TREATMENT OF PULP AND PAPER MILL WASTEWATER BY POLY-ALUMINUM-SILICATE-CHLORIDE (PASIC) THROUGH COAGULATION-FLOCCULATION PROCESS

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ABSTRACT

The coagulation-flocculation process of new inorganic polymer coagulant, Poly-Aluminum-Silicate-Chloride (PASiC) in the treatment of pulp and paper mill wastewater has been studied. The experiments were carried out in jar tests with PAlSiC dosages range of 10-45 mg/L, pH range of 5-9, rapid mixing at 200 rpm for 2 min, followed by slow mixing at 40 rpm for 15 min and settling for 30 min. The effectiveness of PASiC was measured based on the reduction of turbidity and Chemical Oxygen Demand (COD). PASiC is found to give the highest efficiency in the treatment of the pulp and paper mill wastewater among the other coagulants. It can achieve greater than 90% of turbidity and COD reduction at an optimum dosage of 40 mg/L and pH of 7. A comparison of PASiC performance with that of alum and poly aluminum chloride (PAC) showed that the coagulation efficiency of PASiC is more effective than alum and PAC. The optimum dosages of PASiC, PAC and alum in the removal of turbidity and COD reduction are 45, 150 and 200 mg/L with 93.13, 82.86 and 80.64% for turbidity removal and 91.12, 80.43 and 75.64% for COD reduction respectively. This result suggests that single-polymer system can be used alone in the coagulation-flocculation process due to the efficiency of the PASiC.

KEYWORDS: Pulp and Paper Mill Wastewater, Coagulation and Focculation, PASiC, COD, Turbidity

معالجة مياه المخلفات الناجمه عن معمل الورق باستخدام البولي المنيوم سليكات كلورايد بواسطة عملية التخثير والتلبيد

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الخلاصه

في هذا البحث تم دراسة عملية التخثير –التكتيل في معالجة مياه المخلفات الصناعيه الناجمه عن معامل الورق وباستخدام مخثر بوليمري غير عضوي يدعى البولي المنيوم سليكات كلورايد. وقد اجريت التجارب باستخدام اختبار الجره وبمدى جرع تتراوح بين ١٠-٤٥ ملغم/لتر لمادة البولي المنيوم سليكات كلورايد وبداله حامضيه ضمن مدى يتراوح بين ٥-٩ ومزج سريع ٢٠٠ دوره/دقيقه لمدة دقيقتين يليه مزج بطيء بمعدل ٤٠ دوره/دقيقه لمدة ١٥ دقيقه ومن ثم تركيد لمدة ٣٠ دقيقه. وقد قيست فعالية البولي المنيوم سليكات كلورايد استنادا الى الانخفاض في العكوره ومتطلب الاوكسجين الكيمياوي. وقد وجد ان استخدام البولي المنيوم سليكات كلورايد يعطي كفاءة معالجه افضل من المخثرات الاخرى كالبولي المنيوم كلورايد والشب حيث وجد ان استخدام البولي المنيوم سليكات كلورايد ينجز كفاءة ازاله للعكوره و ومتطلب الاوكسجين الكيمياوي بنسبه تتجاوز ٩٠% بجرعه مثلى مقدارها ٤٠ ملغم/لتر وداله حامضيه تساوي ٧. ان نتائج المقارنه بين اداء البولي المنيوم سليكات كلورايد واداء البولي المنيوم كلورايد والشب بينت ان اداء المخثر الاول افضل من اداء المخثرين الاخرين حيث ان نسبة الازاله في متطلب الاوكسجين الكيمياوي عند استخدام البولي المنيوم سليكات كلورايد والبولي المنيوم كلورايد والشب كانت ٩١.١٢ و ٨٠.٤٣ و ٧٥.٦٤% على الترتيب، بينما كانت نسبة الازاله في العكوره ٩٣.١٣ و ٨٢.٨٦ و ٨٠.٦٤ % على الترتيب وبجرع مثلى ٤٥ و ١٥٠ و ٢٠٠ ملغم/لتر على الترتيب. ان النتائج المستحصله في هذا البحث ترجح امكانية استخدام مخثر واحد فقط في اجراء عملية التخثير –التكتيل من دون الحاجه الى استخدام مساعدات التكتيل وذلك بسبب الكفاءه العاليه لمادة البولي المنيوم سليكات كلورايد

INTRODUCTION

Increased knowledge about the environmental effects of industrial activities has led to a need for developing better techniques and more efficient waste management systems in order to reduce their environmental impact. The pulp and paper mills industry employs large amounts of water and produce equally large amounts of wastewater, which constitutes one of the major sources of aquatic pollution.

Such wastewater contains a large amount of pollutants characterized by Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Suspended Solids (SS), toxicity and colorants which cause bacterial and algal slime growths, thermal impacts, scum formation, color problems and a loss of both biodiversity and aesthetic beauty in the environment (**Pokhrel and Viraraghavan, 2004**).

Several biological, chemical and physic-chemical processes are available for the treatments of pulp and paper mills wastewater. Many studies have been carried out on the treatment of pulp and paper mills wastewater by biological processes such as conventional aerobic and anaerobic treatment methods (**Rintala, 1991; Rintala and Puhakka, 1994 and Yu and Gu, 1996**). On the other hand, the pulp and paper mill wastewater has low BOD/COD ratio usually between 0.02-0.07 (**Thompson et al., 2001**). The low ratio of BOD/COD makes the biological treatment methods inappropriate for pulp and paper mills wastewater (**Morais et al., 2006**). Chemical processes, such as chemical oxidation, are usually expensive because of the large amount of chemicals required and their application has therefore been determined by economic factors. Physico-chemical processes, an interesting option for pulp and paper mills wastewater since they are relatively cheap and based on the coagulation-flocculation process of small particles followed by an adjusted settling time.

Coagulation/flocculation is a frequently applied process in the primary purification of industrial wastewater. Chemical coagulation, using alum, ferric chloride, ferric sulphate and lime have been studied extensively in the treatment of pulp and paper mill wastewater (**Beulker and Jekel, 1993 and Stephenson and Duff, 1996**). Several research efforts have been devoted to improve the efficiency of coagulation–flocculation process. The tendency was the production of coagulants with improved properties in comparison with the conventional ones, such as aluminum sulfate, or aluminum chloride.

Recently, it was reported that under certain conditions poly aluminum chloride (PAC) and activated silica, a polysilicate (PSi), could be combined to get Poly aluminum silicate Chloride (PASiC). This new type of inorganic polymer coagulant has an enhanced aggregating power and bigger and denser flocs' formation (**Gao et al., 2003; Bi et al., 2004; Jia et al., 2004**).

Poly aluminum silicate chloride has shown superior coagulation performance than alum and PACl in water or wastewater treatment (**Gao, et al., 2007**). Its advantages can be summarized as the better coagulation performance for lower additions of used coagulant and wider effective pH range, than the conventional or pre-polymerized coagulants. Furthermore, the residual aluminum concentration which remains in the treated sample is significantly lower, in comparison with the conventionally applied coagulants.

In the present work, coagulation-flocculation by PASiC is applied to pulp and paper mill industry effluents. The optimum dosage and pH are studied. The turbidity and COD concentrations are used as evaluating parameters. The main purpose was to define whether the application of composite coagulants can exhibit septic advantages for the physic-chemical treatment of pulp and paper mill wastewater and to determine the appropriate dosage of PASiC and optimum pH, as well as the comparison with conventional coagulants PAC and alum.

EXPERIMENTAL WORK:

Wastewater:

The wastewater was collected from the wastewater treatment plant of a paper mill 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 (**APHA, 1998**).

Chemicals:

All reagents used are analytically pure chemicals except water glass is commercial grade product. All reagents were purchased from R&M chemicals; Essex, U.K. Deionized water was used to make all solutions. Table 2 shows the important properties of the chemicals that used in research.

EXPERIMENTAL PROCEDURES:

Preparation of PASiC:-

Water glass solution (sodium silicate, Na_2SiO_3) was diluted to a concentration of 0.5M. Then the diluted water glass solution was neutralized to pH 2.0 by 0.5M HCl. 0.25M $AlCl_3$ was prepared using de-ionized water. The prepared $AlCl_3$ solution was very slowly titrated with 0.5 M NaOH solution. During titration the solution was vigorously stirred to ensure that homogeneous solution was obtained. The solution was mixed with polysilicic acid aged for 2 h. The prepared coagulant sample was capped, sealed and stored overnight before jar test was conducted.

Coagulation Experiment:

Coagulation/flocculation tests were conducted using a conventional jar test apparatus (Stuart Science Flocculatormodel, SWI) (**Fig. 1**). In each run, 1 L samples was poured into six jars (1.8 L). Different dosages of PASiC were then added and the coagulation began with rapid mixing of 200 rpm for 2 min, followed by slow stirring of 40 rpm for 10min. The flocs formed were then allowed to settle. The end of sedimentation was set at a time when no appreciable floc settlement was observed. Finally, supernatant was withdrawn with a plastic syringe from near 2 cm below the liquid–air interface for chemical analysis. All the experiments were carried out at ambient temperature of 20-25°C.

In the pH optimization (control) test, after initial addition of coagulant, the beaker was placed on a magnetic stir and effluent pH was adjusted to the designated value by adding concentrated HCl or NaOH solution.

Analytical Methods:

Turbidity was measured by a Turbid meter manufactured by Eutech (Model 2100A) (**Fig. 2**). Turbidity was measured by putting 10 ml of sample into turbidity vial and place it in turbidity meter to measure turbidity.

Chemical oxygen demand (COD) was determined by the 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 (**Fig. 3**) and heat 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 (**Fig. 4**). The above-mentioned parameters were measured according to the standard method for examination of water and wastewater. The pH value was determined with a bench-scale pH meter. Calibration was regularly carried out with standard buffers.

RESULTS AND DISUSSION

Coagulation test was conducted for pulp and paper mill wastewater. Wastewater samples were treated with poly aluminum silicate chloride, poly aluminum chloride and alum as well. The comparison of results was made for the three coagulants mentioned above based on two parameters; turbidity and chemical oxygen demand. All results were shown in **Tables 3, 4, 5 and 6.**

Effect of pH:

First the impact of pH variation on the coagulation performance was examined for constant initial concentration of PASiC 25 mg/L using jar test. **Figure 5** shows the effect of pH on the quality of the final water under treatment, parameters such as turbidity and COD concentration, were utilized. According to the data in **Fig. 5**, the lowest remaining turbidity and COD values were observed at $6 < pH < 8$. Therefore, the best pH chosen is 7.0 in this experimental condition. From the observation, the pH does affect the coagulation properties of PASiC like other conventional coagulants but the effect is not much in comparison with poly aluminum chloride and alum.

Effect of PASiC dosage:

The optimal dosages of the PAlSiC are based on the reduction of turbidity and COD. 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. The results obtained from the jar test experiments for turbidity reduction of PASiC are shown in **Fig. 6**. The percentage turbidity reduction of the PASiC is seen to increase with the PASiC dosage. After the PASiC reaches the highest reduction efficiency, there is no significant difference in turbidity reduction efficiency with further increase in PASiC dosages. This can be attributed to the nature of pulp and paper mill wastewater which consist of many different compounds. The dosage beyond which there is no significant enhancement in reduction efficiency with further addition of coagulant is denned as the optimum dosage. The optimum dosage of PASiC was 45 mg/L. The efficiency of the PASiC in the reduction of turbidity is impressive, even at low dosage. The percentage turbidity reduction of more than 68% can be achieved at dosage of 10 mg/ L. The turbidity reduction efficiency of up to 93.13% is obtained by 45 mg/L dosage. The percentage of COD removal by PASiC at various dosages is shown in **Fig. 6**. The removal trend of the COD is similar to that of the turbidity removal. The COD were reduced when the PASiC dosage was increased until it achieved optimum dosage. In **Fig. 6**, the optimum dosage of the PASiC in the removal of COD is 45 mg/L with 90.72% removal.

Comparison of PASiC with PAC and Alum:

Figure 7 shows that the efficiency of turbidity removal for paper pulp wastewater for PASiC, PAC and alum. From this figure it is clear to see that about 93% of turbidity removal is achieved using PASiC as coagulant with dosage of 45mg/L.

In comparison with alum, the positive effect of using PASiC could be clearly observed for low coagulant dosage of 45 mg/L since much greater reduction efficiency is achieved when the alum is used. The reduction efficiency of turbidity is improved from 58-93% for the same dosages of alum and PASiC. This means that lower quantities of PASiC are needed to obtain an acceptable reduction in turbidity. The other coagulant, PACl, also shows lower performance with dosages of 50, 100 and 200 mg/L, although the performance is not as small as in the case of alum. The performance of PAC and PASiC in terms of turbidity reduction is 69.3% and 93% respectively for same dosages.

Figure 8 shows the comparison between PASiC and conventional coagulants, alum and PAC, in terms of the reduction efficiency of COD. The results show that the COD reduction is gradually improved with increasing coagulant dosage. The PASiC coagulant has the greatest performance in reducing COD concentration. In addition, the dosage required to reduce COD is so small in case of PASiC in comparison with alum and PAC. The maximum reduction in COD is 91.12% with PASiC dosage of 45 mg/L.

Alum and PACl exhibit low COD reduction efficiency (>72% for PAC and >58 for alum) at the lowest dosage applied (50 mg/L). The improvement of alum and PAC require many quantities of these coagulants. The maximum reduction in COD achieved by alum and PAC are 80.43 and 75.65% with dosage of 150 and 200 mg/L respectively. This indicates that the use of PASiC lowers the coagulant dosage needed to obtain a satisfactory reduction in COD.

CONCLUSION

Reduction of turbidity and COD has been studied using PASiC as a coagulant for treating pulp and paper mill wastewaters. The results have been compared with conventional coagulants like alum and PAC. The results show that PASiC is more effective than alum and PAC. It can achieve 93.13% of turbidity reduction and 90.12% of COD reduction at the optimum dosage of 45 mg/L. The PASiC produces compacted and dense flocs that can settle faster. 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 PASiC is remarkable.

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Table 1 Chemical characteristics of the wastewater used.

Parameters	Value
pH	6.80
Turbidity (NTU)	235.00
COD (mg L̃1)	20300.00
BOD (mg Ḷ̃1)	636.00

Table 2 Important properties of chemicals.

Chemicals	Chemical formula	MW g/gmol	Purity
Water glass solution	Na2SiO3	142.07	5% water
Aluminum chloride	AlCl3	241.43	pure
Poly aluminum chloride	(Aln(OH)mCl 3m-n)x	Not available	Al2O3 17% Chlorides 20% Basicity 40%
Alum	Al2SO4	342.15	pure

Table 3 PH influence on the coagulation of pulp and paper mill effluent by PASiC.

pH	Turbidity removal %	COD removal %
5	80.6084	70.5659
6	81.409	78.5657
7	82.2285	79.2171
8	80.2635	76.4652
9	76.2984	62.9147

Table 4 Turbidity and COD reduction of pulp and paper mill effluent by PASiC at various dosages

PAlSiC dosage, mg/l	Turbidity removal %	COD removal %
10	68.51923	54.7
15	78.55769	63.64
25	82.2285	79.2171
35	91.05769	88.12
40	93.14423	90.72
45	93.13462	91.12

Table 5 Turbidity and COD reduction of pulp and paper mill effluent by PAC at various dosages

PAC dosage, mg/l	Turbidity removal %	COD removal %
50	69.3	71.49
100	74.64	75.96
150	82.86	80.43
200	82.38	80.75

Table 6 Turbidity and COD reduction of pulp and paper mill effluent by alum at various dosages

Alum dosage, mg/l	Turbidity removal %	COD removal %
50	58.58	57.58
100	66.07	70.07
150	74.6	73.6
200	80.64	75.64

Figure 1 Jar test apparatus

Figure 2 Turbid meter

Figure 3 COD digestion reactor

Figure 4 COD spectrophotometer

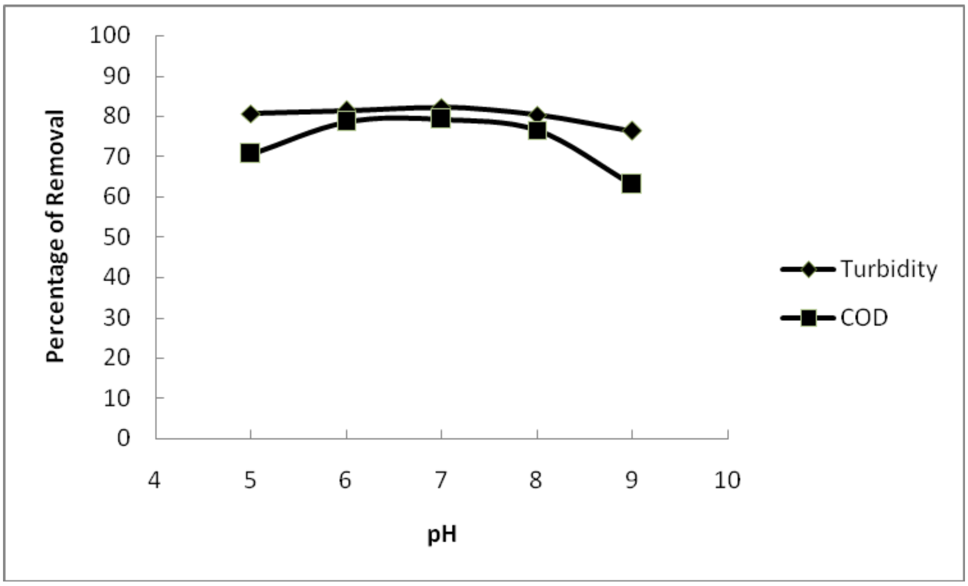

Figure 5 PH influence on the coagulation of pulp and paper mill effluent by PASiC.

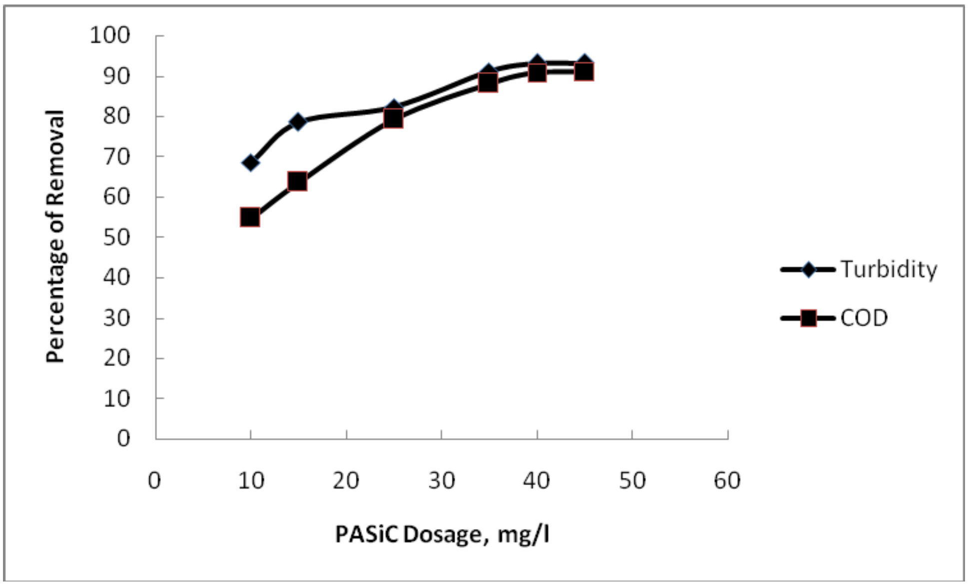

Figure 6 Turbidity and COD reduction of pulp and paper mill effluent by PASiC at various dosages.

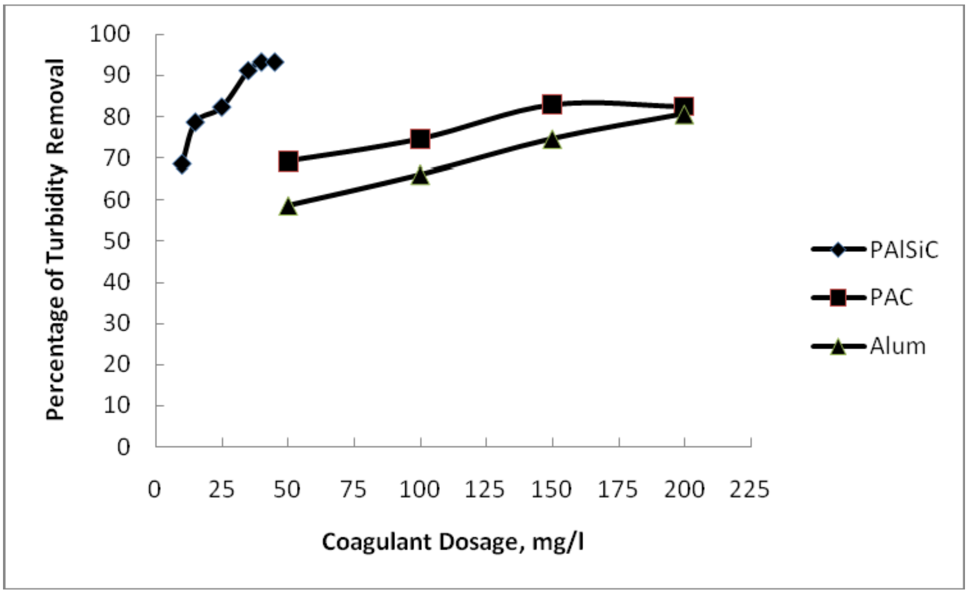

Figure 7 Percentage of turbidity removal by PASiC, PAC and alum for pulp and paper mill wastewater.

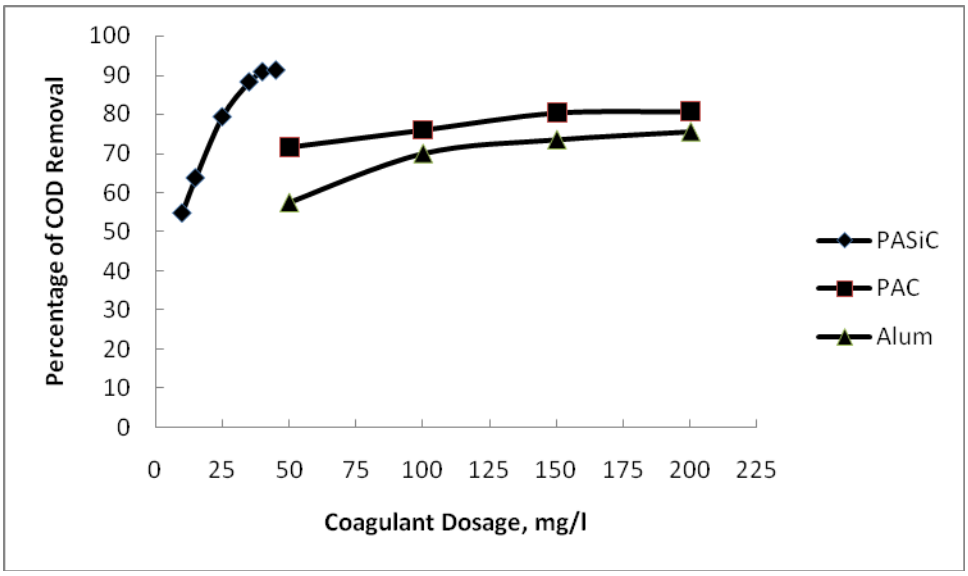

Figure 8 Percentage of COD removal by PASiC, PAC and alum for pulp and paper mill wastewater.