Journal of Hazardous Materials B135 (2006) 378–388

Journal of Hazardous Materials

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

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Received 8 September 2005; received in revised form 22 November 2005; accepted 30 November 2005

Available online 23 January 2006

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.

Keywords: Flocculation; Coagulation; Polyelectrolyte; Cationic polyacrylamide; Anionic polyacrylamide

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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doi:10.1016/j.jhazmat.2005.11.076

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).