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Treatment of pulp and paper mill wastewater by polyacrylamide (PAM) in polymer induced flocculation

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Abstract

The flocculation performances of nine cationic and anionic polyacrylamides with different molecular weights and different charge densities in the treatment of pulp and paper mill wastewater have been studied. The experiments were carried out in jar tests with the polyacrylamide dosages range of 0.5–15 mg l^{-1}, rapid mixing at 200 rpm for 2 min, followed by slow mixing at 40 rpm for 15 min and settling time of 30 min. The effectiveness of the polyacrylamides was measured based on the reduction of turbidity, the removal of total suspended solids (TSS) and the reduction of chemical oxygen demand (COD). Cationic polyacrlyamide Organopol 5415 with very high molecular weight and low charge density is found to give the highest flocculation efficiency in the treatment of the paper mill 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 the optimum dosage of 5 mg l^{-1}. SVI values of less than 70 ml g^{-1} are found for all polyacrylamide at their respective optimum dosage. Based on the cost evaluation, the use of the polyacrylamides is economically feasible to treat the pulp and paper mill wastewaters. This result suggests that single-polymer system can be used alone in the coagulation–flocculation process due to the efficiency of the polyacrylamide. Sedimentation of the sludge by gravity thickening with settling time of 30 min is possible based on the settling characteristics of the sludge produced by Organopol 5415 that can achieve 91% water recovery and 99% TSS removal after 30 min settling.
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1. Introduction

The pulp and paper industry is a very water-intensive industry and can consume as high as 60 m^3 of freshwater per tonne of paper produced [1]. The generation of wastewater and the characteristics of pulp and paper mill effluent depend upon the type of manufacturing process adopted. Hence, the treatments of the wastewaters from different mills become complicated because no two paper mills discharge identical effluents due to different combination of unit processes involved in the manufacturing of pulp and paper.

Wastewater from pulp and paper mills constitutes a major source of aquatic pollution since it contains high organic substances causing high biochemical oxygen demand (BOD) and chemical oxygen demand (COD), extractives (resin acids), chlorinated organics (measured as adsorbable organic halides, AOX), suspended solids, metals, fatty acids, tannins, lignin and its derivatives, etc. [2,3]. Lignin and its derivatives can form highly toxic and recalcitrant compounds and are responsible for the high BOD and COD. Alkylphenol polyethoxylates (APEOs) or nonylphenolic compounds can also be found in the pulp and paper mills effluent [4]. The effluent is toxic to aquatic organisms and exhibits strong mutagenic effects and physiological impairment. Varieties of responses were reported in fish populations living downstream of bleached kraft pulp mills [5–7]. Consequently, a new approach in the wastewater treatment technology should be developed to face more stringent environmental regulations on the quality of the effluent entering receiving waters.

Many studies have been carried out on the treatment of pulp and paper mills wastewater by biological method such as conventional aerobic and anaerobic treatment methods [8–12]. Godkay and Dilek [13] and Wu et al. [14] reported that pulp and

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paper mill wastewater can be treated by white-rot fungi. Numerous physico-chemical processes such as ozonization, electron-beam and ultrafiltration have also been developed [15–18], often in combination with coagulation. Chemical coagulation, using alum, ferric chloride, ferric sulphate and lime have been studied extensively [19–21]. The above mentioned methods have their respective weaknesses and limitations.

Recently, the use of synthetic polyelectrolytes as flocculants for suspended solids removal in wastewater treatment has grown rapidly [22,23]. Acrylamide is a crystalline and relatively stable monomer which is soluble in water and many organic solvents. Acrylamide is a polyfunctional molecule that contains a vinylic carbon–carbon double bond and an amide group. The electron deficient double bond of acrylamide is susceptible to a wide range of chemical reactions including nucleophilic additions, Diels–Alder and free radical reactions [24]. The flocculations of the suspended particles occur via the double bond. Polyacrylamide (PAM) is a commonly used polymeric flocculant because it is possible to synthesize polyacrylamides (PAMs) with various functionalities (positive, neutral or negative charge) which can be used to produce a good settling performance at relatively low cost.

The advantage of polymeric flocculants is their ability to produce large, dense, compact and stronger flocs with good settling characteristic compared to those obtained by coagulation. It can also reduce the sludge volume. Furthermore, the polymer performance is less dependent on pH. There are no residual or metal ions added such as Al^{3+} and Fe^{3+}, and the alkalinity is maintained. The flocculation performance of flocculants primarily lies on the type of flocculant and its molecular weight, ionic nature and content, on the suspension content in the wastewater and the type of wastewater [25].

The use of polymeric flocculants or polyelectrolytes, especially those of high molecular weight, has resulted in tremendous performance improvement for industrial separation processes [26,27]. According to Ovenden and Xiao [28], a good clay flocculation is observed when colloidal alumina (cationic microparticles) is used in conjunction with cationic and nonionic PAMs but a synergetic effect is observed in conjunction with anionic PAM. Recently, a photometric dispersion analyzer (PDA) was successfully applied to monitor a flowing suspension of paper-making filler flocculated by cationic polymer and microparticle system [29].

Technological advancements in polymer chemistry have improved the flocculant technology to provide polyelectrolytes with greater purification efficiency. However, flocculation optimization practices in industry are still reliant, to a very large extent, performed on a trial and error basis due to the highly complex nature of the flocculation process and the large variety of polyelectrolyte available. A better understanding on how polymer molecular weight and charge density distribution affect the flocculation performance may lead to improved flocculant manufacturing processes and better choice of flocculants for the users in specific industrial application.

The main objectives of the present study are to investigate the flocculation efficiencies of various types of PAM flocculant in the treatment of pulp and paper mill wastewaters and to select the most appropriate flocculant scheme with the technical analysis criteria. The optimum dosage, type and psychical attributes of the flocculant such as molecular weight, charge density and functional group are studied to gain a better understanding of the flocculation mechanism. The turbidity, TSS and COD concentrations are used as evaluating parameters. The settled sludge volume, SVI, sludge settling characteristics and water recovery are also investigated.

2. Experimental

2.1. Materials

The wastewater was collected from the wastewater treatment plant equalization tank of a paper mill in Penang, Malaysia. Tissue papers are the main product of the mill with a monthly capacity of 3000 metric tonnes. The wastewater produced by the plant was 96 m^3/tonne of paper produced. The wastewater samples were characterized and the analyses are given in Table 1. These parameters were measured based on the *Standard Methods for the Examination of Water and Wastewater* [30].

Various cationic polyacrylamides (C-PAM) and anionic polyacrylamides (A-PAM) of commercial grade in a wide range of molecular weight and charge density were used. Organopol 5415, Organopol 5020, Organopol 5470, Organopol 5450 and Organopol 5540 were supplied by Ciba Speciality Chemicals. Chemfloc 1515C and Chemfloc 430A were supplied by Chemkimia. AN 913 and AN 913SH manufactured by SNF Floerger were provided by Kempro. The properties of the polyacrylamides used are as shown in the Table 2. Distilled water

Table 1
Chemical characteristics of the wastewater used

Parameters	Value[a]
TCOD[b] ($mg\,l^{-1}$)	3087
SCOD[c] ($mg\,l^{-1}$)	318
Suspended solids ($mg\,l^{-1}$)	5240
Turbidity (NTU)	4770
pH	7.3–8.3

[a] Values show the average values of 20 samples.
[b] Total chemical oxygen demand.
[c] Soluble chemical oxygen demand.

Table 2
The properties of the polyacrylamide used

Polyelectrolytes	Molecular weight	Charge	Charge density
Organopol 5415[a]	Very high	Cationic	Low
Organopol 5020[a]	Low	Cationic	Medium
Organopol 5470[a]	High	Cationic	High
Organopol 5450[a]	High	Cationic	Medium
Organopol 5540[b]	Very high	Anionic	Low
Chemfloc 1515C[a]	Medium	Cationic	Medium
Chemfloc 430A[b]	High	Anionic	High
AN 913[b]	High	Anionic	Low
AN 913SH[b]	Very high	Anionic	Low

[a] Cationic polyacrylamide (C-PAM).
[b] Anionic polyacrylamide (A-PAM).

was used to prepare all the polacrylamide feedstock solutions of 0.1%.

2.2. Experimental procedure

Jar test procedures were performed with the conventional jar apparatus (Stuart Science Flocculator model, SWI) using 500 ml wastewater samples with the C-PAM and A-PAM dosages of 0.5, 2.0, 3.5, 5.0, 10.0 and 15.0 mg l^{-1}, respectively, and keeping other variables constant. The selected polyelectrolyte dosage was added to 500 ml of wastewater and it was stirred for a period of 2 min at 200 rpm. It was followed by a further slow mixing of 15 min at 40 rpm. The flocs formed were allowed to settle for 30 min. After settling, the turbidity, TSS and COD of the supernatant were determined. The remaining portion of the treated wastewater samples was used to determine the sludge volume index (SVI). The experiments were repeated two times to get the average value. The parameters were determined according to the APHA method. A statistical approach to compare the differences of the trends of each PAM on the removal of TSS, reduction of turbidity and reduction of COD was carried out using the one-way ANOVA test available in the SPSS 12.0 software.

Once the optimum polyacrylamide dose that gave the highest flocculation efficiency had been determined, the best PAM was chosen. The jar tests were repeated for the best flocculant at its optimum dosage with 1500 ml of wastewater samples. Settling characteristics tests were then performed on the treated samples. The settling characteristics tests were carried out in a settling column with 1 m in height and 4.5 cm in diameter. The heights of the sludge were recorded at fixed time intervals and the percentage TSS removals were determined. The settling time remained at 30 min as in the jar test procedures.

2.3. Analytical techniques

A calorimetric method with closed reflux was developed for the measurement of COD. Spectrophotometer (Cecil 1000, Cecil Instrument, Cambridge, England) at 600 nm was used to measure the absorbance of COD samples. A pH meter model 320 (from WTW, Germany) was used to measure the solution pH. Turbidity was measured by a turbidity meter (model TN100, Eutech, Singapore). The TSS concentration was determined by filtering a well-mixed sample through a glass fiber filter (Whatman 934AH) and then the residue retained on the filter was weighed after drying it in the oven at 103 °C for 60 min. The SVI were measured using a 1000 ml Imhoff cone.

3. Results and discussion

3.1. Effects on turbidity

In order to clearly illustrate the effect of various PAMs, the PAM were divided into two main categories: C-PAM and A-PAM in the following discussion. The optimal dosages of the flocculants are based on the reduction of turbidity and COD and the removal efficiency of TSS. Turbidity is a measure of the light-transmitting properties of water with respect to colloidal and residual suspended matter. Colloidal matter scatters or absorbs light and thus prevents its transmission [31]. The turbidity of wastewaters fluctuates according to TSS. The results obtained from the jar test experiments for turbidity reduction of C-PAM are shown in Fig. 1. The percentage turbidity reduction of the C-PAM is seen to increase with the PAM dosage except Organopol 5470. A drop in turbidity reduction occurred at the dosage of 2 mg l^{-1} for Organopol 5470 where the lowest turbidity reduction, 63%, was recorded. The turbidity reduction efficiencies of Organopol 5415, Organopol 5020, Organopol 5450 and Chemfloc 1515C increase with flocculant dosage. After each of the C-PAM reaches the highest reduction efficiency, there is no significant difference in turbidity reduction efficiency with further increase in C-PAM dosages. The dosage beyond which there is no significant enhancement in reduction efficiency with further addition of polyacrylamide is defined as the optimum dosage. The optimum dosages of Organopol 5415, Organopol 5020, Organopol 5470, Organopol 5450 and Chemfloc 1515C are 5 mg l^{-1}, 10 mg l^{-1}, 15 mg l^{-1}, 15 mg l^{-1} and 10 mg l^{-1}, respectively.

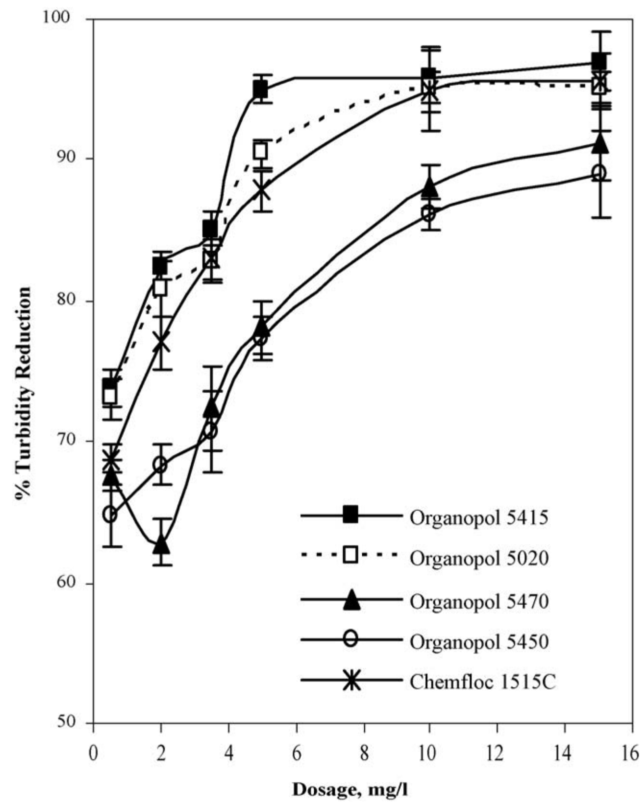

Fig. 1. Turbidity reduction of C-PAM at various dosages.

The efficiency of the C-PAM in the reduction of turbidity is impressive, even at low dosage. The percentage turbidity reduction of more than 60% can be achieved at dosage of as low as 0.5 mg l^{-1} by all of the C-PAM studied. The turbidity reduction efficiency of up to 74% is obtained by the Organopol 5415 at this lowest dosage. Organopol 5415 is a C-PAM with very high molecular weight and low charge density. It is the best among the C-PAM studied since it can achieve 95% reduction of turbidity at the dosage of 5 mg l^{-1}. Organopol 5450 is the least efficient

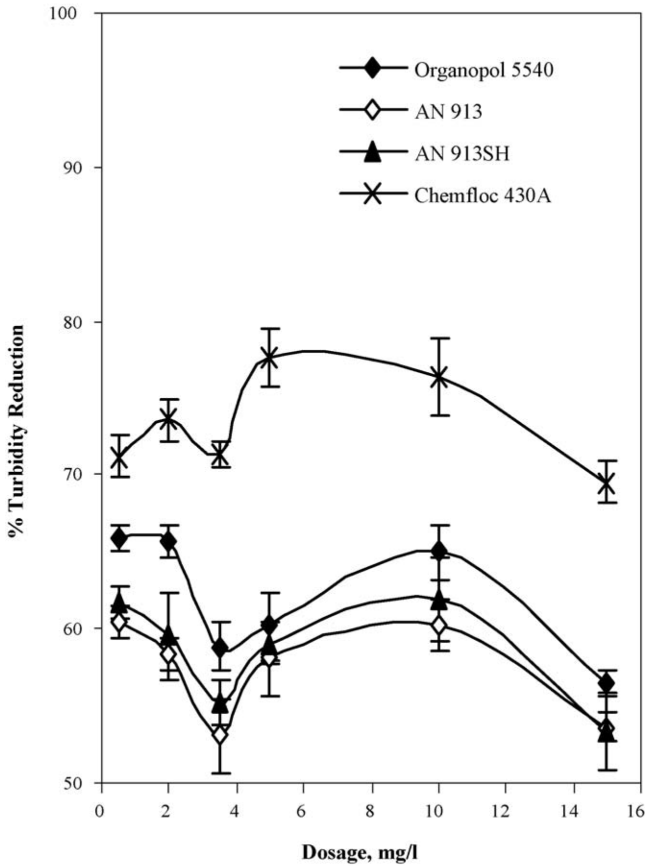

Fig. 2. Turbidity reduction of A-PAM at various dosages.

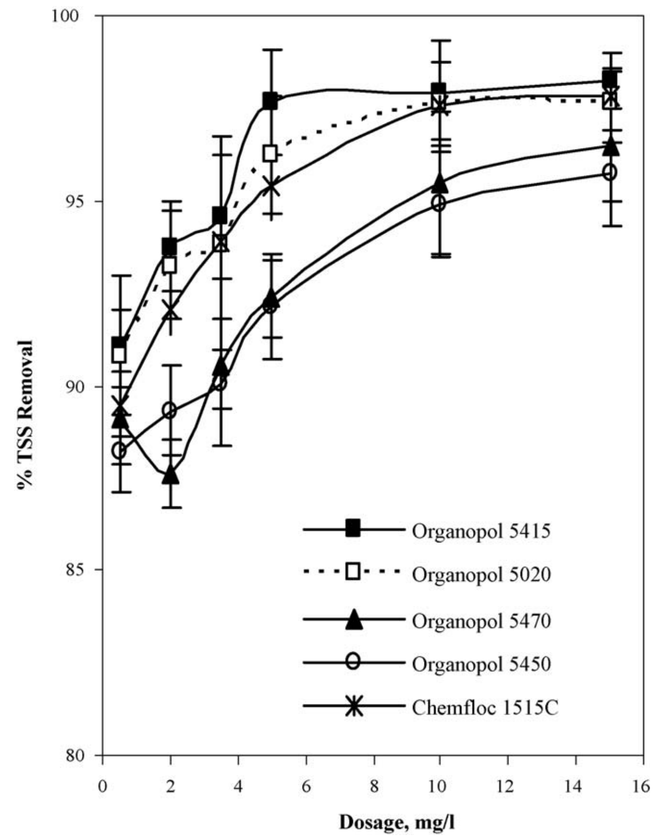

Fig. 3. TSS removal of C-PAM at various dosages.

among the C-PAM studied. It can only achieve 89% turbidity reduction at a dosage of 15 mg l^{-1}.

Fig. 2 shows the turbidity reduction obtained with the A-PAM. For all the four A-PAM studied, it can be seen that there is a drop in the percentage reduction of turbidity at the dosage of 3.5 mg l^{-1}. This result suggested that the A-PAM may have two optimum dosages between 0.5–15 mg l^{-1}, one obtained at the lower dosage range and the other at the higher dosage range. After the fall, the reduction efficiency of turbidity increases until the optimum value and then decreases towards the following dosage. It can be seen clearly from Fig. 2 that the A-PAM are not as effective as C-PAM in the reduction of turbidity. The highest reduction of turbidity is only 78% recorded by the anionic Chemfloc 430A with high molecular weight and high charge density at the dosage of 5 mg l^{-1}. The optimum dosage obtained for the A-PAM is 5 mg l^{-1} with Chemfloc 430A and 10 mg l^{-1} with Organopol 5540, AN 913 and AN 913SH, respectively.

3.2. Effects on TSS

The percentage TSS removal of C-PAM and that of A-PAM at various dosages are shown in Figs. 3 and 4. The removal trends of the TSS are similar to those of the turbidity removal for both C-PAM and A-PAM. The TSS were reduced when the PAM dosage was increased stepwise except for some PAM which showed a drop before it achieved optimum dosage. In Fig. 3, the optimum dosages of the C-PAM in the removal of TSS are:

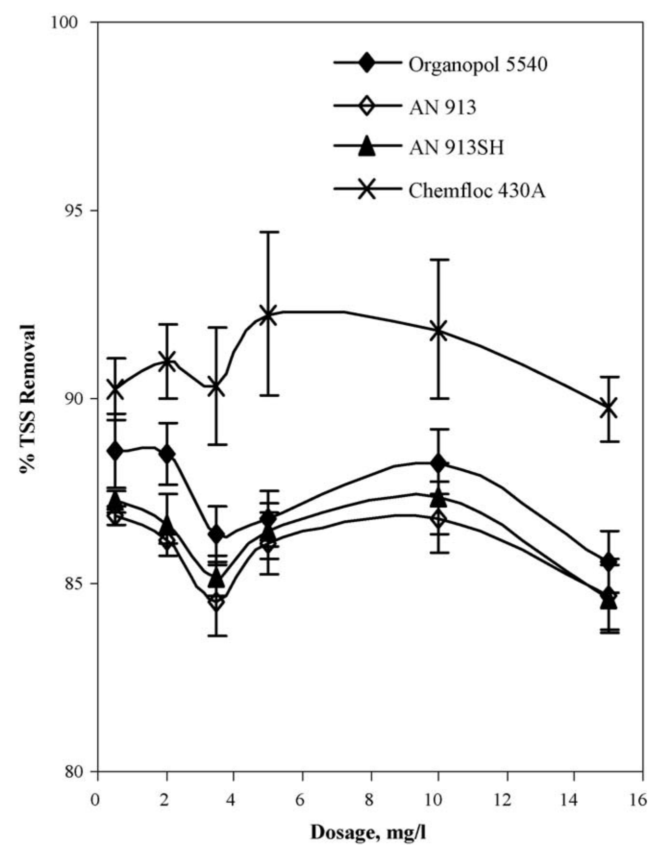

Fig. 4. TSS removal of A-PAM at various dosages.

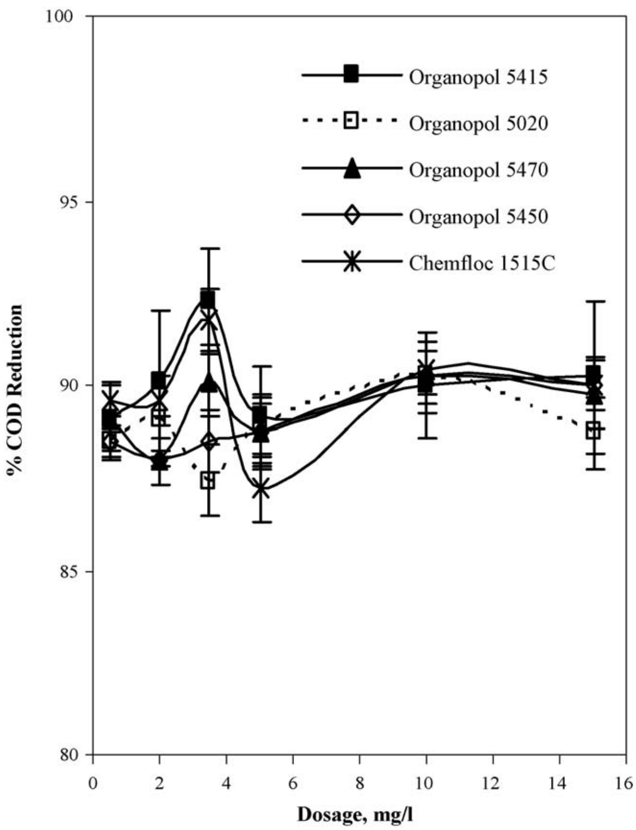

Fig. 5. COD reduction of C-PAM at various dosages.

Organopol 5415 at 5 mg l^{-1} with 98% removal, Organopol 5020 at 10 mg l^{-1} with 98% removal, Organopol 5470 at 15 mg l^{-1} with 96% removal, Organopol 5450 at 15 mg l^{-1} with 96% removal and Chemfloc 1515C at 10 mg l^{-1} with 98% of removal, respectively. The optimum dosages obtained with the A-PAM are: 5 mg l^{-1} with 92% TSS removal by Chemfloc 430A, 10 mg l^{-1} with 91% TSS removal by Organopol 5540, 10 mg l^{-1} with 86% TSS removal by AN 913 and 10 mg l^{-1} with 87% TSS removal by AN 913SH, as shown in Fig. 5. Though the A-PAM exhibit encouraging results in terms of TSS removal, but the C-PAM show much better removal efficiency than A-PAM in the TSS removal.

The removal efficiencies of TSS with C-PAM and A-PAM are more than 88% and 85%, respectively, at each dosage applied and even at a dosage as low as 0.5 mg l^{-1} as shown in Figs. 3 and 4. This is probably due to the fact that the flocculation efficiency is dependent on the original concentration of suspended solids of the wastewater. Barany and Szepesszenentgyorgyi [32] described that for the optimum aggregation of more concentrated suspensions, a lower amount of polymer is needed, and the addition of this amount results in a high degree of flocculation. The physical removal of contaminant particles from water can be represented by the equation: $dN/dt = \alpha k N^2$, where N is the number of particles, t the time, α the fraction of successful collisions and k is the mixed rate constant [33]. It is reasonable as the coagulation–flocculation process relies mainly on the collision frequency between the coagulant or flocculant and suspended solid particles. The wastewater currently used in this system contained very high concentration of suspended solids (more than 5000 mg l^{-1}). The high efficiencies of the C-PAM and A-PAM in the TSS removals may be due to the high collision frequency between the PAM and the suspended solid particles.

Based on the reduction and removal efficiencies of the turbidity and TSS by the PAM studied, the flocculation performances of the PAM are influenced by its molecular weight and charge density as can be seen from Figs. 1–4. In the case of C-PAM, the C-PAM with very high, medium or low molecular weight performed better than high molecular weight C-PAM. Medium and low charge density are the most appropriate charge densities for the C-PAM to obtain better turbidity reduction and TSS removal. The molecular weights of the A-PAM have no significant effect on the turbidity reduction and TSS removal. From Figs. 2 and 4, A-PAM with very high molecular weight (Organopol 5540 and AN 913SH) and high molecular weight (Chemfloc 430A and AN 913) show great differences though their molecular weights are same. The charge density of the A-PAM is the main influencing factor on the reduction and removal efficiencies of the turbidity and TSS by the A-PAM. The A-PAM with high charge density (Chemfloc 430A) shows the best reduction and removal efficiency in turbidity and TSS.

3.3. Effects on COD

The percentage COD reductions of C-PAM and A-PAM at various dosages are shown in Figs. 5 and 6, respectively. It can be

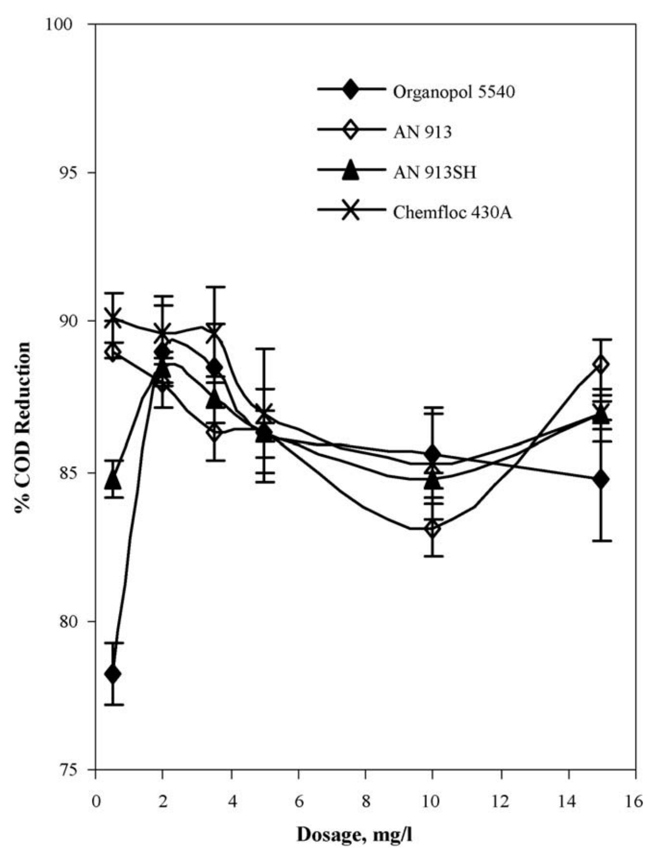

Fig. 6. COD reduction of A-PAM at various dosages.

observed that the trends of the COD reduction efficiency of both C-PAM and A-PAM are different from that obtained in the reduction of turbidity and removal of TSS. In Figs. 5 and 6, it is easily seen that the COD reduction is minimum at which the turbidity and TSS removals are maximum. The reduction trends of COD with different C-PAM and different A-PAM are almost similar and the differences are not significant. This result indicates that the COD reduction efficiency is not influenced by the molecular weight or charge density of the flocculants. Further increase in the dosage does not improve the reduction efficiency. This behavior suggests that floc breakup occurs due to charge reversal and dispersion when there is an excessive or overdosing of flocculants [34]. However, the percentage reduction of COD with PAM is very significant even at the lowest dosage of 0.5 mg l^{-1}. The use of C-PAM results in more than 87% reduction of COD while more than 78% reduction of COD is obtained with A-PAM at all dosages used. These results are better than those of ref. [35], who found that under the optimal conditions of pH 3 and initial polyaluminium chloride (PAC) dosage of 3000 mg l^{-1}, about 80% of COD reduction was obtained in the treatment of pulp and paper mill wastewaters. These results suggest that the use of PAM reduces the amount of flocculant required for the treatment and lowers the cost of the coagulation–flocculation process. The optimum dosages obtained by the C-PAM are 3.5 mg l^{-1} with Organopol 5415 and Chemfloc 1515C (92% of COD reduction) and 10 mg l^{-1} with Organopol 5020, Organopol 5470 and Organopol 5450 (90% of COD reduction, respectively). The optimum dosage of all the A-PAM studied is below 3.5 mg l^{-1}. The optimum dosages of the A-PAM in terms of COD reduction are 2 mg l^{-1} with Organopol 5540, 0.5 mg l^{-1} with AN 913 and Chemfloc 430A and 3.5 mg l^{-1} with AN 913SH, respectively.

3.4. Statistical analysis

Based on the concentration of TSS, turbidity and COD remaining in the supernatants after the treatment by various C-PAM and A-PAM, a statistical approach to compare the differences of the trend of each PAM on the removal of TSS, reduction of turbidity and COD was carried out using the one-way ANOVA test available in the SPSS 12.0 software. The one-way ANOVA procedure produces a one-way analysis of variance for a quantitative dependent variable by a single factor (turbidity, TSS or COD) variable. The analysis of variance is used to test the hypothesis that several means of the turbidity, TSS and COD are equal. The Levene statistics obtained for the TSS, turbidity and COD to test for the equality of group variances are given in Table 3. In Table 3, the significance values of the TSS and turbidity are same (0.002) and the significance value for the COD is 0.073. The Levene statistics of the TSS and turbidity with the significance value of less than 0.05 rejects the null hypothesis that the group variances are equal. The TSS and the turbidity concentrations of the supernatant obtained by various C-PAM and A-PAM are diverse. Meanwhile, the Levene statistic of COD is greater than 0.050 (0.073) which indicates that the group variances of the COD are equal and all PAM show almost similar effect on the removal of COD. These results are corroborated with the finding as shown in Figs. 5 and 6.

Table 3
Levene statistics of TSS, turbidity and COD

	Levene statistic	Significance
TSS	3.825	0.002
Turbidity	3.851	0.002
COD	1.967	0.073

The reduction of turbidity and COD and the TSS removal by PAM as discussed in the previous paragraphs show that differences exist among the means, post hoc range tests and pair wise multiple comparisons can determine which means differ. Range tests identify homogeneous subsets of means that are not different from each other. Pair wise multiple comparisons test the difference between each pair of means, and yield a matrix that indicates significantly different group means at an alpha level of 0.05. In order to compare the group mean and the trends of every PAM with that of other, the post hoc pair wise multiple comparisons were carried out. From the Levene statistics of TSS and turbidity, both have shown the same significant value with the same trends; therefore, only TSS and COD are chosen to compare in the post hoc test since TSS and COD are the main concern parameter in the flocculation process. The Tamhane's T2 comparison is a conservative pair wise comparisons test based on a *t*-test and this test is appropriate when the variances are unequal. The Tamhane's T2 comparison is used for the TSS since the variances across the TSS group are significantly different. COD with equal group variances is compared using the Tukey comparison.

The Tamhane's T2 comparisons of the PAM for TSS are as shown in Table 4. Table 4 shows the respective significant value of every pair of the PAMs listed in the (I) column and (J) column. The removal or the reduction trends are different when the significant level of the duo PAMs is less than 0.05 whereas the trends are similar when the significant level of the duo PAMs is greater than 0.05. From Table 4, there are significant differences between the C-PAM and A-PAM on the TSS removal. The trends of all of the C-PAM (excluding Organopol 5450 and Organopol 5470) are significantly different than the A-PAM of Organopol 5540, AN913 and AN913 SH with the significant value of less than 0.05 except Chemfloc 430A. Chemfloc 430A is the only A-PAM that shows no significant difference compared to the C-PAM with significant level of more than 0.05. The effect of Chemfloc 430A on the removal of TSS is same as that of Organopol 5450 and Organopol 5470 since the significant level is equal to 1.000 when compared with these two C-PAM. Significant value of 1.000 means there are no differences existing among the removal trend of the PAMs. Though Chemfloc 430A is in the same group as Organopol 5540, AN913 and AN913 SH, but Chemfloc 430A is significantly different from all other A-PAM. When Chemfloc 430A is compared to the other PAMs, Chemfloc 430A–AN 913 gave significant value of 0.000, Chemfloc 430A–AN 913SH gave significant value of 0.001 and Chemfloc 430A–Organopol 5540 gave significant value of 0.014. The significant value of 0.000 means the removal trends of Chemfloc 430A and AN 913 are quite distinct from each other. These results confirm that the Chemfloc 430A is

Table 4
The Tamhane's T2 comparisons of the PAMs for the TSS variables

(I) PAM	(J) PAM	Significance[a]
Chemfloc 430A	AN 913	0.000
	Chemfloc 1515C	0.813
	Organopol 5020	0.282
	Organopol 5415	0.405
	Organopol 5450	1.000
	Organopol 5470	1.000
	Organopol 5540	0.014
	AN 913SH	0.001
AN 913	Chemfloc 430A	0.000
	Chemfloc 1515C	0.032
	Organopol 5020	0.006
	Organopol 5415	0.011
	Organopol 5450	0.144
	Organopol 5470	0.227
	Organopol 5540	0.850
	AN 913SH	1.000
Chemfloc 1515C	Chemfloc 430A	0.813
	AN 913	0.032
	Organopol 5020	1.000
	Organopol 5415	1.000
	Organopol 5450	0.999
	Organopol 5470	1.000
	Organopol 5540	0.074
	AN 913SH	0.038
Organopol 5020	Chemfloc 430A	0.282
	AN 913	0.006
	Chemfloc 1515C	1.000
	Organopol 5415	1.000
	Organopol 5450	0.897
	Organopol 5470	0.975
	Organopol 5540	0.013
	AN 913SH	0.007
Organopol 5415	Chemfloc 430A	0.405
	AN 913	0.011
	Chemfloc 1515C	1.000
	Organopol 5020	1.000
	Organopol 5450	0.945
	Organopol 5470	0.989
	Organopol 5540	0.022
	AN 913SH	0.012
Organopol 5450	Chemfloc 430A	1.000
	AN 913SH	0.144
	Chemfloc 1515C	0.999
	Organopol 5020	0.897
	Organopol 5415	0.945
	Organopol 5470	1.000
	Organopol 5540	0.432
	AN 913SH	0.186
Organopol 5470	Chemfloc 430A	1.000
	AN 913	0.227
	Chemfloc 1515C	1.000
	Organopol 5020	0.975
	Organopol 5415	0.989
	Organopol 5450	1.000
	Organopol 5540	0.561
	AN 913SH	0.283
Organopol 5540	Chemfloc 430A	0.014
	AN 913	0.850
	Chemfloc 1515C	0.074
	Organopol 5020	0.013
	Organopol 5415	0.022
	Organopol 5450	0.432
	Organopol 5470	0.561
	AN 913SH	0.994
AN 913SH	Chemfloc 430A	0.001
	AN 913	1.000
	Chemfloc 1515C	0.038
	Organopol 5020	0.007
	Organopol 5415	0.012
	Organopol 5450	0.186
	Organopol 5470	0.283
	Organopol 5540	0.994

[a] The mean difference is significant at the 0.05 level.

more efficient than the other A-PAM and its efficiency in the removal of TSS is comparable to those of C-PAM.

The Tukey comparisons of the PAMs for the COD are shown in Table 5. There is no significant difference between the PAMs on the reduction of COD. The significant levels among the PAMs are mostly greater than 0.05. Significant differences are found among the C-PAM: Organopol 5415, Organopol 5450, Organopol 5470 and Chemfloc 1515C, and the A-PAM: Organopol 5540 and AN 913SH, with significance of each pair is less than 0.05. The statistical analysis of the reductions trends of the COD supports the results of the COD reductions obtained by the PAMs as shown in Figs. 5 and 6.

3.5. Sludge volume index

The SVI is the volume of 1 g of sludge after 30 min settling. A value of 100 ml g^{-1} is considered a good settling sludge. Thus, SVI values below 100 are desired [32]. The SVI values obtained at the optimum dosages for C-PAM and A-PAM are shown in Figs. 7 and 8, respectively. As can be seen from these figures, all SVI values are less than 70 ml g^{-1}. This result exhibits that the use of PAM improves the sludge settling characteristics. The SVI values of the C-PAM are averagely low (less than 30 ml g^{-1}) except Organopol 5470 and Organopol 5450 with high molecular weight at their optimum dosages of 15 mg l^{-1}. This behavior suggests that as the dosages of the C-PAM increase, the high molecular weight C-PAM may be following bridging flocculation mechanism. Flocs which are formed via bridging flocculation stay apart when broken up, since polymer tails and loops bridging across two or more particles are physically severed by the shearing forces [36]. The lowest SVI value of 14 ml g^{-1} is recorded for Organopol 5415 at 5 mg l^{-1}. For the case of A-PAM, all SVI values are less than 50 ml g^{-1} at their optimum dosages. There is one exceptional observation found between the Organopol 5540 and the AN 913SH, both with the same molecular weight and the same charge density. The SVI value of AN 913SH is 44% higher than that of Organopol 5540. This may be due to the different compositions of the PAM during the manufacturing processes.

Table 5
The Tukey comparisons of the PAMs for the COD variables

(I) PAM	(J) PAM	Significantce[a]
Chemfloc 430A	AN 913	0.976
	Chemfloc 1515C	0.817
	Organopol 5020	0.999
	Organopol 5415	0.608
	Organopol 5450	0.994
	Organopol 5470	0.962
	Organopol 5540	0.289
	AN 913SH	0.855
AN 913	Chemfloc 430A	0.976
	Chemfloc 1515C	0.202
	Organopol 5020	0.709
	Organopol 5415	0.097
	Organopol 5450	0.602
	Organopol 5470	0.411
	Organopol 5540	0.902
	AN 913SH	1.000
Chemfloc 1515C	Chemfloc 430A	0.817
	AN 913	0.202
	Organopol 5020	0.993
	Organopol 5415	1.000
	Organopol 5450	0.998
	Organopol 5470	1.000
	Organopol 5540	0.006
	AN 913SH	0.082
Organopol 5020	Chemfloc 430A	0.999
	AN 913	0.709
	Chemfloc 1515C	0.993
	Organopol 5415	0.947
	Organopol 5450	1.000
	Organopol 5470	1.000
	Organopol 5540	0.068
	AN 913SH	0.437
Organopol 5415	Chemfloc 430A	0.608
	AN 913	0.097
	Chemfloc 1515C	1.000
	Organopol 5020	0.947
	Organopol 5450	0.977
	Organopol 5470	0.997
	Organopol 5540	0.002
	AN 913SH	0.035
Organopol 5450	Chemfloc 430A	0.994
	AN 913SH	0.602
	Chemfloc 1515C	0.998
	Organopol 5020	1.000
	Organopol 5415	0.977
	Organopol 5470	1.000
	Organopol 5540	0.046
	AN 913SH	0.339
Organopol 5470	Chemfloc 430A	0.962
	AN 913	0.411
	Chemfloc 1515C	1.000
	Organopol 5020	1.000
	Organopol 5415	0.997
	Organopol 5450	1.000
	Organopol 5540	0.021
	AN 913SH	0.199
Organopol 5540	Chemfloc 430A	0.289
	AN 913	0.902
	Chemfloc 1515C	0.006
	Organopol 5020	0.068
	Organopol 5415	0.002
	Organopol 5450	0.046
	Organopol 5470	0.021
	AN 913SH	0.988
AN 913SH	Chemfloc 430A	0.855
	AN 913	1.000
	Chemfloc 1515C	0.082
	Organopol 5020	0.437
	Organopol 5415	0.035
	Organopol 5450	0.339
	Organopol 5470	0.199
	Organopol 5540	0.988

[a] The mean difference is significant at the 0.05 level.

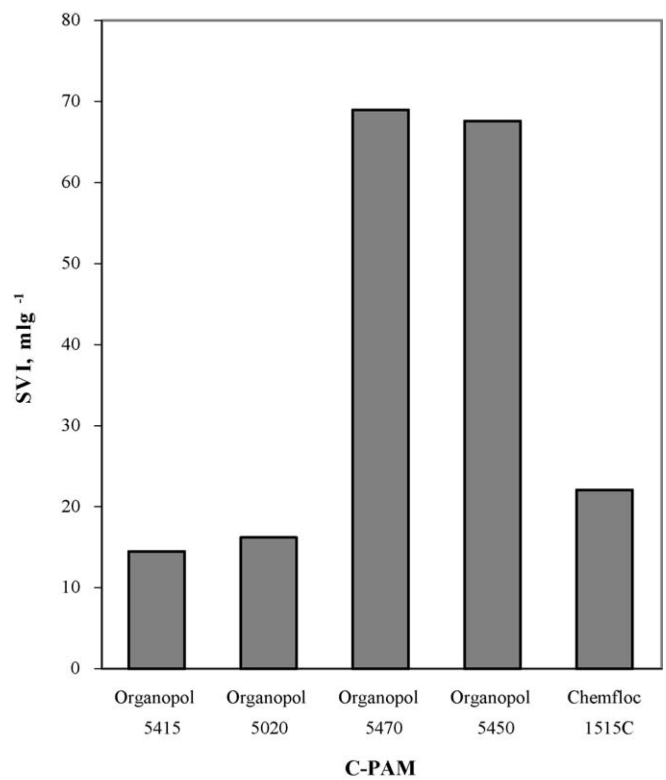

Fig. 7. SVI obtained at the respective optimum dosages of various C-PAMs.

3.6. Cost evaluation

A cost evaluation of using PAM has been done and the results are shown in Table 6. The polymer costs are based on the applying of the PAM at its respective optimum dosage for the treatment of 1 metric tonne of wastewater feed. The prices of the C-PAM are higher than those of the A-PAM except Organopol 5415. Organopol 5415 is the cheapest PAM since it yields high turbidity and COD reduction and high TSS removal and it also produces less sludge with the lowest dosage applied. The use of PAM can be considered as economical in treating the pulp and paper mill wastewaters.

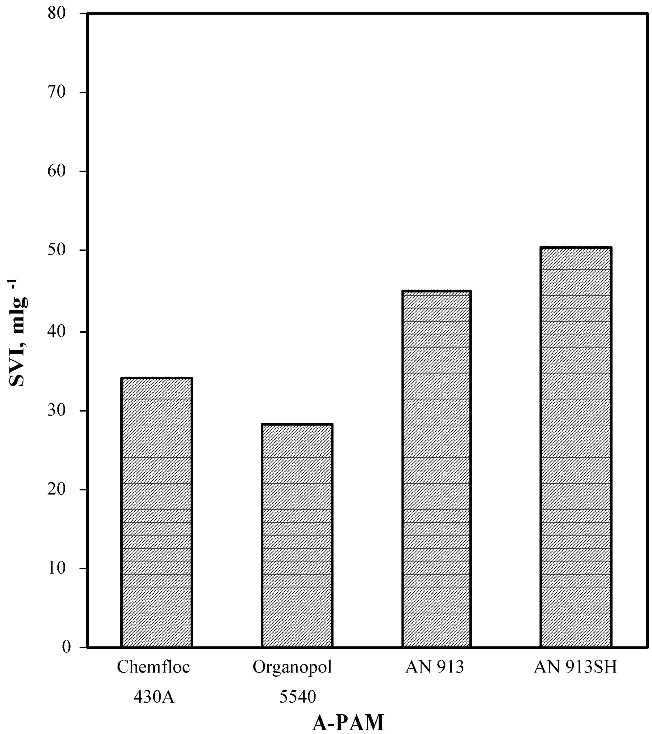

Fig. 8. SVI obtained at the respective optimum dosages of various A-PAMs.

3.7. Sludge settling characteristics

The flocs produced from the flocculation process were removed through the gravity sedimentation process. The primary purpose of the sedimentation is to produce a clarified effluent, but it is also necessary to produce sludge with a solids concentration that can be handled and treated easily. The solid phase of the flocculated sludge must be free settling under quiescent or laminar flow conditions when introduced to the settling zone. Thus, the settling characteristics of the flocculant were studied after the optimum dosage was obtained. The best polyacrylamide chosen is the cationic Organopol 5415 with very high molecular weight and low charge density, after taking into consideration its removal efficiency with respect to turbidity, TSS and COD and also SVI. The optimum dosage of Organopol 5415 is 5 mg l^{-1}.

Fig. 9 shows the water recovery, sludge recovery and sludge volume versus time for Organopol 5415 at the optimum dosage

Table 6
Estimated costs to treat 1 metric tonne of the wastewater feed at the optimum dosages of each PAM

PAM	Cost/kg	Cost per metric tonne of wastewater
Organopol 5415	US$3.80	US$0.019
Organopol 5020	US$4.50	US$0.045
Organopol 5450	US$4.00	US$0.060
Organopol 5470	US$4.25	US$0.064
Organopol 5540	US$3.45	US$0.035
Chemfloc 1515C	US$4.50	US$0.045
Chemfloc 430A	US$3.80	US$0.019
AN913	US$2.80	US$0.028
AN913 SH	US$2.80	US$0.028

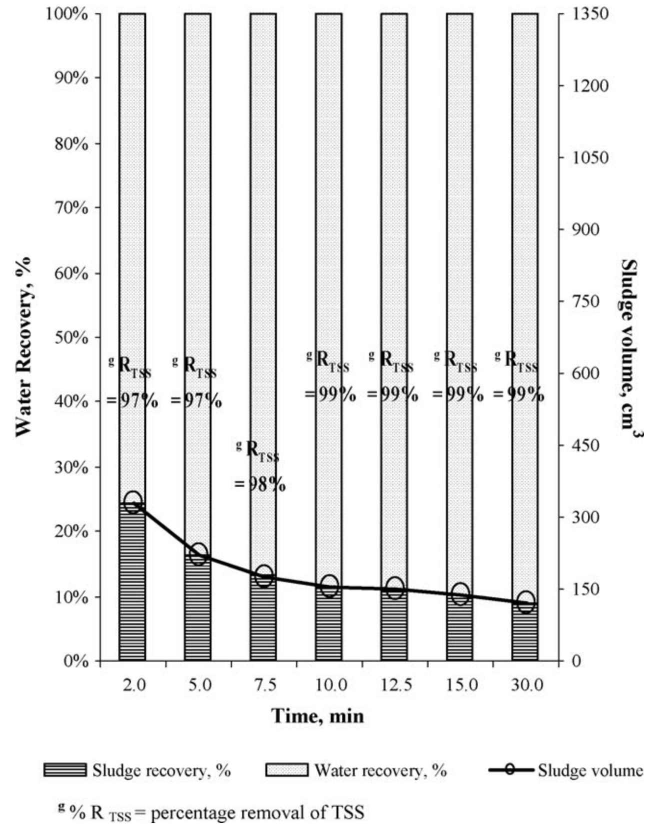

Fig. 9. Water recovery and sludge volume with time of Organopol 5415 at optimum dosage of 5 mg l^{-1}.

of 5 mg l^{-1} obtained after performing in the sludge characteristics experiment. Each of the columns in Fig. 9 represents the actual conditions of the settling column used in the experiment at fixed time intervals. The clear water zone and the sludge zone can be differentiated clearly. During the settling, the rise of water out of the sludge zone as the particles move toward the bottom is observed. The particles were floated to the surface with the rise of the water and this make the sludge zone only can be seen clearly after 2 min settling. The efficiency of the Organopol 5415 is quite satisfactory. It can achieve 97% of TSS removal and 76% water recovery after only 2 min settling.

The percentage water recovery increases with time as the sludge settles down and the maximum water recovery obtained is 91% after 30 min settling of the sludge. Nevertheless, the sludge volume decreases with time until a time that it remains unchanged. The sludge volume obtained after 30 min settling is 120 cm^3. The percentage removal of TSS is 99% after settling for 10 min. The type of settling occurs in the sedimentation process can be classified into three categories: zone settling, phase settling and compression. The curve obtained for Organopol 5415 in Fig. 9 is similar to the shape of the curve of phase settling described by Schwoyer [37]. This result suggests that gravity thickener is applicable because the solids do not settle freely in the beginning of the sedimentation period. In order to allow the sedimentation to proceed, upward flow through the solids mass must be eliminated so that the primary force exerted on the solids is the pull of gravity and gravity thickeners can be designed to allow this to occur [37]. The settling time of 30 min is a rational suggestion since all the sludge settles within 30 min.

4. Conclusion

Reduction of turbidity and COD and the removal efficiency of TSS have been studied using C-PAM and A-PAM as flocculants in treating pulp and paper mill wastewaters. The results show that C-PAM are more effective than A-PAM. Organopol 5415 with very high molecular weight and low charge density is the best flocculant with highest flocculation efficiency for the treatment of the pulp and paper mill wastewater. It can achieve 95% of turbidity reduction, 98% of TSS removal, 93% of COD reduction and SVI of 14 ml g^{-1} at the optimum dosage of 5 mg l^{-1}. The C-PAM produces compacted and dense flocs that can settle faster. Based on the cost evaluation, the use of the PAM is economically feasible to treat the pulp and paper mill wastewaters. The percentage water recovery, sludge recovery and the volume of sludge produced by Organopol 5415 are also satisfactory. This result suggests that single-polymer system can be used alone (without combination with inorganic coagulant) in the coagulation–flocculation process since the efficiency of the polyacrylamide is remarkable. Sedimentation of the sludge by gravity thickening with settling time of 30 min is suggested based on the sludge settling characteristics obtained.

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