Cent. Eur. J. Chem. • 10(1) • 2012 • 127-136
DOI: 10.2478/s11532-011-0121-8

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Central European Journal of **Chemistry**

Coagulation and UF treatment of pulp and paper mill wastewater in comparison

Research Article

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Received 23 May 2011; Accepted 21 September 2011

Abstract: A study using coagulation–flocculation and ultrafiltration (UF) methods for pulp and paper mills' wastewater (WW) was carried out. The reduction efficiencies of turbidity and chemical oxygen demand (COD), the removal efficiency of total suspended solids (TSS) and absorbance at 254 nm were the main evaluating parameters. Using coagulation-flocculation, the efficiencies of alum and polyaluminum chloride (PACl) were studied, when used alone and when coupled with flocculant aids. During the coagulation–flocculation process, use of a single coagulant, the coagulant dosage, and the pH, play an important role in determining the coagulation efficiency. At the optimum PACl dosage of 840 mg L^{-1} and optimum pH of 9.0, turbidity reduction was found to be 94.5%. A combination of inorganic coagulant and flocculant, or polymer was applied, in which PACl was used coupled with the polyelectrolytes Organopol WPB20 and WPB40. PACl coupled with Organopol WPB20 by optimal pH 9 gave a 98.3% reduction of turbidity, 91.9% removal of TSS, and a 60.2% reduction in COD. Ultrafiltration trials were carried out on a pilot scale. A tubular module was used with ceramic membrane. This membrane is a multi-channel membrane with an active surface layer made of Al_2O_3 and ZrO_2. Within the acidic range, the turbidity and TSS were removed at above 99%.

Keywords: *Flocculation • Ceramic membrane • Colloidal particles • Turbidity • COD • TSS*

1. Introduction

The production and use of paper has a number of adverse effects on the environment. Pulp and paper are among the larger industrial polluters of air, water, and land.

The pulp and paper industry is also among the biggest water consumers and, therefore, they create huge amounts of wastewater. The manufacturing process can consume as much as 60 m^3 of freshwater per ton of produced paper [1]. The Wood-pulping and the production of paper products generate a considerable amount of pollutants when untreated or poorly treated effluents are discharged into the recipient waters. Common pollutants include suspended solids (SS), colour compounds, heavy-metals, organic and inorganic substances, phenol, chloro-organics, cyanide, sulphides, and other soluble substances [2]. These effluents cause slime growth, thermal impacts, colour problems, and a loss of environment's aesthetic beauty. They also increase the amount of toxic substances in the water, causing death to the plankton and fish, as well as profoundly affecting the terrestrial ecosystem.

Therefore, the treatment of the wastewater from the pulp and paper industries is necessary. Consequently, new approaches in wastewater treatment technology need to be developed in order to comply with the more stringent environmental regulations on the quality of effluent entering recipient waters.

Several treatment methods are available. The wastewater can be improved by using adsorption, advanced oxidation, membrane filtration [3], coagulation and flocculation [4], solar photo-catalysis [5], electro coagulation [6], catalyzed ozonation [7], or solar photo-Fenton processes [8].

Pulp and paper mills' wastewater contains fibre and can cause unique solid/liquid separation challenges. Eliminating the colloidal suspended-matter (pitch) is one of the main production and environmental problems for the pulp and paper industries, causing a decrease in pulp quality, thus causing mill closures. The colloidal pitch is formed by so-called wood extractives (*i.e.*, those compounds that are extractable from wood using organic solvents). The lipophilic compounds are the most problematic and they include free fatty acids, resin acids,

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waxes, fatty alcohols, sterols, sterol esters, glycerides, ketones, and other oxidized compounds [9]. These substances are released during the digestion of the wood and some of them (*e.g*. waxes, sterols, and sterol esters) do not form soluble soaps nor dissolve during wood cooking, forming colloidal particles that may be deposited on the pulp or machinery, forming sticky deposits or remain suspended within the process waters [10,11].

Chemical coagulation followed by sedimentation is a probed technique for the treatment of high suspended solids wastewater, especially those formed by colloidal matters. According to Aguilar *et al.* [12], anionic polyacrylamide when added to ferric sulphate or polyaluminum chloride led to a significant increase in the settling speed. In earlier work, done by Stephenson and Duff [13], it was found that removals of total carbon, colour, and turbidity of up to 88%, 90% and 98% respectively, were observed during the treatment of mechanical pulping-effluent using ferric chloride, ferrous sulphate, aluminum chloride, and aluminum sulphate.

Recently, the use of synthetic polyelectrolytes as flocculants for suspended solids' removal during wastewater treatment has grown rapidly [14,15]. Girma *et al.* [16] reported that an electron-deficient double-bond of acrylamide is susceptible to a wide-range of chemical reactions, including nucleophilic additions, Diels-Alder, and free radical reactions. Flocculation of suspended particles occurs on account of a charged amide or carboxylic groups. Polyacrylamide (PAM) is a commonly-used polymeric flocculant because it is possible to synthesize it with various functionalities (positive, neutral, or negative charges), which can be used to produce a good settling performance at relatively low cost.

Polymeric flocculants have the ability to produce large, dense, compact, and stronger flocs with good settling characteristic compared to those obtained by coagulation. Wong *et al.* [17] reported the results of flocculation studies with different PAMs, on the treatment of pulp and paper mills' wastewater. They came to the conclusion, that C-PAM is more effective than A-PAM. Organopol 5415 with a very high molecular weight and low-charge density is the best flocculant with the highest flocculation efficiency for the treatment of pulp and paper mills' wastewater. It can achieve 95% of turbidity reduction, 98% of TSS removal, 93% of COD reduction, and sludge volume index (SVI) of 14 mL g^{-1} at an optimum dosage of 5 mg L^{-1}.

Chemical coagulation and flocculation followed by sedimentation are widely-used processes for the removal of suspended solids and these processes have been applied to pulp and paper effluents as a tertiary treatment [18]. Ahmad *et al.* [4] reported the results of treating pulp and paper mills' wastewater using alum and PACl coagulant, coupled with PAMs flocculant. At a fixed amount of alum or PACl, and increased dosages of PAMs, reduction efficiencies of turbidity and COD and the removal efficiency of TSS were more than 90%. At the fixed amounts of PAMs and increased dosages of alum and PACl, they obtained 96%, 99%, and 89% turbidity, TSS, and COD removal efficiencies, respectively.

Several researchers have investigated the performance of membrane processes, such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) during the treatment of pulp and paper industries effluents [19-21]. Membrane processes effectively reduce BOD, COD, total dissolved solids (TDS), total suspended solids (TSS), adsorbable organic halogens (AOX), and colour from pulp and paper effluents [20,22].

Bhattacharjee *et al.* [23] reported, that by using ultrafiltration or adsorption after coagulation with alum for the treatment of wastewater from the digester houses of pulp and paper industries, a slightly greater reduction in BOD and COD was achieved by using ultrafiltration, when compared to adsorption. Leiviskä *et al.* [24] reported the results of treating pulp and paper mills' wastewater before (influent) and after (effluent) biological wastewater treatment, using microfiltration and ultrafiltration with different pore-sizes. The turbidity disappeared with a 0.22 μm fraction per effluent. The reduction in TOC and COD was 60–70%.

To our knowledge, only a few articles have been published on the topic of ceramic membranes. Pizzichini *et al.* [20] reported, that the best filtration performances were obtained with a ceramic MF membrane, having a cut-off of 0.14 μm, which assured a good and stable productivity of 150-200 L m^{-2} h^{-1} with low fouling indexes. On the contrary, spiral-wound polymeric modules, both of MF and UF, showed low productivity and high fouling indexes. MF (pore size of 0.14 μm) rejected all suspended solids and reduced COD and TOC by about 20%. The wastewater composition, having a high content of suspended solids, was unsuitable for spiral-wound conformation.

The objectives of the present coagulation-flocculation study were to investigate the efficiencies of alum and PACl when used alone and coupled with PAMs in the treatment of pulp and paper mills' wastewater and to select the most appropriate coagulant–flocculant scheme using the technical analyses criteria. The effects of coagulant dosage, flocculant dosage, and pH were studied. Further, UF trials were carried out on a pilot-scale. A tubular module with ceramic membrane is used for UF. The membrane area is 0.23 m^2. This membrane

Table 1. Measured parameters, standard analytical methods and apparatus.

Parameter	Standard method	Apparatus	Discharge limits
COD (mg L^{-1} O_2)	ISO 6060	Titration	200 mg L^{-1}
pH	DIN 38 404	pH-meter, MA 5740	6.5-9
Conductivity κ (μS $(cm)^{-1}$)	ISO 7888	Conductometer LF 537	-
Turbidity turb (NTU)	ISO 7027	Turbiditymeter 2100P, HACH	-
Absorbance A (m^{-1})	ISO 7887	Spectrophotometer	-
TSS (mg L^{-1})	ISO/DIS 11923	Filtration (pore size 0,45 μm)	35 mg L^{-1}

was a multi-channel membrane with an active surface layer made of Al_2O_3 and ZrO_2. The pore diameter was 50 nm. The effect of pH was studied. The turbidity, TSS, and chemical oxygen demand (COD) concentrations were used as evaluating parameters. High pressures were used for backwash and this is the reason why ceramic membranes were applied.

2. Experimental procedure

2.1. Real wastewater

Wastewater was collected from the wastewater treatment plant equalization tank of a paper mill. The samples were taken to the laboratory for analysis and further treatment. The pollutants were characterized by chemical oxygen demand (COD), total suspended solids (TSS), turbidity, and absorbance at 254 nm. The measured parameters, standard analytical methods and apparatus used, are shown in Table 1.

2.2. Materials

The $Al_2(SO_4)_3.18\ H_2O$ (alum) was purchased from Merck, Germany, polyaluminum chloride (PACl) from Sotom, Slovenia, polyacrylamides Organopol WPB20 and Organopol WPB40 from Tehnobiro, Slovenia and the Superfloc 567 from Cyanamid, USA. Alum (10 g L^{-1}) and PACl (10% w/w solution) were used as coagulants and very high molecular weight cationic polyacrylamide (C-PAM), Organopol WPB20 (2 g L^{-1}), and Organopol WPB40 (2 g L^{-1}), with high charge density, and low molecular weight cationic polyacrylamide (C-PAM), Superfloc 567 (1% aq. solution), with high charge density were used as flocculants. The zeta potential measurements were determined using Nano Zeta Sizer (ZEN 3600, Malvern inc., UK) at 25ºC.

2.3. Experimental

2.3.1. Jar test

Jar tests were performed on a laboratory scale. The equipment used was a laboratory flocculator: the solutions were observed in 4 parallel jars. Different combinations of pH (6, 7, 8, 9, 10), PACl dosage (200-1000 mg L^{-1}), alum dosage (200-1000 mg L^{-1}), and PAMs dosage (5, 10, 20, 50 mg L^{-1}) were tested. The selected coagulant dosages were added to 1000 mL pH adjusted wastewater samples and then stirred for a period of 1 min at 100 rpm. The selected PAM dosage was then added to the same solution, followed by a further slow mixing of 20 min at 20 rpm. The formed flocs were allowed to settle for 30 to 60 min. After settling, the supernatant water sample was withdrawn and analyzed for parameters.

2.3.2. UF

UF trials were carried out on a laboratory scale. For UF, a tubular module with ceramic membrane was purchased from Tehnobiro, Maribor, Slovenia. The membrane area was 0.23 m^2. This membrane is a multi-channel membrane with an active surface layer made of Al_2O_3 and ZrO_2. Nominal pore diameter was determined at 50 nm. The ceramic membrane was mechanically stable. It was cleaned with backwash at 3 bars after each experiment. No chemical cleaning was necessary during the whole trial.

3. Results and discussion

3.1. Coagulation-flocculation

In order to clearly illustrate the effects of various coagulants and flocculants, the results were divided into two main categories: the effect when single coagulant or flocculant was used and the combination of coagulant with different flocculants. Firstly, the coagulants and flocculants were tested separately. After discarding the low efficiency-ones, the higher-efficiency flocculants were combined with the high-efficiency coagulant for further testing. The optimal dosages of the coagulants or/and flocculants were firstly based on the reductions in turbidity and absorbance at 254 nm. When the best results were achieved, the experiments were repeated by measuring also the removal efficiencies of COD and TSS, respectively.

Table 2. Results after different PACl amounts were added into the wastewater.

PACl (mg L^{-1})	pH_1	pH_2	κ (μS $(cm)^{-1}$)	turb (NTU)	A (at 254 nm)
WW	8.36	/	1419	174.00	2.563
540	6.02	4.06	1463	138.80	2.553
540	7.00	5.31	1520	41.10	2.164
540	10.00	8.10	1503	40.50	2.092
600	8.35	4.69	1559	38.60	1.709
600	9.40	4.76	1577	33.00	1.679
600	10.24	4.99	1633	35.40	1.685
720	9.11	2.57	1606	26.20	1.618
720	9.91	4.70	1633	26.40	1.624
840	7.75	4.52	1623	9.82	1.256
840	9.19	4.54	1653	9.64	1.244
840	9.99	4.65	1694	10.41	1.249
920	9.41	4.53	1684	11.95	1.247

3.1.1. Coagulation with PACl

In order to study the effects of the PACl dosage and pH on the turbidity and absorbance reductions, jar tests were conducted using PACl dosages of 240, 480, 540, 600, 720, 840, 920, and 1000 mg L^{-1} and pH adjusted from 6.0 to 10.0.

Table 2 shows only the best results from different dosages of PACl and pH. pH_2 is the pH after adding PACl.

The turbidity and absorbance at 254 nm reduction efficiencies increased with any increase in coagulant dosage and pH until it reached its highest value, optimum pH, after which the reduction and removal efficiencies started to decrease. The turbidity reduction efficiency started to drop at pH 10.0 and at PACl dosage 920 mg L^{-1}. The value for turbidity did not decrease for dosages lower than 480 mg $L^{-1}$of PACl. The highest turbidity reduction achieved by PACl was 94.5% and the lowest 76.7%.

The absorbance of the samples was determined at 254 nm. At 254 nm the light is mainly absorbed by organic substances (aromatic components). The highest absorbance reduction was 51.5%.

The conductivity has increased by almost 1.2%. The PACl performance depends on the pH, there were Al^{3+} ions present, and therefore, the alkalinity decreased.

The optimum PACl dosage and pH are 840 mg L^{-1} and 9.0, respectively.

3.1.2. Coagulation

The Alum used had the following composition: $Al_2(SO_4)_3{\bullet}18H_2O$.

In coagulation–flocculation processes the use of an inorganic coagulant, the coagulant dosage and the pH play an important role in determining the coagulation efficiency. In wastewater treatment using inorganic coagulants an optimum pH range, in which metal hydroxide precipitates occur, needs to be determined. The addition of metal coagulants depresses the wastewater pH to a lower value. Jar test experiments with alum were run, using pulp and paper mills' wastewater with pre-adjusted pHs from 6.0 to 10.0, for each pH value, with alum dosages of 240, 480, 540, 600, 720, 840, 920, and 1000 mg L^{-1}.

Recently, high molecular weight long-chain polymers have been used as replacements for alum and ferric chloride during the flocculation of suspended solids. The advantages of polymers are: the lower dosage requirements, reduced sludge production, easier storage and mixing, both the molecular weight and charge densities can be optimized creating "designer" flocculant aids, no pH adjustment is required, polymers bridge many smaller particles, and improved floc resistance to shear forces [25].

The results show that reduction in parameters were very similar to those obtained when using PACl. However, the settling time was twice as long, as well as the sludge volume being higher in comparison with PACl, therefore PACl was used in further experiments.

3.1.3. Flocculation

Only C-PAMs were used in this study, because they are more effective than A-PAMs [17].

In order to study the effects of the C-PAM (Organopol WPB20, Organopol WPB40, and Superfloc 567) dosage and pH on the turbidity reduction and absorbance at 254 nm removal, jar tests were conducted using PAM dosages of 5, 10, 20, and 50 mg L^{-1} and a fixed pH of wastewater of 8.36, because polymer performance is less dependent on pH a PACl and alum. There were no residual or metal ions added, such as Al^{3+} and Fe^{3+}, and the alkalinity was maintained.

The results with flocculant WPB20 are shown in Table 3.

Table 3. Measurements when using flocculant WPB20.

WPB20 (mg L^{-1})	pH	κ (μS (cm)$^{-1}$)	*turb* (NTU)	A (at 254 nm)
WW	8.36	1419	174.0	2.563
5	8.29	1372	167.0	2.755
10	8.19	1363	161.0	2.723
20	8.17	1350	64.0	1.916
50	8.08	1347	48.5	1.605

Table 4. Measurements when using WPB20 and WPB40 in combination with PACl.

PACl (mg L^{-1})	WPB20 (mg L^{-1})	pH	κ (μS (cm)$^{-1}$)	turb (NTU)	A (at 254 nm)
WW		7.07	1253	183.00	2.745
540	3	5.62	1408	5.80	1.227
540	6	5.98	1394	10.10	1.259
600	3	5.81	1402	14.80	1.297
600	6	7.08	1239	49.90	1.551
	WPB40 (mg L^{-1})				
540	3	5.66	1404	6.17	1.167
540	6	5.73	1399	6.96	1.164
600	3	5.91	1403	17.20	1.463
600	6	6.20	1424	16.60	1.302

When adding the Organopol WPB20, the largest dosage gave the highest turbidity reduction 72.1%, which was not as efficient as when adding only PACl. In that case the turbidity reduction was 94.5%. The absorbance at 254 nm reduction was only 37% and the conductivity decreased by 5%.

The results using Organopol WPB40 were almost the same as those using WPB20 with the same amounts of flocculants added.

When using Superfloc 567, the turbidity removal efficiency was considerably lower, therefore, it was not used in further experiments.

3.1.4. Effect of flocculant dosage

PACl was used coupled with C-PAM (Organopol WPB20 and WPB40). Another wastewater sample was taken from the equalization tank. The effect of cationic flocculant dosages on the reduction of turbidity and absorbance at 254 nm was investigated. The flocculant dosages were 3.0 and 6.0 mg L^{-1} and the PACl dosages were 540 and 600 mg L^{-1}. The initial pH of the wastewater was 7.07 and all measurements were made at the same pH, as shown in Table 4.

The removal of turbidity and absorbance at 254 nm efficiencies were calculated from the turbidity and absorbance at 254 nm initial concentration in the raw wastewater, and the final concentration in the supernatant.

The results obtained for PACl + Organopol WPB20 and PACl + Organopol WPB40 treatments showed, that lower dosage of C-PAM, and also of PACl, provided better removal efficiencies than higher dosages.

It can be seen that increasing flocculant dosage does not always improve the reduction or removal rates. Overall, the reduction efficiency of turbidity was more than 96% and the absorbance at 254 nm was 55% even at a low PACl (540 mg L^{-1}) dosage. The conductivity increased by 12%.

The performance of PACl + Organopol WPB20 in terms of turbidity reduction was the best combination coagulant + the flocculant system, from among all the combinations investigated.

3.1.5. Zeta potential measurements

Fig. 1 presents the Zeta potential measurements of Organopol WPB20. It can be seen that within low pH values Zeta potential decreased from 20 mV at pH 3 to value 0 at pH 5, whilst it seemed to settle at around the zero point of charge up to pH=9. Zeta potential of Organopol WPB40 was practically the same as that of WPB20 under the same conditions as the points of WPB20 are covered by the points of WPB40. The zeta potential of Superfloc was not determined since the flocculation effect using this flocculant was worse.

3.1.6. Turbidity reduction, TSS removal and COD reduction by coagulation + flocculation

The best combination coagulant + flocculant system in terms of turbidity reduction was PACl + Organopol WPB20. Optimum efficiency was achieved by adding 540 mg L^{-1}of PACl and 3 mg L^{-1} of WPB20.

The test with the optimum dosage of PACl and Organopol WPB20 was repeated in terms, in order to also measure TSS removal and COD reduction.

Table 5. Measurements when using PACl and Organopol WPB20 at different pH's.

PACl (mg L⁻¹)	WPB20 (mg L⁻¹)	pH_1	pH_2	κ (μS (cm)⁻¹)	turb (NTU)	A (at 254 nm)	COD (mg L⁻¹)	TSS (mg L⁻¹)
WW		7.07	/	1253	183.00	2.745	1030	270
540	3	8.98	8.54	1692	3.19	1.164	410	22
540	3	7.07	6.54	1243	5.80	1.167	450	24
540	3	2.75	3.03	1943	5.66	1.343	500	31

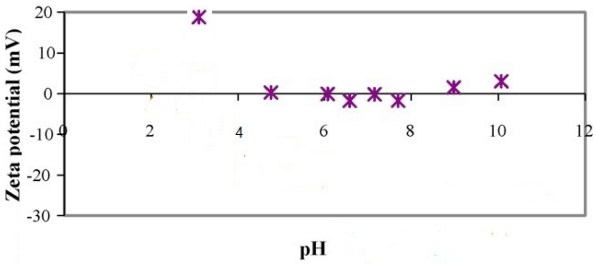

Figure 1. Zeta potential of WPB20 (denoted as x) and WPB40 (denoted as I) as a function of pH.

The measurements were repeated within different pH ranges, in neutral pH, in alkaline at pH = 9, and in acidic at pH = 3, as can be seen in Table 5.

At optimum pH 9, the turbidity was removed by up to 99%, COD was lowered by 60%, TSS by 92%, absorbance by 58%, and the conductivity increased by 35%. At pH 7 turbidity reduction was almost 97%, COD reduction 56%, TSS removal 91%, absorbance reduction almost 58%, and conductivity lowered by almost 1%.

The results were the best within the alkaline region. However, the efficiencies were only up to 5% better than those obtained within the neutral pH range. The pH of the treated water before discharged into the recipient waters needs to be between 6.5 and 9, but even after adding PACl at pH 7, the pH of the treated water did not go below 6.5.

3.2. Ultrafiltration

In order to study the effects of UF and pH on turbidity and absorbance reductions, TSS removal, and COD reduction, tests were conducted at the pilot-plant within different pH ranges: in neutral pH, in alkaline at pH = 8.3, and in acidic at pH = 5.6. The wastewater was pre-treated using mechanical treatment – conventional filtration (F1).

The results are shown in Tables 6-8.

From the measurements it can be seen, that the optimum pH of the water was around 6 – in this case the water was in carbonate equilibrium and the minimum dosage of calcium carbonate, that clogs the membrane, precipitated.

The calculations from the Langelier's saturation index (LSI) showed values from -0.2 to -0.5 for the acidic samples. In that case the parameters had optimal values, which made the UF more efficient. If the pH was acidic, the conductivity increased, whilst the highest turbidity and TSS decreases were determined for the acid samples. The neutral and alkaline pHs of wastewater were unfavourable in terms of precipitated calcium carbonate, which clogs the membrane, and the amount of TSS was greater than in alkaline permeate. In the acidic, COD was lowered by up to 75%, absorbance by up to 81% whilst turbidity and TSS were above 99%, respectively. From Tables 6-8, it can be seen that the values for COD, TSS and pH after UF treatment are in accordance with the legislation (see Table 1, last column).

3.2.1 The membrane fouling

Ceramic instead of polymer membrane was used due to their lower fouling index [20].

Fluxes of distilled water, wastewater, and distilled water after backwashing under different transmembrane pressures (TMP) are shown in Fig. 1. The results show, that the membrane was not fouling irreversibly, because it would be easily cleaned with the backwash using distilled water, which can be seen from a comparison of the fluxes of distilled water and distilled water after backwash. The fluxes of distilled water after backwash maintain values from 88% to 91% of the flux values of the distilled water, which had been filtered before wastewater. The flux of wastewater decreased significantly in comparison with the distilled water, because of the composition of the wastewater. The colloidal matters and suspended solids accumulated on the membrane surface and caused fouling.

The permeate flux of the ceramic membrane at TMP = 1.6 bar remained stable at 75 L h^{-1} m^{-2}. As can be seen from Fig. 2, the ceramic membrane had already reached 100 L h^{-1} m^{-2} flux of wastewater at TMP = 2 bars. At TMP = 3 bars, the flux value reached 164 L h^{-1} m^{-2}.

The degree of reversible fouling FR_{rev} was calculated by following Eq. 1:

$$FR_{rev} = (J_3 - J_2) / J_1 \qquad (1)$$

The degree of irreversible fouling FR_{ir} was calculated by following Eq. 2:

$$FR_{ir} = (J_1 - J_3) / J_1 \qquad (2)$$

Table 6. Measurements for neutral samples.

Parameter	pH	κ (μS (cm)$^{-1}$)	*turb* (NTU)	A (at 254 nm)	COD (mg L^{-1})	TSS (mg L^{-1})
WW	7.0	1253	174.0	2.14	880	240
F1	7.3	1203	5.0	1.64	830	95
UF	7.4	1104	0.7	0.53	420	0.9

Table 7. Measurements for acidic samples.

Parameter	pH	κ (μS (cm)$^{-1}$)	*turb* (NTU)	A (at 254 nm)	COD (mg L^{-1})	TSS (mg L^{-1})
WW	7.0	1253	174.0	2.14	880	240
F1	5.6	2054	13.4	1.67	830	60
UF	6.1	1712	0.2	0.40	220	0.4

Table 8. Measurements for alkaline samples.

Parameter	pH	κ (μS (cm)$^{-1}$)	*turb* (NTU)	A (at 254 nm)	COD (mg L^{-1})	TSS (mg L^{-1})
WW	7.0	1253	174.0	2.14	880	240
F1	8.3	1240	9.8	1.87	830	70
UF	8.5	990	1.0	0.58	200	0.5

Table 9. The degree of reversible, irreversible and total fouling.

TMP (bar)	FR_{rev}	FR_{ir}	FR
3.0	0.6037	0.0926	0.6963
2.5	0.6105	0.0947	0.7052
2.0	0.5946	0.1081	0.7027
1.6	0.6111	0.1111	0.7222
1.0	0.5938	0.1250	0.7188

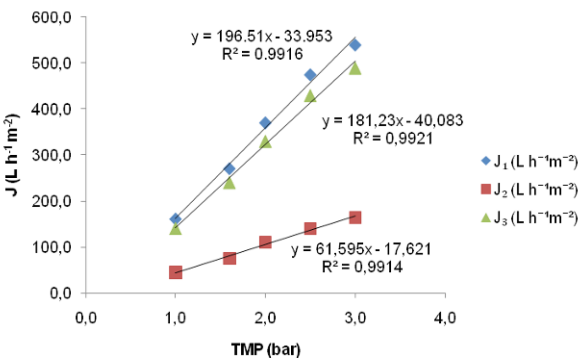

Figure 2. Flux of distilled water J1, wastewater J2 and distilled water after backwash J3, as a function of TMP.

Where

J_3 = pure water flux after wastewater treatment and backwash

J_1 = pure water flux before wastewater treatment

J_2 = wastewater flux

The total degree of fouling *FR* ws calculated as the sum of FR_{rev} and FR_{ir} (Table 9).

The total flux decrease was high due to the cake-layer, and fouling was attributed to the adsorption of organics, such as fatty acids, sterol esters, glycerydes, and other oxidized compounds. However, all could easily be reversed by hydraulic cleaning alone. Thus the reversible fouling was high and the irreversible fouling was much lower.

Hermia [26] developed four empirical models that correspond to the four basic types of fouling: complete blocking, intermediate blocking, standard blocking, and cake-layer formation. These models were developed for dead-end filtration and are based on constant pressure filtration laws:

$$\frac{d^2t}{dV^2} = K\left(\frac{dt}{dV}\right)^n \tag{3}$$

Where:

t = time (s)

V = accumulated permeate volume (m^3)

K = constant (unit depending on the parameter n)

Complete blocking model ($n = 2$):

$$\ln J = \ln J_0 - K_C t \tag{4}$$

Intermediate blocking model ($n = 1$):

$$\frac{1}{J} = \frac{1}{J_0} + K_i t \tag{5}$$

Standard blocking model ($n = 3/2$):

$$\frac{1}{J^{1/2}} = \frac{1}{J_0^{1/2}} + K_S t \tag{6}$$

Cake layer formation model ($n = 0$):

$$\frac{1}{J^2} = \frac{1}{J_0^2} + K_d t \tag{7}$$

Where:

J_0 = initial permeate flux (m s^{-1})

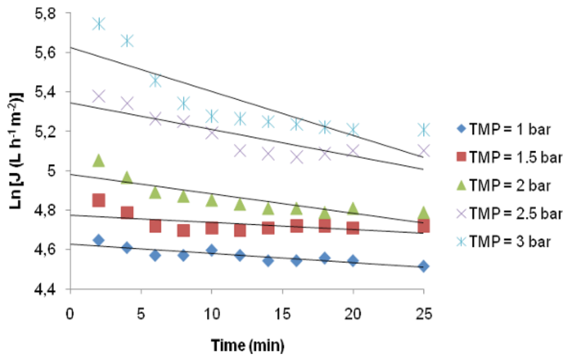

Figure 3. Permeate flux predicted by the complete blocking model.

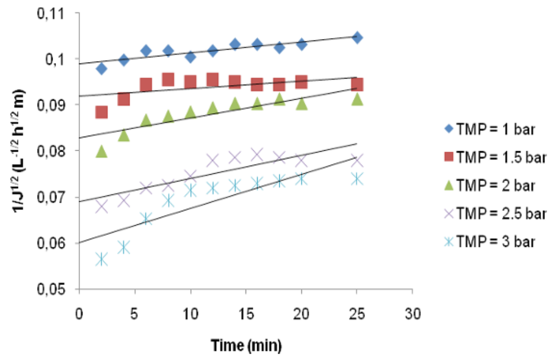

Figure 5. Permeate flux predicted by the standard blocking model.

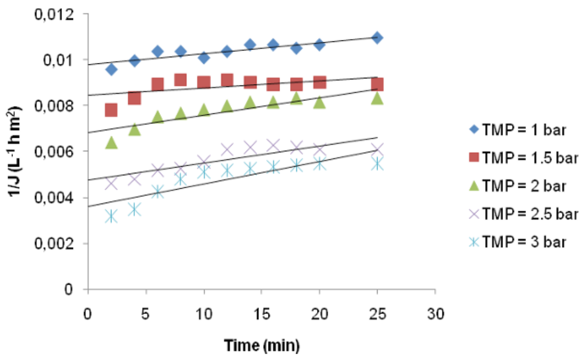

Figure 4. Permeate flux predicted by the intermediate blocking model.

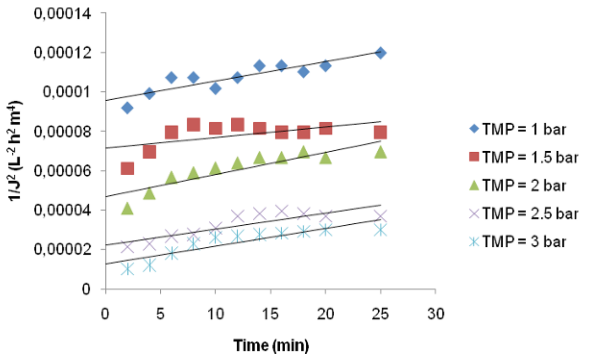

Figure 6. Permeate flux predicted by the cake layer formation mode.

Table 10. Comparison of the results for coagulation + flocculation, and ultrafiltration.

Parameter	Coagulation + flocculation	Ultrafiltration
Reduction in turbidity	98.3%	99.7%
Reduction in A (at 254 nm)	57.6%	81.3%
Reduction in COD	60.2%	75.0%
Removal in TSS	91.9%	99.8%

J = permeate flux (m s^{-1})
K_c = constant in Eq. 4 that corresponds to the complete blocking model (s^{-1})
K_i = constant in Eq. 5 that corresponds to the intermediate blocking model (m^{-1})
K_s = constant in Eq. 6 that corresponds to the standard blocking model ($m^{-1/2}$ $s^{-1/2}$)
K_d = constant in Eq. 7 that corresponds to the cake layer formation model (s m^{-2})

Hermia's models were used to interpret the fouling phenomenon occurring during ultrafiltration experimental tests of the pulp and paper wastewater.

Fig. 3 shows the fitting of the experimental results to the complete blocking model, according to Eq. 4. High deviations between the experimental and predicted flux declines were observed for high TMPs of 2.5 and 3 bar. The complete blocking model considered that this type of fouling occured when the sizes of the suspended molecules in the feed solution were greater than the membrane pores. Therefore, suspended molecules did not enter the membrane pores and did not arrive at the permeate side. For this reason, the differences between the experimental data and the fitted results can be related to the fact that some molecules permeated through the membrane at high TMPs. In our case, the R-squared values were only between 0.7 and 0.77 for all TMPs.

Fig. 4 shows the fitting of the experimental permeate flux to the intermediate blocking model for all the experimental conditions tested, according to Eq. 5. The intermediate blocking fouling mechanism occured when the membrane pore size was similar to the sizes of the suspended molecules. The membrane pores were blocked near their entrance on the feed side. However, the intermediate blocking model did not provide a better agreement with the experimental data than the complete blocking model (R^2 between 0.74 and 0.78). The highest deviations between the experimental and predicted flux decline were observed for high TMPs of 2.5 and 3 bars, as in the case of the complete blocking model.

Fig. 5 shows the fitting of the standard blocking mechanism to the experimental results, according to Eq. 6. Internal pore blocking was produced due to the adsorption of the suspended molecules onto the membrane pores' walls. High deviations between the experimental and predicted flux decline were observed for the highest TMPs of 2.5 and 3 bar and the deviations (R^2 between 0.73 and 0.78) were comparable with those obtained by the complete and intermediate blocking models.

Fig. 6 shows the fitting of the cake layer formation model to the experimental results obtained during this work, according to Eq. 7. The model predictions were observed to be accurate due to the fact that most of the colloidal particles, pitch, and suspended solids were retained by the membrane for the experimental conditions tested. Higher TMPs did not result in a higher deformation of the molecules and the cake-compression was not higher, therefore similar predictions were obtained for all TMPs. The molecular deformation was influenced by the applied TMP. However, the deviations were comparable to those obtained by the complete, intermediate, and standard blocking models.

3.3. Comparison between coagulation + flocculation and ultrafiltration

The reduction of turbidity, absorbance (A) and COD, and the removal of TSS efficiencies, are shown in Table 10.

As can be seen from Table 10, the reductions in turbidity and absorbance, COD, and the removal of TSS were better when using UF. Also, a greater reduction of absorbance at 254 nm could be seen using UF. This means that more of the aromatic substances had been removed.

4. Conclusions

The treatment of pulp and paper mills' wastewater using PACl coagulant coupled with PAMs enhanced the reduction/removal of turbidity, TSS, and COD when compared to the results obtained when the coagulants and flocculants were used alone. However, any increase in the PAMs dosage does not have a significant effect on PACl coagulation. PACl, coupled with Organopol WPB20 was the best system from among all the systems studied and showed the highest efficiency in terms of reduction in turbidity, the removal of TSS, and the reduction in COD. The additions of PAM improved the treatment performances. At optimum pH 9, optimum dosages of PACl (540 mg L^{-1}), and Organopol WPB20 (3 mg L^{-1}), turbidity was removed by up to 99%, COD was lowered by 60%, TSS by 92%, and absorbance by 58%. UF membrane presented better performance and the highest retentions were achieved at pH 6: turbidity was removed by up to 99%, COD was lowered by 50%, TSS by 99% and absorbance at 254 nm by 81%, respectively, within the acidic range. The calculations of Langelier's saturation index (LSI) showed values from -0.2 to -0.5 in the acidic samples. In this case the water was in carbonate equilibrium and the minimum dosage of calcium carbonate, that clogs the membrane, precipitated.

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