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Coagulation-Flocculation process to treat Pulp and Paper Mill Wastewater by Fenugreek Mucilage Coupled with Alum and Polyaluminum Chloride

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Abstract

The wastewater arising from pulp and paper mills is highly polluted and has to be treated before discharged into rivers. Coagulation-flocculation process using natural polymers has grown rapidly in wastewater treatment. In this work, the performance of alum and Polyaluminum Chloride (PACl) when used alone and when coupled with Fenugreek mucilage on the treatment of pulp and paper mill wastewater were studied. The experiments were carried out in jar tests with alum, PACl and Fenugreek mucilage dosages range of 50-2000 mg/L, 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 Fenugreek mucilage was measured by the reduction of turbidity and Chemical Oxygen Demand (COD). The results show that the combination of PACl and Fenugreek mucilage is more effective than alum, PACl and alum + Fenugreek mucilage. It can achieve greater than 97% of turbidity reduction and greater than 98% of COD reduction at low dosage of PACl (50 mg/L) and Fenugreek mucilage (100 mg/L). The results indicate that lower quantities of PACl are needed to obtain an acceptable reduction in turbidity and COD in the treatment of pulp and paper mill wastewater.

Keywords: *Pulp and paper mill wastewater, coagulation and flocculation, fenugreek.*

1. Introduction

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 (resinacids), chlorinated organics (measured as adsorbable organic halides, AOX), suspended solids, metals, fatty acids, tannins, lignin and its derivatives (Ali and Sreekrishnan, 2001; Lacorte et al., 2003).

Pulp and paper mill wastewater is little biodegradable, with BOD/COD ratio values usually around 0.02-0.07 [14]. Morais et al. (2006) report that samples with biodegradability index smaller than 0.3 are not appropriate for biological degradation. According to Chamarro et al. (2001) for complete biodegradation, the effluent must present a biodegradability index of at least 0.40. Consequently, a new approach in the wastewater treatment technology should be developed to face more stringent environmental regulations on the quality of the effluents entering receiving waters.

Flocculation is one of the important treatments given to the industrial e uent before discharging them into rivers to remove toxic waste. Recently, the use of synthetic polyelectrolytes as flocculants for suspended solids removal in wastewater treatment has grown rapidly [13]. 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.

Natural polymers such as starch, Sodium alginate, amylopectin, guar gum, xanthum gum, Kendu gum and Chitosan [12, 15, 6, 5], find extensive application as flocculants. Recently, the use of Fenugreek mucilage, a food grade natural polysaccharide, has been reported as a flocculant for tannery effluent treatment [11].

In the present study, coagulation-flocculation by alum and PAC when coupled with Fenugreek mucilage is applied to pulp and paper mill industry effluents. The effects of coagulant dosage, flocculant dosage and pH are studied. The turbidity and COD values are used as evaluating parameters.

2. Experimental Work

2.1. Wastewater

The wastewater samples used in this study were obtained from Pascorp Paper Sdn. Bhd. which is situated in Bentong, Pahang, Malaysia. The samples were taken after the physical treatment plant facility. 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 [2].

2.2. Chemicals

Polyaluminium Chloride (PACl): PACl is a Synthetic polymer, which is yellow in color. This chemical is used as a coagulant in this research. The PACl used in this research was manufactured by R&M Chemicals Marketing, Essex, U.K.

Aluminium Sulphate (alum): Alumium Sulphate, or alum is an inorganic coagulant, in a molecular form. The alum used in this research was manufactured by R&M Chemicals Marketing.

Fenugreek mucilage: Fenugreek mucilage, an amorphous natural poly-saccharide is composed of D-galactose and D-mannose in 1:1 ratio and 1:1.2 ratio. Extraction of the milled seeds with cold water yielded a thick mucilaginous solution. This material is used as flocculant aid in this research. It is added during the slow mixing period in jar test experiments. To prepare Fenugreek mucilage, 50 g of Fenugreek seeds were dissolved in 1 L of distilled water. This solution was then stirred for 24 hours. The homogenous solution was then centrifuged to purify fenugreek mucilage.

2.3. Experimental Procedures

Jar test procedures were performed with the conventional jar apparatus (Stuart Science Flocculator model, SWI) using (1L) wastewater. Different combinations of pH (3, 6, 9), alum and PAC dosages (50, 100, 500, 1000, 1500, 2000 mg/L) and

Table 1,
Chemical Characteristics of Wastewater Samples.

Parameter	pH	Turbidity (NTU)	COD ($mg\ L^{-1}$)	BOD ($mg\ L^{-1}$)
Value	6.80	235.00	20300.00	636.00

Fenugreek muciluge dosage (50, 100, 500, 1000, 1500 and 2000 mg/L) were tested. The selected coagulant dosage was added to 1 L 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 after the selected Fenugreek dosage was added to the same solution. The pH of the solution was adjusted accordingly. The flocs formed were allowed to settle for 30 min. After settling, the turbidity and COD of the supernatant were determined. All parameters were determined according to the APHA method.

2.4. Analytical Methods

Turbidity was measured by a turbid meter manufactured by Eutech (Model 2100A). Turbidity was measured by putting 10 ml of sample into turbidity vial and place it in turbidity meter to measure turbidity.

COD was determined by potassium dichromate method by adding 2 ml of treated wastewater into COD digestion reagent. Then, the vial was capped tightly and inverted several times to mix. After that, the vial was placed in the preheated COD digestion reactor and heated for two hours. Then, the COD reactor was switched off and the vial was left to cool to room temperature. Finally, COD was measured by spectrophotometer, HATCH DR/2400. The above-mentioned parameters were measured according to the standard method for the examination of water and wastewater.

3. Results and Discussion

3.1. Treatment by Alum

Coagulant dosage and pH play an important role in determining the optimum conditions of coagulation flocculation process. In wastewater treatment using inorganic coagulants, an optimum pH range in which metal hydroxide precipitates occur, should be determined. The effects of pH adjustment and coagulant dosage by alum on turbidity and COD are illustrated in Figures 1 and 2, respectively.

Figures 1 and 2 show that turbidity and COD reduction efficiencies increase with the increase in coagulant dosage till it reaches its highest value after which the reduction and removal efficiencies start to decrease. It can be seen that the optimum dosage is approximately 1000 mg/L and the optimum pH is approximately 6.0. At these optimum dosage and pH, turbidity reduction is 91.28% and COD reduction is 95% followed by a further slow mixing of 15 min at 40 rpm after the selected Fenugreek dosage was added to the same solution. The pH of the solution was adjusted accordingly. The flocs formed were allowed to settle for 30 min. After settling, the turbidity and COD of the supernatant were determined. All parameters were determined according to the APHA method.

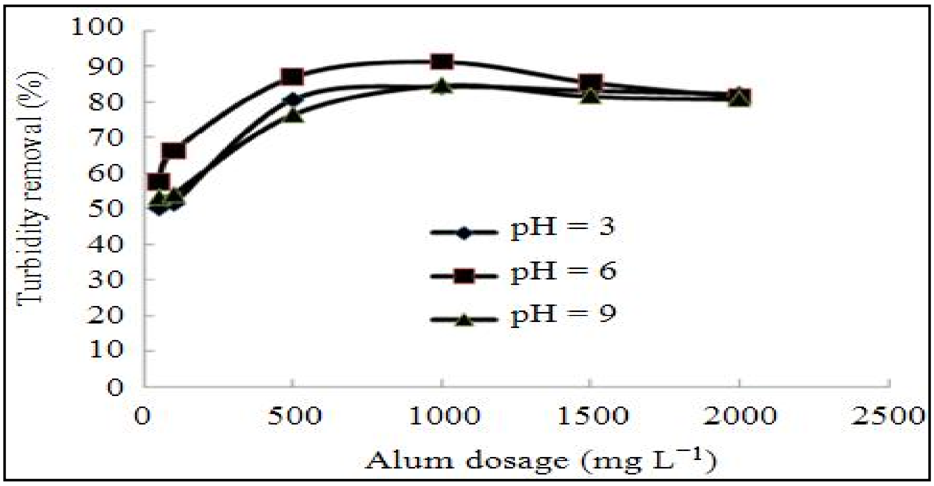

Fig.1. Effect of Alum Dose on Percent Removal of Turbidity at Different pH.

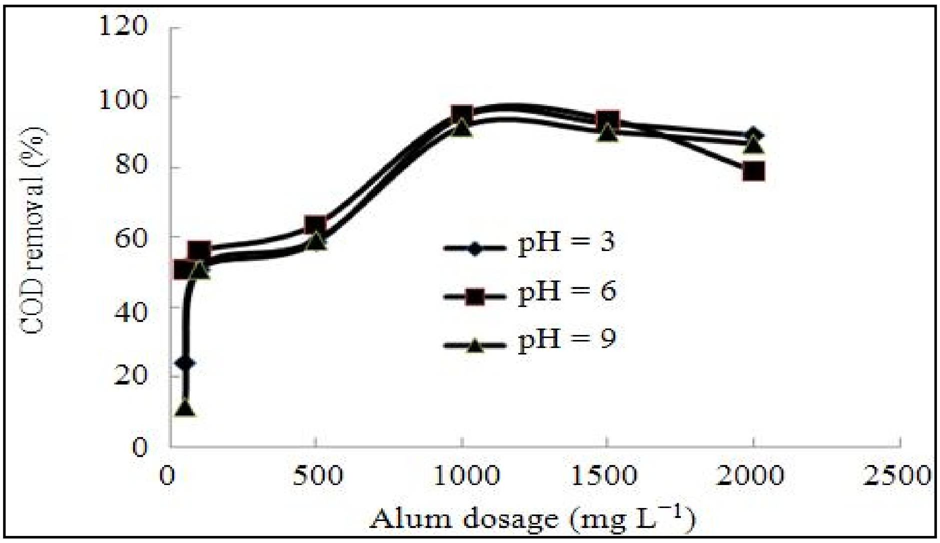

Fig.2 Effect of Alum Dose on Percent Removal of COD at Different pH.

3.2. Treatment by PACl

To study the effects of the PACl dosage and pH on the turbidity reduction and COD reduction, jar tests were conducted with the PACl dosages of 50, 100, 500, 1000, 1500 and 1500 mg/L and pH adjusted to 3, 6 and 9. The results obtained are shown in Fig. 3 and 4. The effects of coagulant dosage and pH with PACl are parallel to the effects observed with alum. The turbidity reduction and COD reduction efficiencies increase with the increase in coagulant dosage and pH till it reaches its highest value after which the reduction and removal efficiencies start to decrease. As shown in Fig.3, the turbidity reduction efficiency at pH 6 is higher than that at pH 3 and 9 at low dosage. The highest turbidity reduction is 95.66%.

Figure 4 shows that the PACl dosage only reveals minor impacts on the reduction efficiencies of COD at pH 9. Nevertheless, pH shows significant effects on the COD reduction at pH 3 and 6. The COD reduction efficiency reaches to more than 95% at PACl dosage and pH 500 mg/L and 6.0, respectively. This result reveals that the optimum coagulant dosage for PACl is less than that of alum but the optimum pH for both coagulants remains the same at pH 6.0.

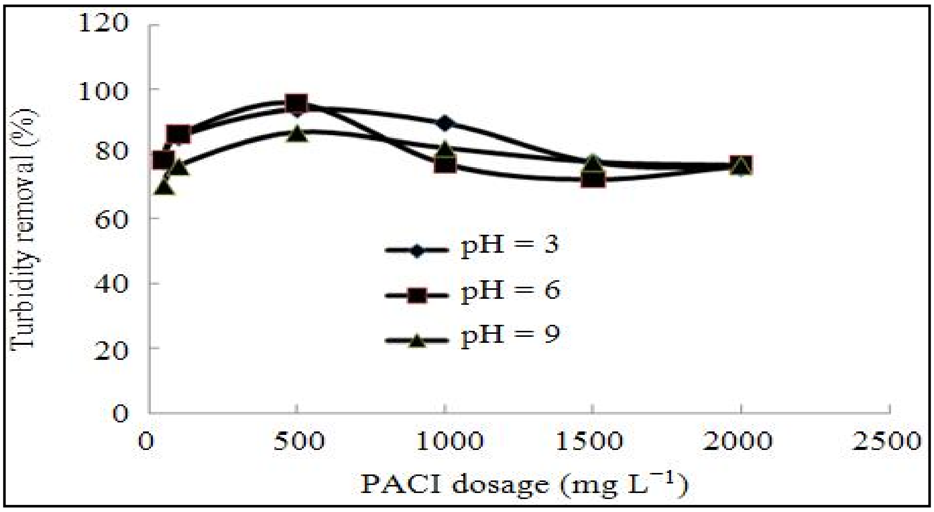

Fig.3. Effect of PACl Dose on Percent Removal of Turbidity at Different pH.

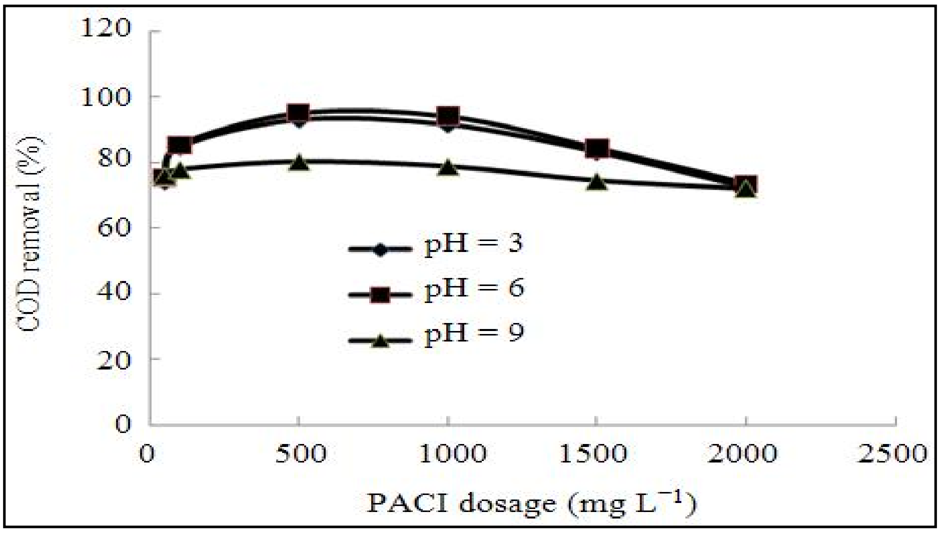

Fig.4. Effect of PACl Dose on Percent Removal of COD at Different pH.

According to Huang and Pan (2002), at lower pH and lower coagulant dosage, the only mechanism for the destabilization of particles is charge neutralization. At low pH and because the aggregates are small in size, the mechanism of colloidal destabilization is mainly charge neutralization. At lower dosage, PACl behaves like the alum salt; therefore, charge neutralization is the principal mechanism for destabilization. As stated by Huang and Pan (2002), PACl is a prehydrolyzed inorganic coagulant. It is prepared by reacting NaOH or Na_2CO_3 with concentrated $AlCl_3$ solution under controlled reaction rate and mild temperature. The extent of prehydrolysis of pure PACl is described in terms of the ligand ratio r, which is the molar ratio of hydroxide (OH-) to the total Al present in solution (Al_{total}).

Theoretically, r is in the range between 0 and 3, or basicity between 0 and 100%. Basicity is the percentage of Al^{3+} acidity satisfied by prehydrolysis or base addition. The major dissolved Al species from PACl available for coagulation is controlled by r. For r < 1 (basicity <33%), monomeric Al species such as Al^{3+} and $AlOH^{2+}$ dominate. Some dimeric Al such as $Al_2(OH)_2^{4+}$ may be present. The basicity of the PACl used in the present study is 30%. Evidently, this indicates that the main Al species present for the destabilization of colloidal particles are monomeric and dimeric Al which functions only through charge neutralization.

3.3. Treatment by Alum with Fenugreek Mucilage

Alum is used in coupled with Fenugreek mucilage to improve the performance of flocculation process. Fenugreek mucilage acts as a flocculent aid which provides more collision opportunity among suspended particles in the wastewater and the inorganic coagulants. This in turn would increase successful collision rate, hence forming larger and denser flocs. The effect of polysaccharide flocculant dosages on the reduction of turbidity andCOD was investigated. Flocculant dosage was increased from 50-2000 mg/L with a fixed amount of alum (100 mg/L). The initial pH of wastewater was adjusted to pH 6.0. The reduction or removal of turbidity and COD efficiencies were calculated from the turbidity and COD initial concentration in the raw wastewater and final concentration in the supernatant. The results obtained for alum plus Fenugreek treatment is depicted in Figs. 5 and 6. The reduction and removal efficiencies of turbidity did not change significantly. On the other hand, the COD reduction efficiency increased appreciably as shown in Fig. 6. The positive effect of using Fenugreek mucilage could be clearly observed for low coagulant dosages of 50, 100 and 500 mg/L since a much greater reduction efficiency in COD is achieved when only the alum is used. The reduction efficiency of COD is improved from 55-95% for alum and Fenugreek mucilage dosage of 100 and 1000 mg/L respectively. This means that lower quantities of alum are needed to obtain an acceptable reduction in COD.

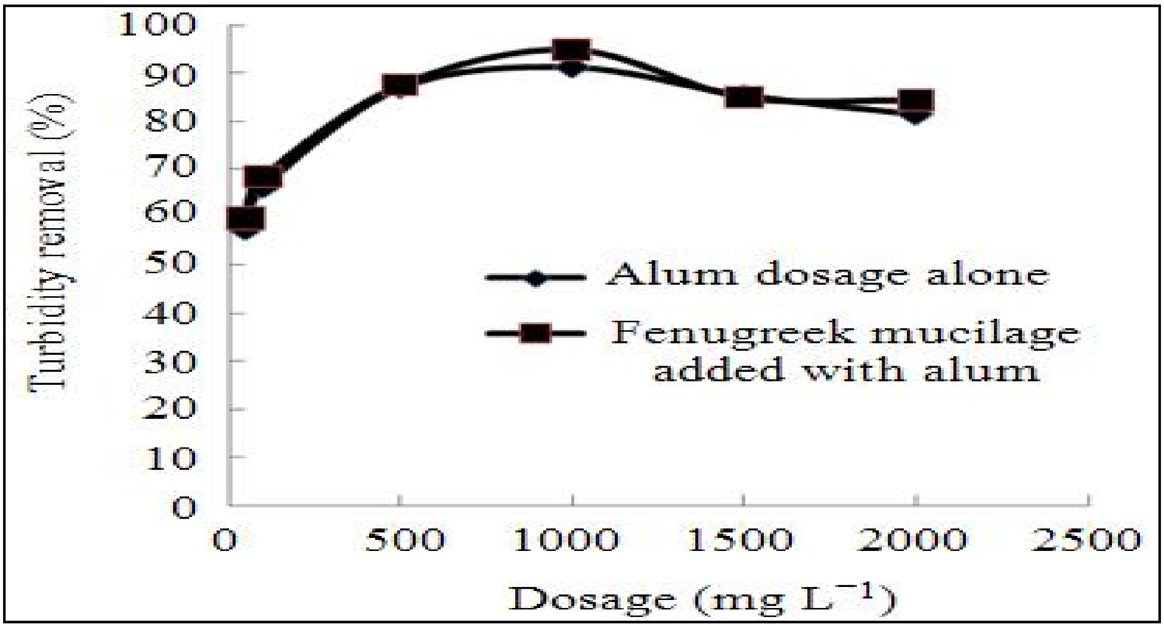

Fig.5. Comparison of % Turbidity Removal with and Without Addition of Fenugreek Mucilage to Alum.

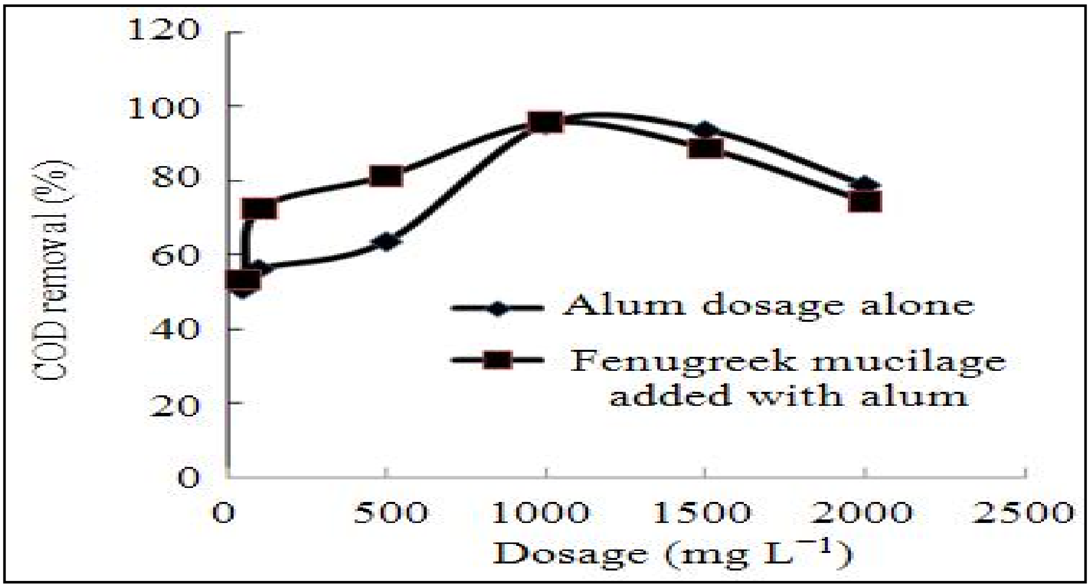

Fig.6. Comparison of % COD Removal with and Without Addition of Fenugreek Mucilage to Alum.

3.4. Treatment by PACl with Fenugreek Mucilage

PACl is used with Fenugreek mucilage to improve the performance of flocculation process. Flocculant dosage was increased from 50-2000 mg/L with a fixed amount of PACl (50 mg/L). The initial pH of wastewater was adjusted to pH 6.0. Figures 7 and 8 show the plots of percent reduction of turbidity and COD vs. polysaccharide dose. It is apparent that the performance of PACl plus Fenugreek mucilage in terms of turbidity reduction is the best combination coagulant + flocculant system in comparison with Fenugreek alum combination.The effect of flocculant addition on turbidity removal is depicted in Fig.7 which shows a similar performance over the entire range of polysaccharide dose.

This combination system achieves more than 97% removal of turbidity when Fenugreek mucilage dosage is greater than 100 mg/L. This means that lower quantities of PACl and Fenugreek mucilage are needed to obtain high reduction in turbidity. This behavior could be explained by the fact that optimal dose of flocculant in suspension causes larger amount of suspended solids to aggregate and settle thus decreasing the total solids in the effluent.

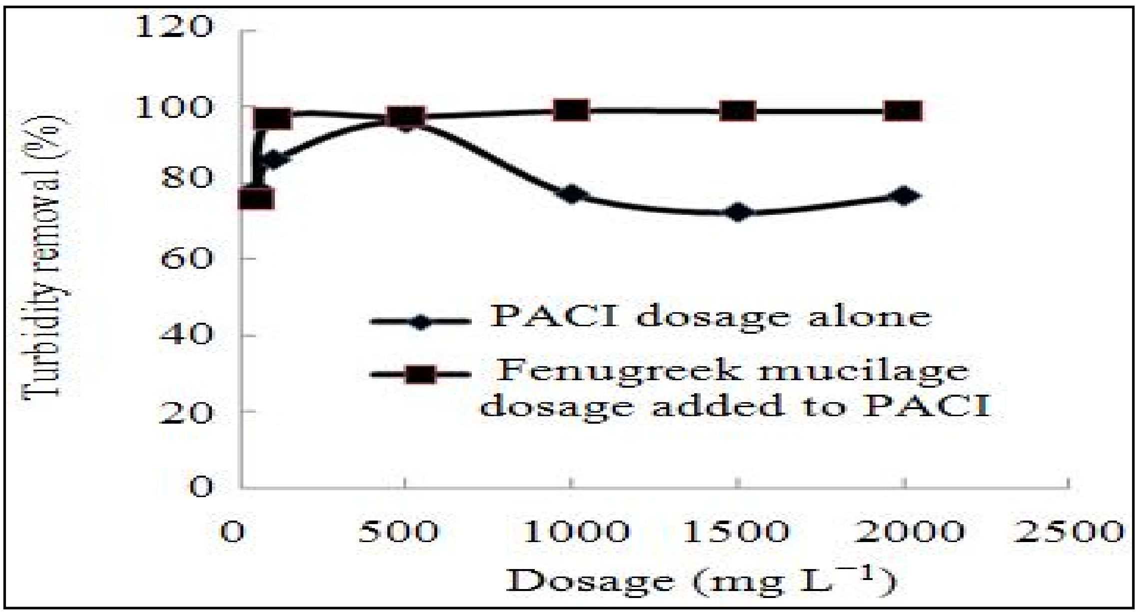

Fig.7. Comparison of % Turbidity Removal with and Without Addition of Fenugreek Mucilage to PACl.

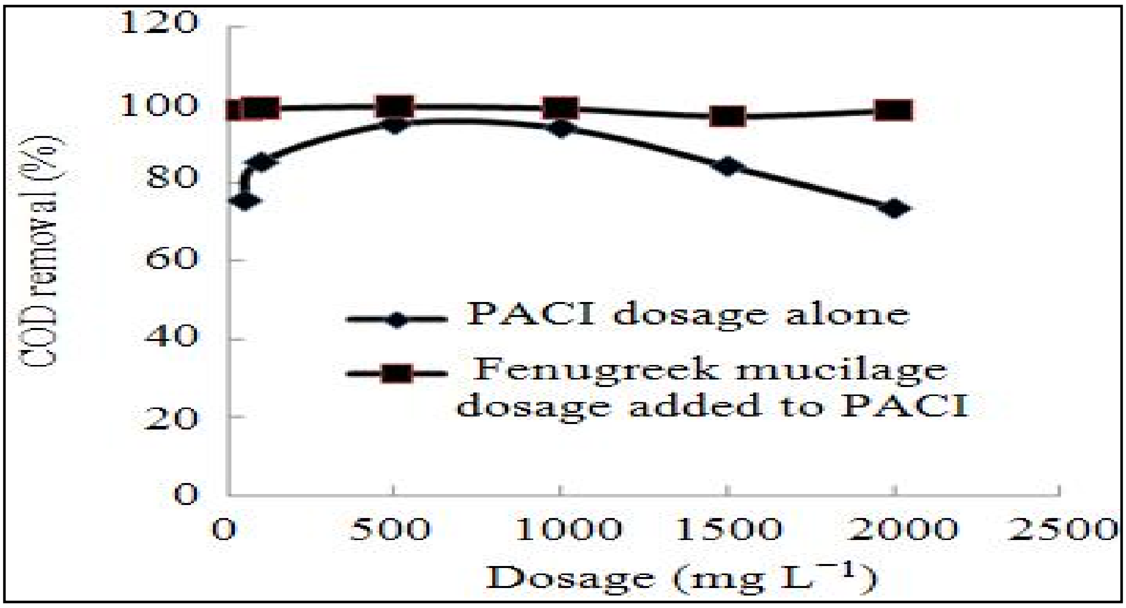

Fig.8. Comparison of % COD Removal with and Without Addition of Fenugreek Mucilage to PACl.

Figure 8 shows the effect of Fenugreek mucilage addition on the reduction efficiency of COD. The results show that the COD reduction is improved over the entire range of Fenugreek mucilage. The addition of flocculant exhibit very high COD reduction efficiency (>98%) even at low dosage of PACl and Fenugreek mucilage. This indicates that the use of flocculant lowers the coagulant dosage needed to obtain a satisfactory reduction in COD.

Obviously, the PACl performs much better than alum in the reduction efficiency of turbidity and COD. These results suggested that the use of Fenugreek mucilage will reduce the usage of PACl coagulant.

4. Conclusion

Reduction of turbidity and COD were studied using alum+Fenugreek mucilage and PACl+Fenugreek mucilage as a combination system for treating pulp and paper mill wastewaters. The results were compared with conventional coagulants like alum and PAC. The results show that the combination of PACl and Fenugreek mucilage is more effective than alum, PACl and alum+Fenugreek mucilage. It can achieve greater than 97% of turbidity reduction and greater than 98% of COD reduction at low dosage of PACl (50 mg/L) and Fenugreek mucilage (100 mg/L). Obviously, the combination of Fenugreek mucilage with PACl performs much better than that with alum in the reduction efficiency of turbidity and COD. These results suggested that the use of Fenugreek mucilage will reduce the usage of PACl coagulant.

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دراسة أداء كل من الشب والبولي ألمنيوم كلورايد مع دبق الحلبة في معالجة مخلفات المياه الناجمة عن معامل الورق

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الخلاصة

تعتبر مخلفات المياه الناجمة عن معامل الورق من المياه الملوثة بدرجه كبيره مما يتطلب معالجتها قبل تصريفها إلى الأنهار. وتعتبر عملية التخثير والتلبيد باستخدام البوليمرات الطبيعية من الطرق التي تزايد استخدامها في معالجة مخلفات المياه. في هذا البحث تم دراسة أداء كل من الشب والبولي المنيوم كلورايد كل على حده و الشب والبولي المنيوم كلورايد مع دبق الحلبه في معالجة مخلفات المياه الناجمة عن معامل الورق. وقد أجريت التجارب باستخدام اختبار الجره وبجرع مختلفة للشب والبولي المنيوم كلورايد ودبق الحلبة تتراوح بين ٥٠-٢٠٠٠ ملغم/لتر ومزج سريع مقداره ٢٠٠ دوره في الدقيقه لمدة دقيقتين متبوع بمزج بطئ مقداره ٤٠ دوره في الدقيقة لمدة ١٥ دقيقه وزمن تركيد مقداره ٣٠ دقيقه. وقد قيست فعالية دبق الحلبة اعتمادا على الانخفاض في العكوره ومتطلب الأوكسجين الكيمياوي. وقد أظهرت النتائج ان استخدام دبق الحلبه مع البولي المنيوم كلورايد يكون أكثر فعالية من استخدام الشب والبولي المنيوم كلورايد من دون إضافة دبق الحلبة والشب مع دبق الحلبه. حيث بلغت نسبة الانخفاض في العكوره اكثر من ٩٧% ونسبة الانخفاض في متطلب الأوكسجين الكيمياوي أكثر من ٩٨% وبجرعه واطئه للبولي المنيوم كلورايد (٥٠ ملغم/لتر) ودبق الحلبه (١٠٠ ملغم/لتر). ان النتائج المستحصله تدل على امكانية استخدام كميات قليله من البولي المنيوم كلورايد للحصول على انخفاض مقبول في العكوره ومتطلب الاوكسجين الكيمياوي لمخلفات المياه الناجمة عن معامل الورق.