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

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A R T I C L E   I N F O

A B S T R A C T

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-diallyl-dimethyl ammonium chloride), ACCEPTA 2047 (high molecular mass (MM) anionic polyacrylamide), ACCEPTA 2111 (high MM cationic polyacrylamide), ACCEPTA 2105 (Low-medium MM cationic poly-acrylamide) 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.

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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$_4$)$_3$·16H$_2$O) (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
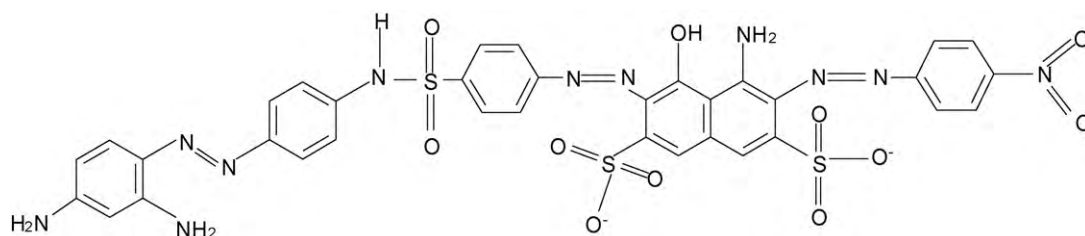
Fig. 1. The structure of C.I. Acid Black 210 dye.

prepare all polymer feedstock solutions according to supplier recommendation. The concentration of the diluted ACCEPTA 2047 polymer solutions is 0.05% while others is 0.1%. The use of Milli-Q water to prepare the solutions is very important since dissolved solids, hardness, and other impurities in water can inhibit complete dissolution of the polymer because these impurities can obstruct the polymer's charged groups from repelling each other.

The properties of the polymers used are shown in Table 2. Conventionally, the low, medium and high molecular mass consist of $<10^5$, 10^5–10^6 and $>10^6$ g/mol respectively. Charge density can be determined using colloid titration. In regard of charge density: low, medium and high charge density polymers have 10%, 25% and 50–100% (mol% of ionic group) [4]. From other experimental work the point of zero charge (pzc) for aluminium sulphate was determined to be about 4.0–5.0 [24] while anionic/cationic polyacrylamide and polyDADMAC was about 4.5–5.0 [25] and 5.73 [26] respectively. For ACCEPTA 2105 and ACCEPTA 2111, the oil emulsion was added to maintain the stability of these polymers. The range of polymer dosage tested in this study was within the optimum range that has been given by the supplier (Table 2); which is suitable for wastewater clarification [27]. To select the best polymer as flocculant aid, jar test experiments were conducted simultaneously with one beaker without addition of polymer as control. Dye removal increment due to the addition of polymer was defined as dye removal due to coagulation of aluminium sulphate with polymer minus dye removal due to coagulation of aluminium sulphate alone after a settling time fixed at 60 min. Addition of polymer might reduce the amount of inorganic coagulant [4]. To examine this, in the next experiments the concentration of aluminium sulphate varied from 0.00025 to 0.00476 M with ACCEPTA 2058 (polyDADMAC) added as flocculant aids and settling time was 120 min.

2.2. Jar tests

For the jar tests, the appropriate volume of dye solution was transferred into the round jar and pH was adjusted accordingly. The pH adjustment was made under vigorous stirring with a magnetic stir bar using solutions of 2 M HCl and 2 M NaOH. Aluminium sulphate was added to the dye solution in the jar, making the total volume of 500 ml. In every experiment, aluminium sulphate solution was less than 5% (v/v) in aqueous solution. This was done to prevent unnecessary dilution effects. A standard jar-test apparatus (Bibby-Stuart Flocculator SW6) equipped with stainless steel paddles and stirrer was used for the coagulation and flocculation tests. The aqueous solution was then rapidly mixed at a paddle speed of 250 rpm for 3 min followed by slow mixing for 20 min at 30 rpm. Polymer dosage of 4–5 ml/l of solution, as recommended by the supplier, was added during the slow mixing step. This is to avoid the breaking of flocs during their growth [28]. After allowing settling to occur (60 min or 120 min), about 25 ml of the liquid was withdrawn using a pipette from a height of about 3 cm below the liquid surface in each jar. This height comprises first 40% of the total height. Experiments were all duplicated to test their repro-

ducibility. All experiments were conducted at room temperature (19–20 °C).

2.3. Residual concentration of dye analysis

Residual concentration of dye (without filtering or centrifuging) was analysed with a UV/Vis-spectrophotometer (UVmini-1240, Shimadzu) by measuring the absorbance at the λ_{max} (460 nm) and final pH of the solution. The absorbance was measured using water Milli-Q as background and the concentration of dye was computed from calibration curves preliminary determined at different pHs. If the reading of absorbance was greater than 1.0, then necessary dilution was made. After every experiment, precision cell (10.00 mm, quartz SUPRASIL® (Hellma GmbH & Co, Germany)) was cleaned by soaking it with Methanol HPLC Grade (Fischer Scientific UK ltd., United Kingdom) overnight. Glassware was cleaned by rinsing with 0.1 M NaOH. The values of the initial and final concentrations of the dye measured as outlined above were used to calculate the removal percentage of the dye using Eq. (1).

$$\text{Dye removal} (\%) = 100 \times \frac{C_0 - C_f}{C_0} \tag{1}$$

where C_0 is the initial dye concentration and C_f is the final dye concentration.

Measurement of solution pH was done using a Jenaway 3540 pH meter. Baseline flatness and wavelength accuracy for the UV-spectrophotometer and pH calibration were carried out daily.

3. Results and discussion

3.1. Effect of initial pH and aluminium (III) concentration

In aqueous solution, Al^{3+} is strongly hydrated and found surrounded by six co-ordinated water molecules in an octahedral configuration. The high positive charge on the central metal ion causes some polarisation of the O–H bonds and there is a tendency for protons to dissociate giving one or more hydroxylated species as shown by Eq. (2).

$$Al(H_2O)_6^{3+} \leftrightarrow Al(H_2O)_5(OH)^{2+} + H^+ \tag{2}$$
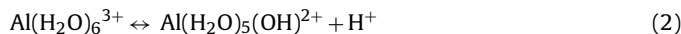
From Eq. (2), it is seen that complexes of Al ions in water act as weak acids [3].

Since each step involves the loss of a proton, increasing pH causes the equilibrium to be shifted to the right [29]. The simplest representation, for Al^{3+}, omitting the hydration shell for convenience, is represented by the following equation [29]:

$$Al^{3+} \rightarrow Al(OH)^{2+} \rightarrow Al(OH)_2^+ \rightarrow Al(OH)_3 \rightarrow Al(OH)_4^- \tag{3}$$
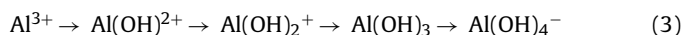
The interdependence of optimum pH, aluminium sulphate concentration and dye removal are shown in Figs. 2 and 3. Fig. 2 shows the removal of C.I. Acid Black 210 dye solution during coagulation with various dosages of aluminium sulphate at an initial pH in the acidic region and Fig. 3 shows the removal patterns at an initial pH in the alkaline region. According to Papic et al. [30], the dye

Table 2
Properties of polymers used (data given by supplier).

Product/chemical description	Charge	Solubility in water	Specific gravity	pH	Viscosity, cps	Operating temperature, °C	Tested dosage, ml of diluted polymer/litre solution
ACCEPTA 2037 (Water–Polyacrylamide (PAM)–Inorganic salt(s))	Cationic/High Molecular Mass	Complete	1.21–1.23	3.0–4.2	<700	Min: −10 Max: 40	1–20 (0.35–7)*
ACCEPTA 2047(Polyacrylamide (PAM) based)	Anionic/High Molecular Mass	Emulsifiable	1.03	7.0–8.0	300–1700	Min: >Freezing temperature	1–5 (0.2–0.9)*
ACCEPTA 2058 (polyquaternary amines (poly-diallyl-dimethyl ammonium chloride)–polyDADMAC)	Cationic/High charge density	Complete	1.02–1.06	4.0–5.0	Not stated	Min: Freezing temperature	1–10 (0.35–3.5)*
ACCEPTA 2105 (Polyacrylamide (PAM) based dispersed in hydrocarbon solvent)	Cationic/Low charge density	Partially miscible	1.03	3.0–5.0	Not stated	Avoid extreme temperature	1–4 (0.35–1.4)*
ACCEPTA 2111 (Polyacrylamide (PAM) based-Hydrocarbon solvent–fatty alcohol etoxylate–water)	Cationic/High molecular Mass/Low charge density	Partially miscible	1.03	4.0–5.0	725	No data	1–4 (0.35–1.4)*

NS = Not stated.
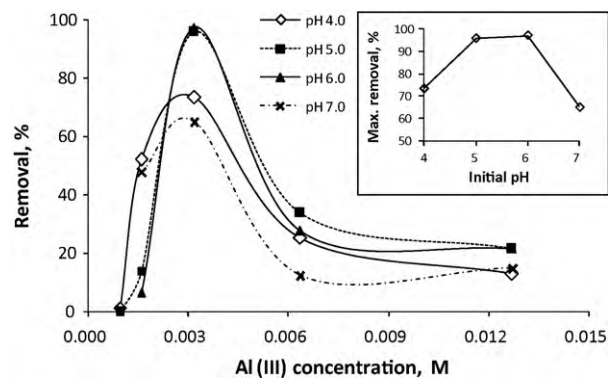* Value in bracket is in mg/l.

Fig. 2. Dye removal of Acid Black 210 dye solution during coagulation with various concentrations of aluminium (III) and initial pH of 4.0, 5.0, 6.0 and 7.0 ± 0.1 (initial concentration of C.I. Acid Black 210 dye: 4 g/l, settling time: 120 min). Small figure shows the effect of initial pH on the maximum dye removal (concentration of Al(III) = 0.0032 M).

removal depends on combination of (i) the decrease of the degree of ionisation of the auxochrome, i.e. sulphonyl, hydroxyl, etc.; with the decrease in solution pH and (ii) the solubility of alum which increases with the decrease of pH. The pattern for acidic region is the same for all pHs studied, i.e. sharp increase up to the maximum removal followed by sharp decrease as the concentration of aluminium sulphate increases.

At 0.002 M, a concentration of aluminium (III), the dye removal for initial pH 4.0, 5.0, 6.0 and 7.0 was about 54%, 21%, 15% and 48% respectively. Higher dye removal in the respect of pH 4.0 because there might be higher soluble aluminium (III) concentration compare to initial pH 5.0, 6.0 and 7.0. However, in the respect of initial pH 7.0, the high dye removal was found compared to pH 5.0 and 6.0 is due to the fact that, at this point the dye solution is more ionised; thus enhanced the coagulation. Papic et al. [30] conducted coagulation of 1 g/l reactive dyes using aluminium chloride. At pH 4, they reported that the C.I. Reactive Red 45 dye removal for 0.0017 and 0.0033 M aluminium was about 84% and 96% respectively. In similar study, at pH 4 they observed that the C.I. Reactive Green 8 dyes removal for 0.0017 and 0.0033 M aluminium (III) was 66% and 99%. In respect of this, the initial pH of this study is lower than ours finding might be due to the effect of the number of sulphonyl group in various dyes [31]. The sulphonyl group in C.I. Acid Black 210, C.I. Reactive Red 45 and C.I. Reactive Green 8 is 2, 3 and 5 respectively. The larger number of sulphonyl group also increase the decolourisation due to higher of interaction between dye molecule and Alum (III) [31]. However, at the concentration of 0.00017 M, the C.I. Reactive Green 8 is remove less dye compare to C.I. Reactive Red 45
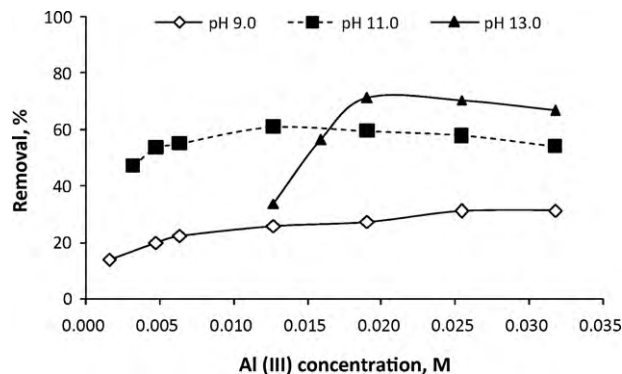

Fig. 3. Dye removal of C.I. Acid Black 210 dye solution during coagulation with various concentrations of aluminium (III) at initial pH of 9.0, 11.0 and 13.0 ± 0.1 (initial concentration of C.I. Acid Black 210 dye: 4 g/l, settling time: 120 min).

because of the molecular structure is more complex [32]. Therefore, our finding and reports from other works suggested that the optimum coagulant concentration also depends highly on the concentration of the dye as well as the type of dye.

As expected, when the concentration of aluminium (III) increases to about 0.003 M, the dye removal also increases. From Fig. 2 (inserted small figure), it can be seen that the maximum colour removal occurred at a concentration of aluminium (III) equal to about 0.003 M for all pH values. At this concentration, the maximum removal percentages were about 75%, 96%, 97% and 65% for initial pH values of 4.0, 5.0, 6.0 and 7.0 respectively. After concentration of 0.003 M, the colour removal decreases rapidly due to the restabilisation of the dye. Restabilisation occurs because at higher concentration of alum, the positive charge ions accumulated at the surface of the dye cause repulsion forces between the dyes, hence aggregation of the particles is hindered [11]. Zonoozi et al. [33] reported pH 5 as the optimum condition for coagulation of C.I. Acid Red 398 using aluminium oxide (Al_2O_3) with 60% dye removal. Using aluminium chloride ($AlCl_3$), pH 6 was reported as optimum for coagulation of reactive dyes, i.e. C.I. Reactive Black 5 and C.I. Reactive Orange 16 with 80% and 99% dye removal [34].

The coagulation of insoluble dyes at acidic pH, especially using aluminium sulphate is thought to have a complex mechanism. Gaydardzhiev et al. [16] reported that there is no good agreement between the aluminium sulphate dosage and the surface charges of the C.I. Acid Blue 113 dye colloids, although charge neutralisation has been verified as the predominant mechanism when ferric chloride was used as the coagulant. In another study, the result of coagulation of aluminium chloride and reactive dyes were in good agreement with colloid charge (measured as zeta potential value) [34]. Therefore, the proposed mechanism of dye removal in an acidic pH could include:

- Aluminium hydrolysis product binding to the anionic sites such as sulpho, amino and hydroxy groups in the dye molecule. Thus, their charge will be neutralised and then the dye solubility will be reduced. For molecules such as C.I. Acid Black 210 dye with medium molecular mass (in this case 938 g/mol), this reaction can lead to precipitation of the aluminium–dye complex [29].
- At pH values of approximately 5–6, the dye molecule is negatively charged [16] while Al hydroxides are positively charged. This condition would give strong adsorption of the dye molecule on the amorphous metal hydroxide precipitates via van der Waals interactions, hydrogen bonding, etc. [29].
- Destabilisation is brought about mainly by complex chemical reactions/chelation between the aluminium (III) and the dye molecules. Then, the precipitates will be formed out of this mechanism [3].

The pattern of the effect of concentration of aluminium sulphate on dye removal in the alkaline region is clearly different from that in the acidic region (Figs. 2 and 3). Fig. 3 shows gradual increase of dye removal with the concentration of aluminium (III) until reaching a maximum value at optimal concentration (0.025 M at pH 9, 0.012 M at pH 11 and 0.019 M at pH 13). This maximum value was sustained with further increase in aluminium (III) concentration.

It can be seen from the figure that the maximum dye removal for an initial pH of 9, 11 and 13 was about 30%, 60% and 71% respectively. Aluminium (III) concentrations of 0.025 M for pH 9, 0.013 M for pH 11 and 0.019 M for pH 13 were required to achieve these removal values. The main mechanism is due to the entrapment/enmeshment of the dye colloid into the gelatinous aluminium flocs, which are aggregated products from hydrolysis of Aluminium (III) ions, and then removed by what is known as "sweep coagulation" [16]. Mohan et al. [35] reported pH 8 as the optimum pH for removing C.I. Acid Red 88 using about 0.00238 M aluminium
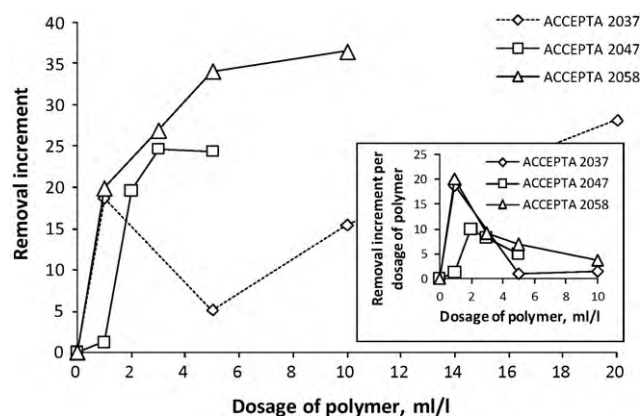

Fig. 4. Dye removal increment of C.I. Acid Black 210 dye solution during coagulation with aluminium sulphate with various types of commercial synthetic polymers: ACCEPTA 2037, ACCEPTA 2047 and ACCEPTA 2058 (Initial concentration of C.I. Acid Black 210 dye: 4 g/l, initial pH: 5.0 ± 0.1; aluminium (III) concentration: 0.0032 M; settling time: 60 min). Small figure shows the dye removal increment per polymer dosage.

sulphate. They found that about 97% of the colour removed probably because of lower concentration of dye, i.e. 50 mg/l. Since pH 5 gave the highest dye removal at an Al(III) concentration of 0.0032 M, the following experiments were carried out at these conditions.

3.2. Selection of polymer as flocculant aid

The average dye removal due to aluminium sulphate alone with settling time of 60 min was about 40%. The concentrations of polymers in this study were selected as recommended by the supplier (Table 2). From Figs. 4 and 5 it can be seen that the dye removal increments were 5–28%, 1–25%, 20–37%, 0–14%, and 5–25% for ACCEPTA 2037, 2047, 2058, 2105 and 2111 respectively. Maximum residual dye in the supernatant were about 1280, 1400, 920, 1840 and 1400 mg/l for ACCEPTA 2037, 2047, 2058, 2105 and 2111 respectively. The figures also show that, generally, as dosage of polymer increased the removal increment also increased. However for ACCEPTA 2037 and ACCEPTA 2111, a decrease in removal increment at dosages 5 and 2 ml/l respectively was observed. This phenomenon might due to the formation of larger aggregates which are too difficult to settle at the stated polymer doses. However, when the polymer doses increase, the density of the aggregates
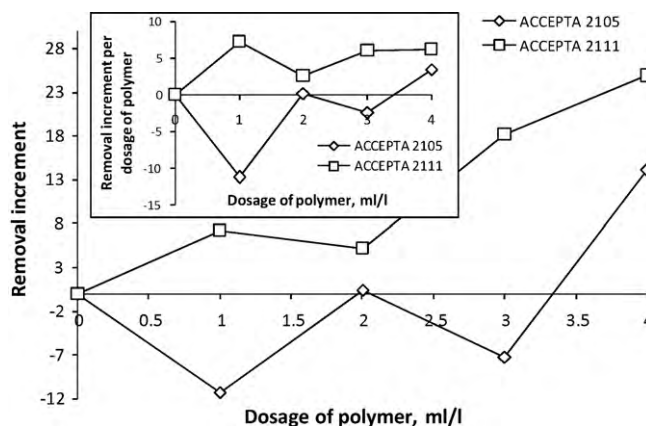

Fig. 5. Dye removal increment of C.I. Acid Black 210 dye solution during coagulation with aluminium sulphate with various types of commercial synthetic polymers: ACCEPTA 2111 and ACCEPTA 2105 (initial concentration of C.I. Acid Black 210 dye: 4 g/l, initial pH: 5.0 ± 0.1; aluminium (III) concentration: 0.0032 M; settling time: 60 min). Small figure shows the dye removal increment per polymer dosage.

would also increase, which explains the better removals obtained for polymer doses higher than those stated above. Wong et al. [36] also reported a reduction in turbidity at a dose of 2 mg/l using cationic polyacrylamide (Organapol 5470) and the turbidity removal enhanced when the polymer dose was increased beyond 2 mg/l.

The highest dye removal was achieved by ACCEPTA 2058 possibly due to its highest charge density (a polyDADMAC) that might be more resistant to shear degradation [3]. During flocculation, coagulated dye particles might transfer to polymer chain via electrostatic interactions [5] and then were adsorbed by the polymer [4]. Chang et al. [37] stated that the main mechanism for adsorption via polyDADMAC is charge neutralisation. Chang et al. [37] also found that coagulation with polyDADMAC was found to be very effective for removing turbidity for tannic acid (molecular mass of 1700 g/mol); compared to higher molecular mass cationic and non ionic polyacrylamide. In another study, Kanokkantapong et al. [38] studied removal of trihalomethanes (THMs) by using alum with three types of cationic polymer; cationic polyacrylamide (CPAM), polydiallyl dimethyl ammonium chloride (polyDADMAC), and epichlorohydrin dimethyl amine (EpiDMA). The highest efficiency in the removal of THM formation potential could be ordered from high to low as: alum with polyDADMAC (39%), alum with EpiDMA (32%), alum with CPAM (21%), and alum alone (18%).

The removal achieved by the composite inorganic salt(s)-high molecular mass PAM (ACCEPTA 2037), high molecular mass anionic PAM (ACCEPTA 2047) and high molecular mass cationic PAM (ACCEPTA 2111) showed maximum dye removal increments of 28%, 25% and 25%. These removal values of the PAMs are lower than polyDADMAC because these polymers are pH sensitive and they function best at pH >6.0 [39]. In this study, the pH of the dye solution turns to be about 4.0 due to pH depression after addition of aluminium sulphate (Eq. (1)). Gao et al. [10] reported that 45 mg/l composite polyferric-polyDADMAC removed 70% of a reactive blue dye, which is in agreement with results obtained in this study.

The adsorption of coagulated dye molecules onto the PAM might due to the dye hydroxyl (–OH) group which forms hydrogen bond with amide groups of PAM (R–CO–NH_2) [4]. According to Bolto and Gregory [4], the high molecular mass polymers promote bridging flocculation. Solberg and Wågberg [6] reported that flocculation of cationic PAM and silica nanoparticles is due to polymer bridging as well.

As expected, ACCEPTA 2105 which is low-medium molecular mass PAM only achieved the lowest increment of dye removal (Fig. 5). No removal increment found when the dosage is less than 3 ml/l. At the dosage of 4 ml/l, the ACCEPTA 2111 and ACCEPTA 2105 shows 25% and 15% of dye removal increment respectively (Fig. 5). The difference of dye removal between high and low-medium molecular mass shows that the mechanism of dye removal using PAM as flocculant aids is due to polymer bridging [4]. It is reported that higher molecular mass polymers were more effective for removing natural organic matter (NOM) from water than lower-medium molecular mass polymers [4].

Thus for colour removal increment, the order of best polymer is as follows:

ACCEPTA 2058 (36.6% at 10 ml/l) > ACCEPTA 2037 (28.2% at 20 ml/l) > ACCEPTA 2111 (24.9% at 4 ml/l) ≈ ACCEPTA 2047 (24.7% at 3 ml/l) > ACCEPTA 2105 (14.0% at 4 ml/l).

Fig. 4 (small figure inserted) shows that the maximum dye removal per dosage of polymer was obtained at 1 ml/l for ACCEPTA 2058 and ACCEPTA 2037, which are cationic polymers. At this dosage the maximum dye removal per dosage of polymer was about 20% per ml/l. However, for the anionic polymer ACCEPTA 2047, the maximum dye removal per dosage of polymer was only 10% per ml/l obtained at a dose of 2 ml/l which is a double of that of the cationic polymer. The dye removal per dosage of polymer then
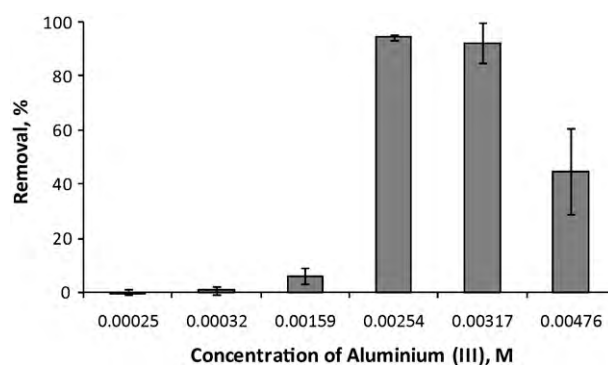

Fig. 6. Dye removal of C.I. Acid Black 210 dye solution during coagulation with aluminium sulphate with ACCEPTA 2058 (10 ml/l) (initial concentration of C.I. Acid Black 210 dye: 4 g/l, initial pH: 5 ± 0.1; settling time: 120 min).

decreases as the dosage of polymer increases for all these polymers. On the other hand, for cationic polymers with low charge density (ACCEPTA 2105 and ACCEPTA 2111), the maximum dye removal per dosage of polymer seem to be obtained at higher dosages of the polymer. This shows that both the type of charge and its density influence very much the removal of the dye that is due to flocs enlargement by the presence of the polymer after the dye was destabilised by aluminium (III).

3.3. Effect of coagulant dose in the presence of polymer

As the concentration of aluminium (III) decreased, the dye removal also decreased significantly (Fig. 6). This result shows that the addition of aluminium sulphate as primary coagulant is vital. As primary coagulant, aluminium sulphate alters the structure of the dye and consequently increases the affinity between polymer segments and dye particles [4]. In a study by Petzorld and Schwarz [40] who did not use an inorganic coagulant, it was found that the coagulation of the dyes they studied with polymers alone as coagulants was also difficult. Beside that, from Fig. 6 it was also found that to achieve > 90% dye removal with ACCEPTA 2058, the optimum concentration of aluminium (III) is about 0.003 M, which is similar to the concentration obtained when the settling time was 60 min. Concentrations higher than this optimum value reduced the final dye removal even though the settling time was doubled.

4. Conclusions

From this study, the addition of a suitable polymer helped to increase the colour removal of C.I. Acid Black 210 dye as compared to using Al(III) alone. This will consequently causes reduction of the size of a sedimentation tank. The optimum conditions for coagulation were: aluminium (III) concentration of about 0.003 M and initial pH of 5–6. The addition of ACCEPTA 2058 (polyDADMAC) showed better colour removal increment up to 37% (final dye concentration about 920 mg/l) as compared to the other polymers. Experiments carried out using a sedimentation time of 120 min showed that the addition of polymers did not significantly improve the final removals of the dye as compared to aluminium sulphate alone. Although the overall maximum removal of the dye was almost 90% (obtained at 120 min settling time), the remaining 10% (400 mg/l) of the dye is still significant. Indeed, after treatment, a visible colour remained in the solution, which requires further treatment. It is thus suggested to use for example a combined process involving coagulation/flocculation and a membrane filtration or ozonation unit so a complete removal can be achieved.

Acknowledgements

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