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Evaluation of several commercial synthetic polymers as flocculant aids for removal of highly concentrated C.I. Acid Black 210 dye

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ABSTRACT

The removal of C.I. Acid Black 210 dye from highly concentrated solutions was studied using a coagulation/flocculation process. Aluminium sulphate was used as a primary coagulant and five commercial polymers were used as flocculant aids. The five commercial polymers were ACCEPTA 2058 (poly-diallyldimethyl ammonium chloride), ACCEPTA 2047 (high molecular mass (MM) anionic polyacrylamide), ACCEPTA 2111 (high MM cationic polyacrylamide), ACCEPTA 2105 (Low-medium MM cationic polyacrylamide) and ACCEPTA 2037 (Composite of high MM cationic polyacrylamide-inorganic salt(s)). The five polymers behaved differently and they showed maximum colour removal increment in the order: ACCEPTA 2058 > ACCEPTA 2037 > ACCEPTA 2111 ≈ ACCEPTA 2047 > ACCEPTA 2105. Results also showed that the aluminium sulphate is important as primary coagulant and settling time has significant effect on the dye removal.

1. Introduction

The presence of residual dyes in surface water is aesthetically undesirable and causes annoyance to the aquatic biosphere due to reduction of sunlight penetration and depletion of the dissolved oxygen. Some dyes are toxic and mutagenic and have potential to release the carcinogenic amines. Due to their toxic properties, dyes can also contribute to the failure of biological processes in wastewater treatment plants [1]. Most dyeing processes are inefficient causing a loss that can reach up to 50% of the input dye. Dyes are generally designed to withstand microbial, chemical and photolytic degradation, hence are difficult to biodegrade in sewage treatment works. Protection of human health and the environment is a priority which requires the removal of dyes before effluent discharge into the environment.

At present, coagulation is the most widely used method for treating coloured wastewater. Aluminium and ferric salts are extensively used as inorganic coagulants in wastewater treatment but the use of inorganic coagulant alone appeared to be less effective, especially for highly concentrated dyes [2].

To improve the coagulation by inorganic coagulant, the addition of polymer as flocculant aid proved to enhance the effectiveness of dye removal by enlarging the size of flocs and consequently causing rapid settling [3]. In addition, the floc that was formed is strong enough to withstand shear forces. Basically, polymers enhances the rate of orthokinetic flocculation when added to a system already destabilised with inorganic coagulants, as shown below [3]:

$$\text{Stable Colloid} \xrightarrow[\text{Coagulant}]{\text{Inorganic}} \text{Unstable Colloid} \xrightarrow[\text{Time}]{\text{Conditioning}} \text{Flocs} \xrightarrow[\text{Conditioning}]{\text{Polymer}} \text{Large Flocs}$$

The enlargement of flocs only happens when there is sufficient adsorption affinity between polymers and the flocs surfaces. The flocs will then undergo polymer bridging or charge neutralisation [3,4]. The polymers should be carefully selected because the effectiveness of flocculant aids depends on the type of the polymer, the process conditions (i.e. pH, temperature), the concentration ratios of each kind of polymer and the type of inorganic coagulant to be used [4], and the size of the molecule that need to be coagulated [5].

The amount of coagulated colloid/pollutant to adsorb to the polymers depends on the polymer type, its surface charge density, the concentration and solubility of the polymer, the chemical affinity of the polymer to the surface, the ionic strength and secondary effect such as pH of the solution [6]. Although several studies have reported the treatability of dyes using inorganic coagulants with polymers as flocculant aids (Table 1); a comparison of different types of polymers as flocculant aids is lacking. Therefore, in this study we aim to evaluate the efficiency of coagulation/flocculation for the removal of a highly concentrated soluble dye using commercial synthetic polymers as flocculant aids with aluminium sulphate as inorganic coagulant.

Aluminium based coagulant was found to be superior in the destabilisation of acid dyes [16] and textile wastewaters [2,15] as compared to other metal based coagulants such as those of

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Table 1
Efficiency of various polymers as flocculant aids in removing dyes as reported in the literature.

Type of dye(s)	Inorganic coagulant	Type of polymer (dosage)	Condition	Performance	References
125 mg/l Polyvinyl alcohol (PVA) + 20 mg/l Reactive Blue (R94H)	Ferric chloride (150 mg/l)	Anionic (2 mg/l)—KURI diafloc Ap-120, Japan	Initial pH 4; Mixing time = 40 min; Settling time = 30 min	COD removal = 66%; Colour removal = 12% (*Ferric chloride ∼ 5 mg/l)	[7]
Real wastewater from cotton synthetic-textile factory	Ferrous sulphate (1000 mg/l)	Anionic (5 mg/l)—HENKEL 23500	Initial pH 9.5; Temperature = 20 °C; Mixing time = 22 min; Settling time = 60 min	Colour removal = 50%; COD removal = 50%; Toxicity removal = 80%	[8]
Real wastewater from cotton synthetic-textile factory	Aluminium sulphate (1500 mg/l)	Anionic (5 mg/l)—HENKEL 23500	Initial pH 7.0; Temperature = 20 °C; Mixing time = 22 min; Settling time = 60 min	Colour removal = 60%; COD removal = 56%; Toxicity removal = 70%	[8]
Dyeing and finishing mill	Polyaluminium chloride (PAC) (100 mg/l) + electrochemical treatment	Unknown polymer (1 mg/l)	Initial pH 3.0; Mixing time = 5 min; Settling time = 60 min	Colour removal = 97%; COD removal = 73%	[9]
100 mg/l Reactive Blue STE	Polyferric chloride*	Cationic (polyDADMAC*)	Initial pH 7.0; Mixing time = 15 min; Settling time = 12 min	Colour removal = 99%	[10]
125 mg/l Direct dye (Ciba-corb Yellow P-6GS)	Aluminium sulphate (70 mg/l)	Cationic (31 mg/l)	Mixing time = 21 min; Settling time = 10 min	Colour removal = 50%; COD removal = 50%	[11]
Real textile wastewater	Ferric chloride (56 mg Fe/l)	Cationic (5 mg/l)	Mixing time = 32 min; Settling time = 30 min	Colour removal = 92%; Turbidity removal = 64%	[12]
Real textile wastewater	Aluminium sulphate (416 mg/l) + lime (213 mg/l)	Unknown polymer (11 mg/l)	Initial pH 10; Mixing time = 35 min; Settling time = 300 min	COD removal = 50%; BOD removal = 23%	[13]
Real textile wastewater	Ferrous sulphate (400 mg/l) + lime, $Ca(OH)_2$ (800 mg/l)	Cationic polymer (8 mg/l)	Initial pH 12.5–13; Mixing time = 22 min; Settling time = 45 min	Colour removal = 80–90%; COD removal = 50–55%	[14]
Real textile wastewater	Aluminium sulphate (20 mg/l)	Cationic polymer (2.5 ml/l)	Initial pH 7; Mixing time = 22 min; Settling time = 30–150 min	Colour removal = 98%; COD removal = 45%; TOC removal = 50%	[15]

* Composite as polyferric-polyDADMAC.

iron, magnesium, calcium, manganese and barium. Beside that, aluminium based coagulant is extensively used in industrial and domestic effluent treatment, due to its inexpensive cost. Although some researchers have criticised the use of aluminium salts due to concerns about the residual metal in treated waters, so far, no readily available alternative coagulant has been developed.

Soluble triazo metalocomplex C.I. Acid Black 210 dye was selected as a model dye in this study because it is frequently used in dyeing of leather, cotton and woollen fabric. C.I. Acid Black 210 dye is irritating to the eye in powder form but not considered as carcinogenic and toxic. However due to the fact that 80–90% of black dye used in the industry is C.I. Acid Black 210 dye [17], improper treatment of the dye will cause both aesthetic and environmental problems in addition to possible failure of wastewater treatment plants due high recalcitrant organic.

The structure of the C.I. Acid Black 210 dye is given in Fig. 1. The treatment of C.I. Acid Black 210 dye, at low concentrations, has been reported by several studies. Dave and Dave [18] used bacteria isolated from contaminated soil, *B. thuringiensis*, to degrade the C.I. Black 210 dye at a concentration of 100 mg/l. Their results showed a 92% decolourisation in 24 h. On the other hand, enzymatic oxidation using recombinant CotA-laccase from *B. Subtilis* was only able to decolourise the dye to about 35% at 37 °C and 7 h of treatment [19]. Full decolourisation of 25–35 mg/l dye was obtained using sequencing batch bioreactor with suspended growth configuration under anoxic-aerobic-anoxic microenvironment in 24 h total cycle period [20]. Using bioluminescent bacteria, *Vibrio harveyi* TEMS1, decolourisation of 100 mg/l dye achieved 94% in 24 h incubation [21]. Sonochemical was also used to decolourise the C.I. Acid Black 210 dye in the presence of exfoliated graphite at about 99% with initial concentration of dye 60 mg/l at pH 1.0, temperature 51 °C and reaction time of 120 min [22]. Full decolourisation obtained by Costa et al. [23] using electrochemical oxidation with initial concentration of 500 mg/l. It was found that the fastest decolourisation was obtained at pH 1.9 and 6.8 when chloride was present, but at pH 11.7 when chloride was not present. Although there are few published studies on the removal of C.I. Acid Black at low concentrations, no published report that deal with the treatment of highly concentrated solutions of this dye is available.

2. Experimental methods

2.1. Materials

C.I. Acid Black 210 dye (Commercial name: Durapel Black NT) was purchased from Town End (Leeds) plc (United Kingdom) and used without further purification. A dye mass of 20 g in powder form was dissolved in Milli-Q Plus, 18.2 MΩ cm (Millipore) water to make 5 l solution at a concentration of 4 g/l. The pH and the conductivity at 18 °C for this solution were about 9.1–9.5 and 3.2 mS/cm respectively.

In order to add polymers as flocculant aids, the optimum initial pH and aluminium (III) concentration should be determined. Jar-tests were performed to determine the optimal coagulation conditions for the removal of dye. The two parameters studied were the initial pH of the dye solution and the aluminium (III) concentration.

The laboratory reagent aluminium sulphate hexadecahydrate ($Al_2(SO_4)_3{\cdot}16H_2O$) (molecular mass of 630.39 g/mol, purity > 96%) was purchased from Fisher Scientific UK ltd. (United Kingdom). Aluminium sulphate solutions were prepared fresh everyday by dissolving appropriate amounts of powder aluminium sulphate in Milli-Q Plus (Millipore) water. Five commercial polymers ACCEPTA 2037, 2047, 2058, 2105 and 2111 were generously given by Accepta (Manchester, United Kingdom). Milli-Q Plus water was used to