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Improvement of alum and PACl coagulation by polyacrylamides (PAMs) for the treatment of pulp and paper mill wastewater

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Abstract

A study using coagulation–flocculation method for the treatment of pulp and paper mill wastewater has been carried out. The efficiency of alum and polyaluminum chloride (PACl) when used alone and in coupled with cationic polyacrylamide (C-PAM) and anionic polyacrylamide (A-PAM) on the treatment of pulp and paper mill wastewater were studied. The reduction efficiency of turbidity and chemical oxygen demand (COD), removal efficiency of total suspended solids (TSS), sludge volume index (SVI) and settling time are the main evaluating parameters. In coagulation–flocculation process using single coagulant, coagulant dosage and pH play an important role in determining the coagulation efficiency. At the optimum alum dosage of 1000 mg/L and optimum pH of 6.0, turbidity reduction is found to be 99.8%, TSS removal is 99.4% and COD reduction is 91%. The optimum dosage and pH for PACl are 500 mg/L and 6.0, respectively, at which it gives 99.9% reduction of turbidity, 99.5% of TSS removal and 91.3% of COD reduction. A combination of inorganic coagulant and flocculant or polymer is applied in which alum and PACl are used coupled with the C-PAM (Organopol 5415) and A-PAM (Chemfloc 430A). Overall, alum coupled with Organopol 5415 is the best system among all systems studied. It gives 99.7% reduction of turbidity, 99.5% removal of TSS and 95.6% reduction of COD, and at the same time with low SVI (38 mL/g) and low settling time (12 s).

Keywords: Coagulation; Flocculation; Polyelectrolyte; Sludge volume index

1. Introduction

The pulp and paper mill is a major industrial sector utilizing a huge amount of lignocellulosic materials and water during the manufacturing process. It can consume as high as 60 m^3 of freshwater per tonne of paper produced [1]. According to Thompson et al. [1], currently the concept of "zero liquid effluent" has been suggested and is applicable in area with extremely limited water sources. However, the recovery and reuse of the water can increase the concentration of organic and inorganic species, which in turn can affect paper formation, bacteria loading or lead to corrosion and odours. Common pollutants include suspended solids (SS), colour compound, heavy metals, organic and inorganic substances, phenols, chloroorganics, cyanide, sulphides and other soluble substances [2]. The wastewater can cause considerable damage to the receiving waters if discharged untreated [3–5].

Unlike freshwater, pulp and paper mills wastewater contains fibre and can cause unique solid/liquid separation challenges. Most solid/liquid separation systems have difficulty operating when the requirements are to produce high quality water, to remove fine particles, to operate continuously and remove high quantities of fibre. Chemical coagulation followed by sedimentation is a probed technique for the treatment of high suspended solids wastewater especially those formed by colloidal matters. Research and practical applications have shown that coagulation will lower the pollution load and could generate an adequate water recovery [6–10]. As a result of the smaller load, the wastewater treatment plant might be designed more energy efficiently at a smaller footprint and might be built at lower investment costs [11].

Coagulation is mainly induced by inorganic metal salts, e.g. aluminum and ferric sulphates and chlorides. Polyelectrolytes of various structures, e.g. polyacrylamides, chitosan, polysaccharides, polyvinyl and many more are usually used as coagulant aids to enhance the formation of larger floc in order to improve the rate of sedimentation. According to Aguilar et al. [12], anionic polyacrylamide when added with ferric sulphate or

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polyaluminum chloride led to a significant increase in the settling speed. In the earlier work done by Stephenson and Duff [13], they found that the removal of total carbon, colour and turbidity of up to 88, 90 and 98%, respectively, were observed in the treatment of mechanical pulping effluent using ferric chloride, ferrous sulphate, aluminum chloride and aluminum sulphate.

Aluminum and iron salts are widely used as coagulants in water and wastewater treatment and in some other applications. Their mode of action is generally explained in terms of two distinct mechanisms: charge neutralization of negatively charged colloids by cationic hydrolysis products and incorporation of impurities in an amorphous hydroxide precipitate so-called sweep flocculation [14]. The relative importance of these mechanisms depends on factors such as pH and coagulant dosage.

Recently, the use of synthetic polyelectrolytes as flocculants for suspended solids removal in wastewater treatment has grown rapidly [15,16]. 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. Girma et al. [17] reported that 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. Flocculations of suspended particles occur via charged amide or carboxylic groups. 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 main objectives of the present study are to investigate the coagulation–flocculation efficiencies of alum and PACl when used alone and in coupled with cationic and anionic PAMs in the treatment of pulp and paper mill wastewaters and to select the most appropriate coagulant–flocculant scheme with the technical analysis criteria. The effects of coagulant dosage, flocculant dosage and pH are studied. The turbidity, TSS and chemical oxygen demand (COD) concentrations and SVI are used as evaluating parameters.

2. Material and methods

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 per tonne of paper produced. 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 [18].

Alum and PACl were used as coagulants and very high molecular weight cationic polyacrylamide (C-PAM), Organpol 5415, with low charge density and high molecular weight anionic polyacrylamide (A-PAM), Chemfloc 430A, with high charge density were used as flocculants. Organopol 5415 was supplied by Ciba Speciality Chemicals and Chemfloc 430A was supplied by Chemkimia. Distilled water was used to prepare all the PAM feedstock solutions of 0.1%.

Table 1
Chemical characteristics of the wastewater used

Parameters	Value[a]
TCOD[b] (mg/L)	3087
SCOD[c] (mg/L)	318
Suspended solids (mg/L)	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.

2.2. Experimental procedure

Jar test procedures were performed with the conventional jar apparatus (Stuart Science Flocculator model, SWI) using 500 ml wastewater samples. Different combinations of pH (5, 6, 7, 8, 9, 10), alum dosage (200, 500, 800, 1000, 1500, 2000 mg/L), PACl dosage (50, 100, 200, 500, 1000, 1500 mg/L) and PAMs dosage (1, 2, 3, 4, 5, 6 mg/L) were tested. The selected coagulant 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 after the selected PAM 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, 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). All parameters were determined according to the APHA method.

3. Results and discussion

3.1. Coagulation with alum

In coagulation–flocculation processes using inorganic coagulant, coagulant dosage and 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, should be determined. The addition of metal coagulants depresses the wastewater pH to a lower value. The jar test experiments with alum, using pulp and paper mill wastewater with pre-adjusted pH of 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0, for each pH value with the alum dosages of 200, 500, 800, 1000, 1500 and 2000 mg/L, were run. The effects of pH adjustment and coagulant dosage by alum on turbidity, TSS and COD are illustrated in Fig. 1(a–c), respectively. In general, decreasing the pH from the alkaline levels to near neutral levels has a strong positive effect on reduction/removal of turbidity, TSS and COD.

Fig. 1 clearly shows that turbidity reduction, TSS removal and COD reduction efficiencies increase with increase in coagulant dosage and pH adjustment till it reaches its highest value, optimum pH, after which the reduction and removal efficien-