therefore be carried out at acidic conditions to increase the aggregation of resin acids and to avoid excessive chemical consumption. Pectins were selectively aggregated. The results indicate that understanding the chemistry of aggregation and flotation is necessary for selection of flocculation chemicals, adjusting process conditions, and for obtaining an acceptable cleaning efficiency.

Application: This study provides valuable information for papermakers who might install a DAF cleaning stage in a TMP process and for optimizing the DAF functions.

Problems related to accumulation of dissolved and colloidal (DisCo) substances have been troubling papermakers since the installation of the first mechanical pulp processes. During mechanical pulping, hydrophilic and lipophilic substances are released and either dissolved or dispersed in the process water. The control of these mostly negatively charged DisCo substances is very important to prevent their negative effects from stretching over the entire papermaking system. Excessive consumption of cationic process chemicals, deposits, and specks in paper can all originate from DisCo released during the pulping process. At present, paper mills are still struggling with these phenomena. The process runnability and product quality are jeopardized with faster paper machines, higher production rates, and legislative and economical pursuit of effluent-free mills.

Alkaline peroxide bleaching has a considerable effect on the noncellulosic constituents of thermomechanical pulp (TMP). The colloidal dispersed pitch droplets lose their steric stability and become sensitive to agglomeration by simple electrolytes [1,2]. In addition, demethylation and dissolution of pectins occur in alkaline conditions, resulting in formation of anionic pectic acids [3]. Peroxide oxidizes lignin and extractives, further increasing the anionic charge of the dissolved and colloidal fraction of the pulp slurry [4].

Different methods of diminishing the negative effects of wood-derived detrimental substances have been developed over time. One way to handle the detrimental material, once it is introduced in the process, is to remove it with the paper [5]. A large variety of commercial fixing agents and retention aids are available for retention of DisCo substances in the sheet. Drawbacks are, however, lower paper quality and carry-over of DisCo to paper recycling plants and subsequent process stages.

Internal cleaning stages can also be installed to purify the circulating waters. Evaporation, membrane filtration, and dissolved air flotation are well-known industrial cleaning techniques. The feasibility of evaporation in purification of TMP process waters is questionable because of high operational costs. The greatest challenge that remains in membrane technology is the fouling of the membranes.

Dissolved air flotation (DAF), also called microflotation, is a common method deinking plants use to clean circulation water. It separates aggregated particles and is not very sensitive to surface properties. Recent studies have investigated removal of extractives by a flotation process resembling flotation deinking, both in chemical and mechanical pulping [6-8]. Extractives attach to air bubbles due to their water-repelling character and float to the surface where they can be mechanically removed. The DAF process is usually accelerated by flocculants that aggregate detrimental substances before actual flotation. Colloidal lipophilic extractives and pectic acids can be effectively removed from bleached TMP water by flotation with coagulants [9,10]. Although some processes already use DAF in internal water purification [11], the flotation technology has not yet achieved larger popularity in TMP mills. A drawback with DAF is its low selectivity, which can lead to considerable fines losses.

This study assessed the removal of lipophilic extractives (pitch) and polygalacturonic acids (pectic acids) from peroxide-bleached TMP water by dissolved air flotation. It compared the aggregation efficiency of different coagulants and flocculants.

A commercial peroxide bleaching stage has an end pH near 8. After bleaching, an acidification with sulfur dioxide (SO_2) water can be used to destroy the residual peroxide. In case the peroxide will be re-used, the pulp goes to press without acidification [12]. Both practices were considered in this work. We also studied aggregation mechanisms and investigated the influence of pH on aggregation-flotation.

EXPERIMENTAL

Materials

A mill in southern Finland using two-stage refining of Norway spruce (*Picea abies*) provided the thermomechanical

pulp for this study. The pulp consistency was about 40%. The pulp was stored in a freezer until used. Analytical grade calcium chloride ($CaCl_2$) and magnesium sulfate ($MgSO_4$) were provided by Panreac Quimica SA. Kemira Oyj provided the commercial grade flocculation chemicals listed in **Table I**.

Preparation of peroxide-bleached TMP water

Portions of TMP (100 g o.d.) were mixed with bleaching chemicals in polyethylene bags at 10% consistency and the initial pH was adjusted to about 11. The peroxide concentration was 3% on o.d. pulp basis [2]. The bags were kept in a water bath at 60°C for 90 min. After bleaching, the samples were acidified to pH 5 or 8 with SO_2^- water. The water was then pressed from the pulp and centrifuged for 30 min at 1500 rpm. The supernatant, free of fibers, containing DisCo substances and microfines, was diluted to 1:10 with distilled water to represent typical TMP process water from a bleaching plant. That TMP water was used as model water in all experiments (**Fig. 1**).

Focused beam reflectance measurement

A Lasentec M500LF for focused beam reflectance measurement (FBRM; Mettler Toledo, Seattle, Washington, USA) was used to assess flocculation. The methodology is based on a highly focused laser beam scanning across particles in a suspension at a fixed speed. The duration of the back-scattered light from these particles is measured. Statistical parameters, such as a value of the particle geometry (mean chord), size distribution, and total counts of suspended solids are obtained. The method has been described by Blanco et al. (2002) [13, 14]. Particles with mean chord over 0.5 µm can be detected. In general, a dispersion can be regarded as colloidal if the size of the particles is in the range 1 nm-1 µm [15]. The FBRM technique has proven to be a rapid and accurate method in providing information about polyelectrolyte-induced aggregation and aggregation kinetics in mechanical pulp slurries [16]. In the peroxide-bleached, centrifuged TMP water, the particle counts per second increase with flocculation. This is because most of the colloidal material is initially below the detection limit. Consequently, the mean chord length also increases.

Determination of chemical doses

The smallest chemical dose that efficiently aggregated DisCo substances was determined for each flocculation chemical before the actual flotation experiments. The chemical doses were determined by FBRM and by assessing aggregation at test tube scale with turbidity measurements. In the latter method, a series of test tubes was prepared for each chemical. We pipetted a bleached TMP water sample of 8 mL into each tube and added different amounts of chemicals. The tubes were agitated by hand and left to stand over night. The next day they were centrifuged (30 min, 1500 rpm) and the supernatant was assessed for turbidity. In FBRM, a sample of bleached TMP water was placed in the glass beaker and agitated at constant velocity during the aggregation. A small portion of flocculation agent was added every 30 s. The minimum quantity of chemical needed to initiate the aggregation was determined by on-line measurement of aggregate formation.

Name	Chemical character	Average molar mass (million g/mol)	Charge (meq/g)
PAC	polyaluminium chloride		medium basicity
PAM0	polyacrylamide	12	-1
PAM1	polyacrylamide	9	0,3
PAM2	polyacrylamide	7	1
PAM3	polyacrylamide	9	2
Bentonite	alkali-activated montmorillonite clay		
FRB	phenol-formaldehyde resin		
PEO	polyethylene oxide	7	nonionic

I. Specification of the flocculation chemicals.

The flotation apparatus

For this study, we used a Flotatest FTH3 DAF apparatus manufactured by Orchidis Laboratoire, France. It consists of three cylinder-conical flotation vessels of 1300 mL, agitators, an rpm-controller, a saturation unit, and a valve for adjustment of air-saturated water. The inlet of air-saturated water and the outlet of sample are located at the bottom of the vessels.

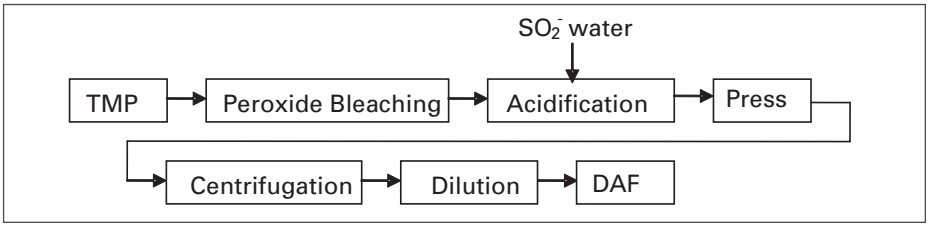
Flotation experiments

Each flotation vessel was filled with 1000 mL peroxide-bleached TMP water at 60°C. The chemicals of determined concentrations were added during rapid agitation (180 rpm). After 30 s the agitation was set to 60 rpm for 6.5 min to facilitate the flocculation process. In case of multi-compound systems, the components were added at intervals of 1 min, maintaining rapid agitation for efficient mixing. The addition orders were polyacrylamide (PAM)-bentonite and magnesium (Mg)-phenol-formaldehyde resin (FRB)-polyethylene oxide (PEO). After that, the agitation was switched off and air-saturated water was introduced into the vessels. Samples were left to stand for 10 min to let the aggregates rise to the surface, followed by sampling of the purified water.

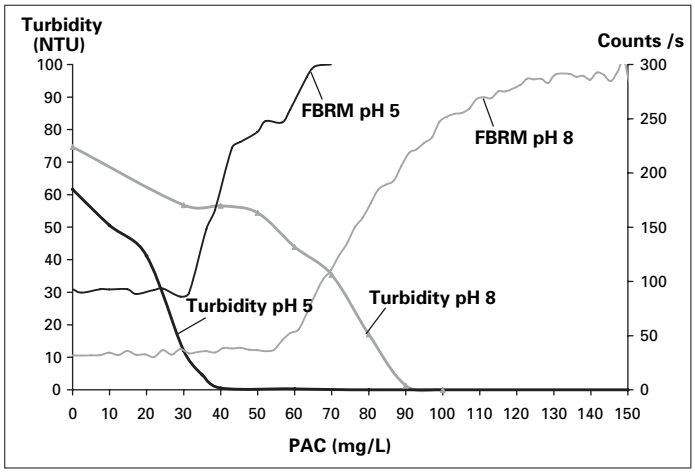
Measurements and analyses

Absorbance was assessed with a Gary 1E UV-visible spectrophotometer (Varian, Australia) at 589 nm, and converted to nephelometric turbidity units (NTU). Total organic carbon (TOC) was determined using a TOC 5050 instrument (Shimadzu Corp., Japan). Lipophilic extractives were determined by extraction with methyl *tert*-butyl ether (MTBE), followed by silylation and analysis by gas chromatography [17].

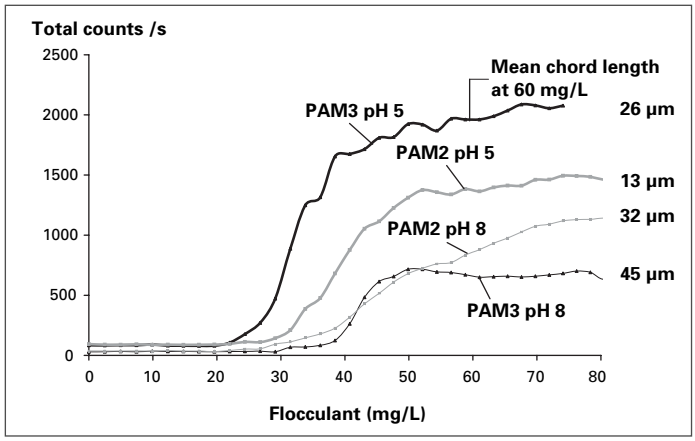
Carbohydrates were determined using acid methanolysis to obtain monomeric methyl glycosides of neutral sugar units and methyl ester glycosides of uronic acids, followed by gas chromatography to determine monomer con-



1. Preparation of peroxide-bleached thermomechanical pulp model water.



2. A higher dose of PAC is needed to aggregate the dissolved and colloidal material at pH 8 than at pH 5.



3. For the studied polyacrylamides, a higher charge density is beneficial for floc formation. Less flocculant is needed and bigger flocs are formed.

centrations [18]. The quantified monomers were arabinose (Ara), xylose (Xyl), galactose (Gal), glucose (Glc), mannose (Man), rhamnose (Rha), 4-O-methylglucuronic acid (4-0-MeGlcA), glucuronic acid (GlcA) and galacturonic acid (GalA). Cationic demand was determined by polyelectrolyte titration with Mütek PCD 03 Particle Charge Detector (Mütek Analytic Inc., Germany). Polybrene (hexadimethrine bromide, SIGMA) was used as the standard polymer.

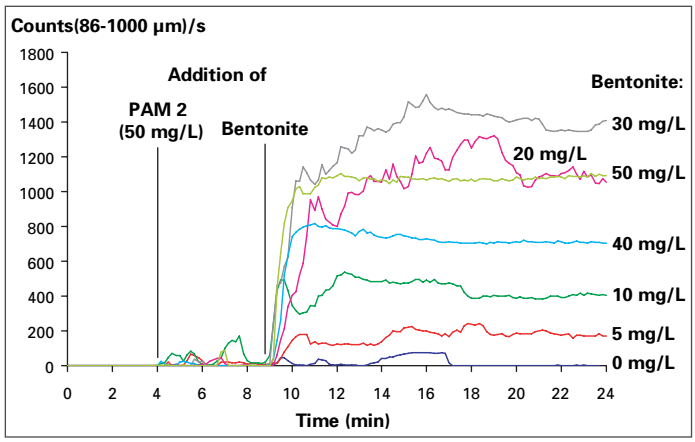
RESULTS AND DISCUSSION

Determination of chemical doses

Table II summarizes the results from determination of chemical doses. Aggregation characteristics of some chemicals are illustrated in **Figs. 2-4**, and in Table II, and are discussed below.

During the process of aggregation, polyaluminum chloride (PAC) hydrolyzes to form a precipitate of aluminum hydroxide that appears as flocs. These flocs have a high surface area that can absorb DisCo substances. The efficiency is best at acidic pH. At high pH values, the hydroxide complexes are too strong, or the complexes built are not beneficial for coagulation, so that the coagulation efficiency decreases [19]. This phenomenon could be verified by both turbidity measurements and FBRM experiments (Fig. 2). The results obtained with both methods were in good accordance, and thus the smallest PAC doses that efficiently aggregated DisCo material could easily be determined: 60 mg/L at pH 5 and 100 mg/L at pH 8 (Table II).

The polyacrylamide doses were determined before studying the PAM/bentonite-system. An anionic polyacrylamide, PAM0, was also tested, but did not cause any aggregation. It could probably be used in a dual flocculation system with a cationic cofactor. The flocs formed by PAM1 were weak and unstable. Even at high polymer doses, no equilibrium state in floc size or floc number was obtained. The aggregation induced by PAM2 or PAM3 was efficiently monitored by FBRM (Fig. 3).



4. The concentration of bentonite has a substantial effect on formation of very big flocs (86-1000 µm).

At pH 5, PAM3 produced more flocs, and bigger flocs, than PAM2, which implies better purification efficiency by DAF. Fewer, but larger flocs were formed with both PAM2 and PAM3 at pH 8 compared to pH 5. In general, flotation is promoted by larger floc size. At pH 8, however, dissolution of some anionic colloidal substances, such as fatty and resin acids, decreases their aggregation and subsequent removal. Thus, an explanation for bigger flocs at pH 8 than at pH 5 could be a lower degree of flocculation of DisCo material.

Furthermore, the larger final floc size at pH 8 could be explained by the partial neutralization of the polymer charge at high concentrations of polysaccharides and resin components. Thus, the adsorption of the polymer on particle surfaces will be weaker, forming tails and loops typical of a bridging mechanism. Consequently, these types of flocs are larger and the number of total counts is lower.

The reason for increasing counts at pH 8 with PAM2 is not clear. The mean chord length remained the same, about 32 µm, even at the highest doses. A higher dose of PAM2 could flocculate more material below 0.5 µm, which becomes visible and gives higher counts per second. This should correspond with a higher DisCo removal. With PAM3, on the other hand, after the threshold dose for flocculation, a stable particle counts level was obtained, which indicates efficient flocculation.

Once the dose of PAM was achieved, the optimal bentonite doses were determined. Figure 4 demonstrates that optimization of the bentonite dose is essential when efficient flocculation is required. The number of very large flocs (about 86-1000 µm) for PAM2 increases steadily as a function of the bentonite dose. The optimal bentonite dose is roughly 20-50 mg/L. The highest counts were obtained at 30 mg/L bentonite. The beginning of the curve after bentonite

Chemical	pH 5 Conc. mg/L	pH 5 Counts/s	pH 5 Mean chord µm	pH 8 Conc. mg/L	pH 8 Counts/s	pH 8 Mean chord µm
$CaCl_2$ (mmol/L)	10	354	18	10	335	17
PAC	60	264	12	100	250	10
	20/60/200			20/60/200		
PEO/FRB/Mg		240	52		138	57
PAM1+B.	80+60	164	113	80+70	132	67
PAM2+B.	30+50	7692	44	40+60	2361	56
PAM3+B.	20+40	6696	61	30+50	4039	46

II. The chemical doses chosen for DAF and the respective agglomerate properties.

addition provides most information, since the PAM/bentonite-system formed quite sticky flocs that attached to beaker walls and to the detector during the experiments. Therefore, the repeatability of long-term experiments at high doses of bentonite is questionable.

The aggregation chemicals studied can be classified according to their flocculation mechanisms. $CaCl_2$ and PAC differ from the other flocculants due to lower mean chord of formed flocs (Table II). In papermaking, these inorganic chemicals are generally known as coagulants. Coagulation is a process in which destabilization is achieved by addition of salts that reduce the electrical repulsion between particles. $CaCl_2$ and PAC coagulate negatively charged particles by electrostatic neutralization. The neutralization of surface charge on the particles results in their cohesion and agglomeration into larger particles, which can be removed by DAF. The shear resistance of flocs formed by coagulation is low, but they reflocculate easily when shear forces decrease.

The term flocculation usually refers to polymers that form bridges or patches between suspended colloidal particles, e.g. aggregation induced by PAMs. The flocs are larger and harder, and the aggregation is partially irreversible if flocs are broken down. The dual system PAM/bentonite forms a flocculation system where the cationic moieties of polyacrylamide interact with anionic DisCo material and with anionic groups on the surface of bentonite.

The PEO/FRB-system flocculates via nonionic interactions. Interactions between the ether oxygens in polyethylene oxide and the phenolic hydroxyl groups in the phenolic resin create a network that captures particles during movement through the dispersion. Mg^{2+} decreases the thickness of electric double layer of colloidal particles, which increases their collision rate and promotes gathering in the network [19].

When pH is increased, deprotonization of acidic groups (mainly carboxyl groups) in DisCo substances occurs and the charge density increases. Thus, the consumption of cationic chemicals increases. This can, in most of the studied chemicals, be noticed as a shift in required chemical doses when pH is changed from 5 to 8 (Table II).

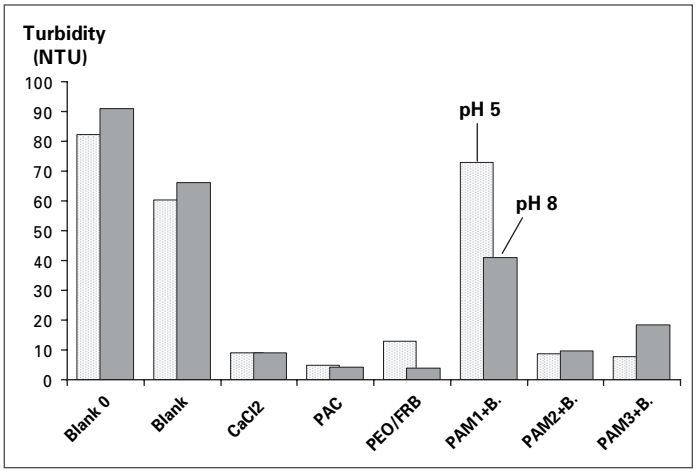
FLOTATION EXPERIMENTS

Blank 0 in the results indicates a reference sample taken before flotation. The blank sample was taken after flotation without any chemical treatment.

Removal of pitch

Dissolved air flotation after flocculation selectively removes pitch from peroxide-bleached TMP water (**Fig. 5, Table III**). Turbidity is directly proportional to the amount of colloidal extractives [20]. Removals of around 80%-90% were obtained with both inorganic and organic aggregation chemicals, regardless of pH. PAM1 and bentonite did not work properly. The charge density of PAM1 was probably too low. The shear forces during flotation caused break-up of the formed weak flocs, which did not reflocculate due to the low charge. At pH 8, the material in the bleached TMP water before DAF was slightly more colloidal. Acidification decreased the repulsive forces between negatively charged colloidal pitch and fibers, thus increasing the adsorption of colloidal material on fibers. Babineau et al. (2003) reported a drastic difference in turbidity of the pressate from acid-treated pulp compared to non-acid-treated pulp [12].

The removal of extractives by flotation with PAM3 and bentonite was lower at pH 8 than at pH 5 (**Fig. 6**). At high pH levels, the fatty and resin acids are dissolved as soaps in the water [21], impair-



5. Turbidity of bleached thermomechanical pulp water can be effectively decreased by flocculation and dissolved air flotation (DAF).

pH5	Free fatty acids mg/L	Resin acids mg/L	Sterols mg/L	Steryl esters mg/L	Triglycerides mg/L	TOTAL mg/L
Blank 0	2.2	3.2	0.4	3.8	7.2	16.9
Blank	1.2	2.8	0.2	2.3	5.4	12.0
$CaCl_2$	0.2	0.9	0.0	0.3	0.7	2.1
PAC	0.2	0.5	0.0	0.2	0.6	1.6
PEO/FRB	0.1	0.8	0.0	0.1	0.2	1.2
PAM1+B.	0.2	1.5	0.1	0.3	0.7	2.8
PAM2+B.	0.1	0.6	0.0	0.2	0.4	1.2
PAM3+B.	0.1	0.7	0.0	0.1	0.5	1.5
pH8						
Blank 0	1.2	3.9	0.4	6.5	13.0	25.1
Blank	1.3	4.4	0.3	4.1	9.2	19.2
$CaCl_2$	0.6	3.1	0.1	0.8	2.1	6.6
PAC	0.2	1.8	0.1	0.5	0.8	3.4
PEO/FRB	0.4	3.4	0.1	0.8	1.5	6.2
PAM1+B.	0.4	3.5	0.0	0.2	0.7	4.9
PAM2+B.	0.3	2.7	0.0	0.2	0.4	3.5
PAM3+B.	0.3	2.9	0.0	0.4	0.7	4.3

III. Residual concentrations of different resin components after DAF.

ing their aggregation and removal by DAF. Especially for resin acids, the shift of pH is drastic, so that removal is about 40% poorer. The same result was obtained with all coagulants and flocculants.

Removal of carbohydrates

Only about 30% of the total carbohydrates were removed at pH 5 by dissolved air flotation, without any chemical addition (**Fig. 7**) and without any selectivity. This could be explained by removal of microfines. The removal was increased by flocculation before flotation. Galacturonic acid units were selectively removed, whereas the other main carbohydrate groups remained in the water. Selective flotation of galacturonic acids after aggregation with $CaCl_2$ has been reported by Sundberg et al. (1995) [9].

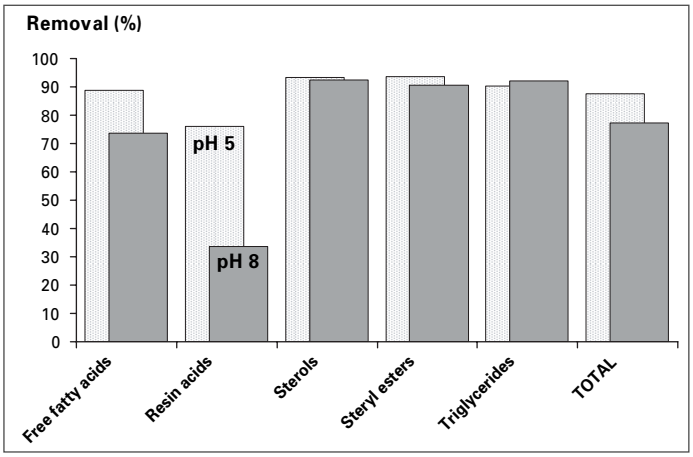
A similar effect was obtained with other inorganic and organic flocculants, also at pH 8. The inorganic flocculants (PAC and $CaCl_2$) removed galacturonic acids more efficiently than the organic multicompound systems (**Fig. 8**). Pectins are known to form gels by calcium bridging. The gel strength increases with increasing Ca^{2+} concentration, resulting in precipitation at high concentrations [22]. In this study, PAC aggregated galacturonic acids even better than did $CaCl_2$ (about 70% were removed).

Figure 9 shows that the galacturonic acid removal increases when the floc size decreases. The highest galacturonic acid removals and the smallest flocs were achieved with highly charged coagulants. The coagulants probably induced charge neutralization of the dissolved substances, followed by aggregation to colloidal flocs, detectable by FBRM. Therefore, a low mean chord value and a high number of counts sometimes mean that there are a lot of aggregated dissolved substances forming small flocs that will be removed by the air bubbles. The increase of the charge density of the polyacrylamides in the PAM/bentonite systems increased the galacturonic acid removal. The PEO/FRB-system did not interact with the dissolved substances, therefore the galacturonic acid removal was very low.

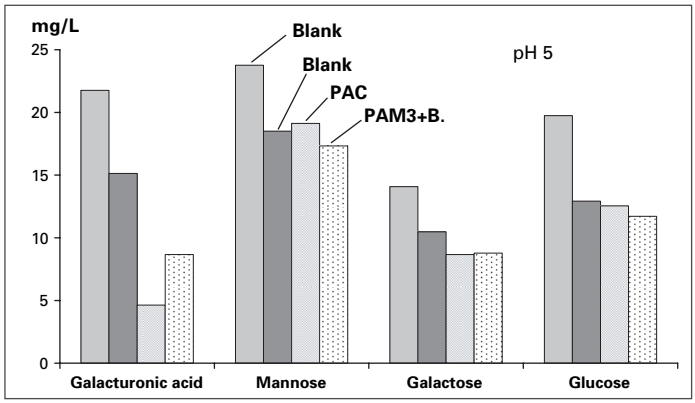
PAM and bentonite did not aggregate galacturonic acids efficiently. PAM3, the polymer with highest charge density, removed about 40% of the galacturonic acids. Nylund et al. (1995) reported that highly charged PAM effectively destabilized dissolved wood polymers, whereas the destabilization progressively decreases towards less charged polymers [23]. The PEO/FRB system with nonionic interaction did not aggregate galacturonic acids. Polygalacturonic acids seemed to be sensitive to aggregation by charge neutralization and were not affected when other aggregation mechanisms dominate. Sundberg et al. (1993) showed that dissolved galacturonic acid can be selectively aggregated by poly-DADMAC, which forms aggregates by patch flocculation or charge neutralization [20].

Cationic demand of bleached TMP water

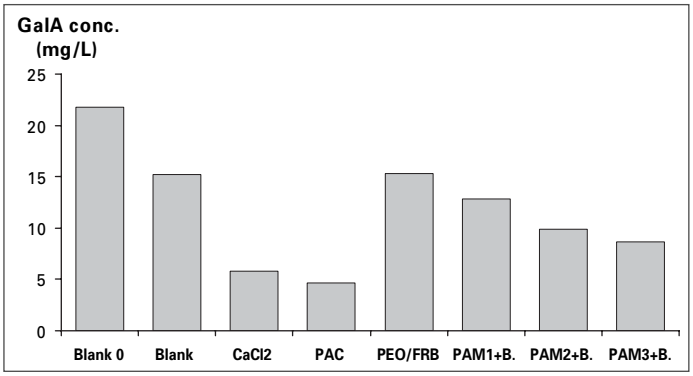
The anionic charge (cationic demand) of bleached TMP water was significantly decreased by DAF and inorganic flocculants, while organic flocculants gave a



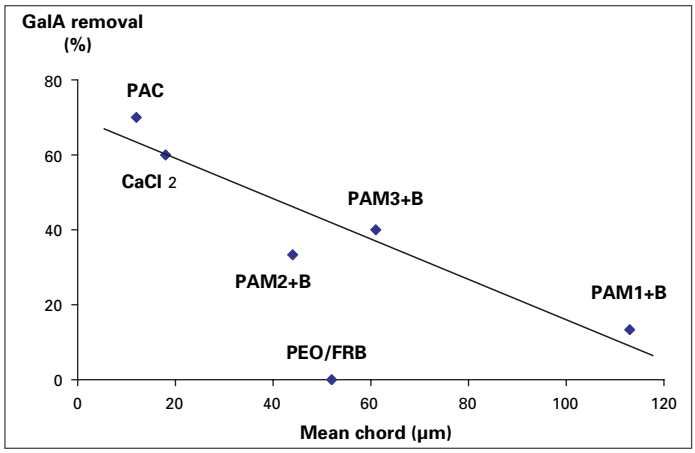
6. Fatty and resin acids were the most difficult extractives to remove from bleached thermomechanical pulp waters at pH 8 by flotation with PAM3+bentonite.



7. Selective removal of galacturonic acids, representing the pectins, was achieved with PAC and PAM3+bentonite at pH 5.



8. Inorganic coagulants aggregated galacturonic acids more efficiently than organic flocculants at pH 5.



9. Galacturonic acid removal was favored by small floc size at pH 5.

lower effect (Fig. 10). The pH has a profound influence on flotation because it affects the ionic character of dissolved and colloidal components. The peroxide-bleached TMP water becomes increasingly anionic as pH is increased from 5 to 8.

The FRB/PEO system did not decrease the cationic demand at pH 8, although it removed pitch well. The interaction between PEO and FRB (resin) is based on nonionic interaction. The charge of FRB is based on pH, at pH 5 it is nonionic and at alkaline pH it is anionic. The anionicity of FRB at pH 8 probably inhibits its interaction with PEO and thus the network formation deteriorates. In general, the cationic demand may not be the most efficient method to assess the purification efficiency, because the added chemicals contribute to the ionic character of the water.

About 30% of the anionic charge of bleached TMP water could be removed by flotation without chemical addition, both at pH 5 and at pH 8. The decrease in anionic charge was lower at pH 8 than that at pH 5 with all coagulants and flocculants.

Bräuer et al. (2001) stated that, depending on the pulp brightness after bleaching, anionic trash accounts for 80%-90% of the detrimental substances measured by polyelectrolyte titration. Silicate accounts for the remaining 10%-20% [24]. Dissolved silica polymerizes at low pH, forming gels. Thus, the retention of silica in pulp increases. Rapid gelling occurs around pH 5-6. Above pH 7, silica begins to dissolve as silicate. At pH 8, no gel is formed since the particles are charged and repel each other. The charge repulsion decreases when salt is present and aggregation as well as gelling occur [12,25]. Thus, silica can account for some of the difference in cationic demand between pH 5 and pH 8.

Sundberg et al. (1999) stated that the anionic charge of TMP suspensions originates mainly in free uronic acids in xylans, arabinogalactans, and pectic acids. The contribution of fatty and resin acids is substantial only for the colloidal fraction [26]. Theoretical anionic charge (carboxyl groups) of TMP waters was assessed on the basis of the concentrations of these substances determined by chromatography (Fig. 10).

Polygalacturonic acids may account for as much as 50% of the cationic demand or potential anionic trash in peroxide-bleached TMP water [21]. In this case the contribution of GalA to total anionic charge was about 30%.

The theoretical charge based on carboxylic groups determined by GC followed the same trend as the charge assessed by polyelectrolyte titration. However, the theoretical amount of carboxylic groups is significantly lower than the cationic demand. Other researchers have reported this behavior and have stated that low-molar-mass lignin, which is dissolved during peroxide bleaching, could adsorb polybrene [26].

Removal of TOC

Only a small fraction of the dissolved organic substances in the bleached TMP waters was removed by flocculation and flotation (**Fig. 11**). Dissolved substances that can not be aggregated can not be removed by flotation. These dissolved substances are mainly hemicelluloses and low-molar-mass lignin. Of dissolved hemicelluloses, only pectins can be aggregated.

CONCLUSIONS

Colloidal extractives can be effectively removed by aggregation and dissolved air flotation. Resin acids were difficult to remove at pH 8, because they occur as soluble soaps and can not be aggregated. Pectic acids made up about 30% of the cationic demand of peroxide-bleached TMP water. They were selectively removed by DAF. Inorganic coagulants aggregated polygalacturonic acids more effectively than did organic flocculants. The PEO/FRB system did not aggregate galacturonic acids efficiently. PAMs aggregated some of the dissolved galacturonic acids. Higher charge density had a positive effect on aggregation. Aggregation by charge neutralization seems to be a more effective mechanism for galacturonic acids than does bridging. Thus, in a papermaking system, less interaction can be expected between galacturonic acids and cationic polymers with high molecular weight and low charge density. Dissolved substances make up the majority of the TOC in bleached TMP water. The decrease in TOC was minimal due to poor aggregation of dissolved substances. Only galacturonic acids can be aggregated and floated. Thus, aggregation and flotation should be carried out at acidic conditions to increase the aggregation of resin acids and to avoid excessive consumption of chemicals. In high-yield pulp mills, if the process water to be purified is not fiber-free, the economical costs related to fines losses during flotation need to be considered. **TJ**

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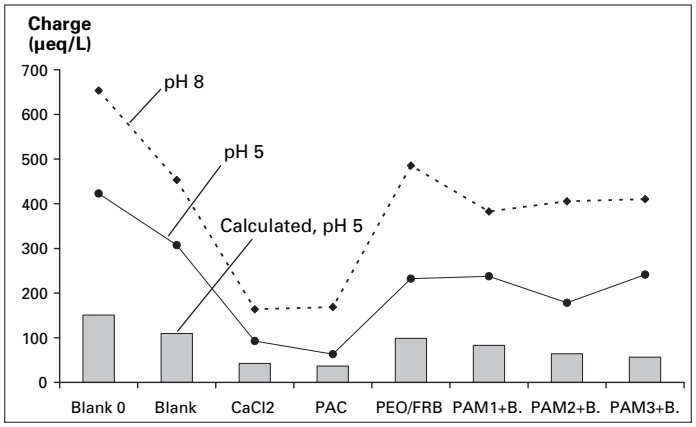
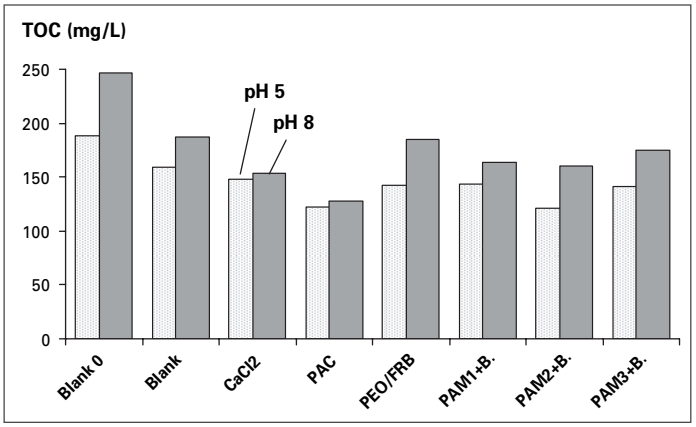


10. The cationic demand of bleached thermomechanical pulp water before and after dissolved air flotation (DAF) with different chemicals at pH 5 and 8. The calculated charge is based on GlcA, 4-0-mGlc, GalA, resin acid, and fatty acid concentrations.



11. Small decreases in total organic carbon (TOC) values imply preferential removal of colloidal particles and only little removal of dissolved substances by dissolved air flotation (DAF).

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INSIGHTS FROM THE AUTHORS

Control of dissolved and colloidal substances, some of which are detrimental, is an essential part of pulp and papermaking.

This study is an extension of previous work at our laboratories. In that, controlled aggregation of dissolved and colloidal substances is combined with flotation studies.

A challenging aspect of this study was to prepare identical peroxide-bleached TMP waters for the different experiments, since that was a prerequisite for determination of the chemical doses and for the successful flotation experiments. This was ensured by very careful preparations.

We found that efficient destabilization and aggregation of dissolved and colloidal material largely determined the removal of this material by flotation. Once well-controlled optimization of aggregation is achieved, the subsequent removal can be carried out by flotation, or other separation techniques.

Monitoring of aggregation of dissolved and colloidal substances by a novel method—focused beam reflectance measurement—can provide optimal conditions for flotation.

As a next step, new means should be developed to selectively separate resin, without losses of fibers and fines, by flotation to purify paper mill process waters by DAF.

Saarimaa, Sundberg, and Holmbom are with Åbo Akademi, Turku, Finland; Blanco, Negro, and Fuente are with Complutense University of Madrid, Spain; e-mail Saarimaa at ville.saarimaa@abo.fi.


Fuente


Holmbom


Negro


Sundberg


Blanco


Saarimaa