Decolorization of dyeing wastewater and characterization of flocs during coagulation by a new composite coagulant

Cuizhen Sun, Yang Zhao, Zhibin Zhang, Yanhao Zhang and Xiaorui Zhang

ABSTRACT

A composite coagulant, polymeric aluminum ferric chloride-poly-epichlorohydrin-ethylenediamine (PAFC-EPI-ETA), was synthesized and then used for the treatment of synthetic reactive brilliant red (RBR) dyeing wastewater. Effects of (Fe + Al) to EPI-ETA mass ratio (P) on the color removal and zeta potential were investigated under different coagulant dosages and initial pHs. Experimental results indicate that the removal of reactive dye and the charge neutralization ability of composite coagulant were improved by increasing the content of organic EPI-ETA. PAFC-EPI-ETA with P = 1 achieved the best color removal percentage and strongest charge neutralization ability. Decolorization efficiency using PAFC-EPI-ETA was quite effecient with pH range of 6.0–7.5 for RBR dye removal. Characteristics of the formed floc were investigated with the dosage of PAFC-EPI-ETA under different P values. The low (Fe + Al) to EPI-ETA mass ratio contributed to the formation of flocs with high growth rate, large size and large size variation.

Key words | coagulation, composite coagulant, decolorization performance, dying wastewater, floc characterization

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INTRODUCTION

Dyeing wastewater from the textile printing and dyeing industry can cause aesthetical problems and impede light penetration, which greatly upsets biological processes in surface water (Rajkumar & Kim 2006; Santhy & Selvapathy 2006; Gul & Silah 2014). In addition, due to its high color and large amount of chemical oxygen demand, dyeing wastewater is considered as a considerable source of environmental pollution (Wang *et al.* 2007; Hassan *et al.* 2009; Amaral *et al.* 2014). More importantly, the widely applied synthetic dye compounds usually have poor biodegradability because of their complex structure (El-Desoky *et al.* 2010; Saratale *et al.* 2010; Ito 2013). For these reasons, decolorization technologies for dyeing wastewater have been receiving great attention for industrial application.

Owing to its relatively simple operation, low cost and high removal efficiency, coagulation/flocculation has been widely used as the pretreatment process to remove dye compounds from dyeing wastewater (Shi *et al.* 2007; Xu *et al.* 2010b). During coagulation/flocculation, coagulants play an important role in the decolorization of dyeing wastewater. In recent years, various coagulants, including inorganic, organic and combined inorganic–organic coagulants, have been applied in color removal. Inorganic coagulants, such as Al(III)- and Fe(III)-based coagulants, have some disadvantages. For example, their color removal efficiency is strongly pH- and dosage-dependent and a high amount of sludge will be produced during treatment (Lan *et al.* 2009; Zhao *et al.* 2014). Compared with inorganic polymers, organic polymeric coagulants, such as polydimethyl-diallyl-ammonium chloride, epichlorohydrin-dimethylamine and poly-epichlorohydrin-ethylenediamine (EPI-ETA), have inherent advantages of being less pH-dependent, having small amount of sludge production and requiring less dosage (Wang *et al.* 2009, 2012), although their high cost has limited their application in wastewater treatment. To achieve a high decolorization efficiency, decrease the cost and improve the floc characteristics in terms of settleability and filterability, inorganic–organic composite flocculants, produced by combining inorganic and organic coagulants, have been widely investigated and applied for dyeing wastewater treatment in recent years (Moussas & Zouboulis 2009; Wei *et al.* 2009, 2010; Gao *et al.* 2011; Ng *et al.* 2012).

During wastewater treatment, the two principal inorganic coagulants applied are Al(III)- and Fe(III)-based

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coagulants. Polymeric aluminum ferric chloride (PAFC) not only has the advantages of poly-ferric, but also has some advantages of poly-aluminum. PAFC has strong adsorption bridging ability, large particle size and a wide pH range (Lan *et al.* 2009). However, there are few studies on the application of PAFC-EPI-ETA in water or wastewater treatments so far. Therefore, research on a new inorganic–organic composite, PAFC-EPI-ETA consisting of inorganic PAFC and organic EPI-ETA, should be carried out so as to advance its practical application.

In this research, a new inorganic–organic composite coagulant, produced from both inorganic PAFC and organic EPI-ETA, was used for the treatment of synthetic dyeing wastewater. During color removal, the flocculation dynamics plays a very important role in investigation of flocculating mechanism and expansion of application range (Vandamme *et al.* 2012). Therefore, the objectives of this study were to: (1) examine the effects of (Fe + Al) to EPI-ETA mass ratio (P value = (Fe + Al)/EPI-ETA weight ratio) and initial pH on the color removal in treating synthetic dyeing wastewater; (2) determine the destabilization ability of coagulants through the examination of the produced flocs' zeta potential and coagulation mechanisms; and (3) investigate the effect of organic EPI-ETA proportion and pH on the flocculation dynamics including floc size, floc growth rate and degree of floc distinguish.

METHODS

Synthesis of coagulants

EPI-ETA was prepared by the reaction of epichlorohydrin and ethylenediamine with trimethylamine (33%, chemically pure) as a modifying agent. The molar ratio of epichlorohydrin to ethylenediamine was 1:2. The reaction was promoted for 3 h with gradually increasing temperature to 95 °C. Finally, the product $P_{(EPI\text{-}ETA)}$ with the intrinsic viscosity value of 350 mPa.s was used in this study.

The inorganic regent (PFAC) used was prepared by dissolving analytical grade $FeCl_3{\cdot}6H_2O$ and $AlCl_3{\cdot}6H_2O$ at 25 ± 1°C. During synthesis, Na_2CO_3 powder was slowly added to the above solution to the predetermined basicity (B = 1.5). Finally, Na_2HPO_4 (analytical reagent) was incorporated into the PFAC solution as a stabilizer ($[Na_2HPO_4]/([Fe] + [Al]) = 0.08$).

The PAFC-EPI-ETA coagulant was prepared through a composite method. During synthesis, a certain amount of $P_{(EPI\text{-}ETA)}$ was introduced into the PAFC solution under magnetic stirring for 2 h to prepare PAFC-EPI-ETA with mass ratios (P) of (Fe + Al) to $P_{(EPI\text{-}ETA)}$ of 1:1, 2:1 and 4:1. The coagulant dosage of PAFC and PAFC-EPI-ETA was calculated by the content of Fe + Al and Fe + Al + EPI-ETA, respectively.

Test water

The tested synthetic dyeing wastewater was prepared by adding 0.5 g of reactive brilliant red (RBR) into 10 L of tap water. The pH was adjusted to the predetermined value by 0.1 mol/L NaOH or HCl. The zeta potential of the synthetic dyeing wastewater was 30.32–38.14 mV.

Experimental set-up

At room temperature, coagulation experiments were carried out. A measured amount of coagulants was added into the synthetic wastewater of 500 mL. Then, the water was mixed rapidly at 120 rpm for 2 min, followed by slow stirring at 40 rpm for 15 min, and finally settled for 30 min. After flocculation, the samples were collected from 20 mm below the surface for measurements. The absorbance values of supernatant and zeta potential values of flocs were measured by a spectrophotometer (UV-754, Shanghai Analytical Instrument Factory, China) and a micro-electrophoresis analyzer (JS94H, Shanghai Zhongchen Digital Technology Equipment Co., Ltd, China), respectively. The color removal efficiencies in the wastewater treatment by flocculation–sedimentation were determined by comparing the absorbance values of supernatant to the absorbance value of raw wastewater at the maximum absorbance wavelength of RBR dye. Color removal efficiency was calculated by comparing the absorbance value for the wastewater sample after treatment to the absorbance value for the original simulated dye wastewater.

On-line monitoring of floc size

The floc size was monitored with a photometric dispersion analyzer (PDA, Mastersizer 2000, Malvern, UK), in which optical signals were transformed to electrical signals, during the coagulation process apart from the setting phase. The suspension was drawn and circulated by a peristaltic pump with a 5 mm internal diameter tube at a flow rate of 1.5 L/h. Size measurements were taken every 0.5 min during the process and were logged on a PC.

The floc aggregation process includes three phases: lag phase, growth phase and steady-state phase (Wang *et al.*

2011). The characteristics of flocs formed were evaluated by three typical parameters, named as the slope (growth rate) of growth region, the time-weighted average ratio (ratio) of growth region and a time-weighted relative standard deviation (TWV) of the steady-state ratio value, calculated from the data collected by PDA. The calculation equations are listed as following (Xu *et al.* 2010a):

$$\text{Growth rate} = \frac{\Delta \text{ratio}}{\Delta \text{time}}$$

$$\text{Ratio} = \frac{\sum_{i=1}^{n} (ratio_i, time_i)}{\sum_{i=1}^{n} time_i}$$

$$\text{TWV} = \frac{\sqrt{\dfrac{\sum_{i=1}^{n}\left[(\text{ratio}_i - \text{ratio})^2 \cdot \text{time}_i\right]}{\sum_{i=1}^{n} \text{time}_i}}}{\text{Ratio}} \times 100\%$$

where ratio_i and time_i are the typical ratio value at a certain flocculation time and the corresponding flocculation time, respectively, Δratio is the floc size variation in the growth region, and Δtime is the growing time in the growth region.

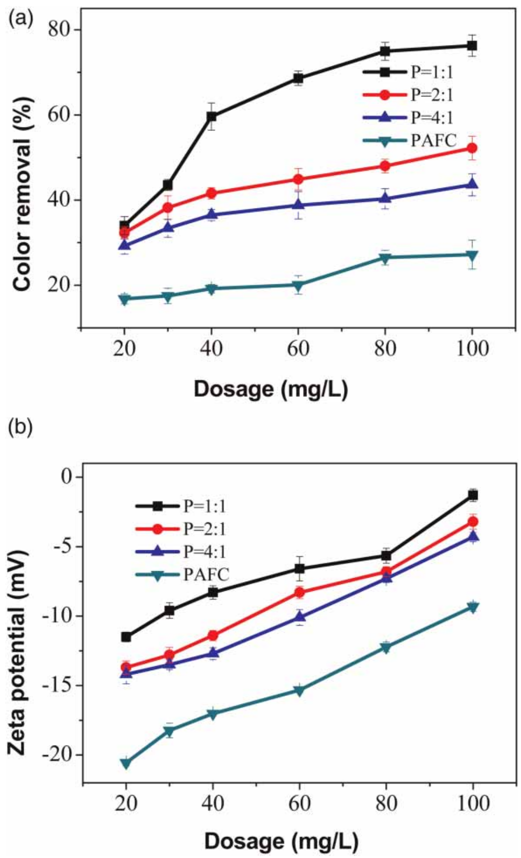

Figure 1 | Color removal efficiency (a) and zeta potentials (b) of flocs by PAFC-EPI-ETA with different P values.

RESULTS AND DISCUSSION

Decolorization performance of composite coagulants with different (Fe + Al) to EPI-ETA mass ratios

The effect of inorganic component proportion on RBR removal and zeta potential of formed flocs was assessed by using PAFC and PAFC-EPI-ETA with different mass ratios (P = 1:1, 2:1 and 4:1).

As shown in Figure 1(a), decolorization efficiency of both coagulants significantly increased as flocculant dosage increased from 20 to 100 mg/L. In addition, the color removal efficiency of PAFC-EPI-ETA increased sharply as P value decreased from 4:1 to 1:1 at the same coagulant dosage. For RBR treatment, the color removal efficiencies of PAFC were all below 25%. The color removal efficiency of PAFC-EPI-ETA could reach about 80%, much higher than that of PAFC.

The color removal efficiency mainly depends on not only the characteristic of the coagulant but also the solubility and chemical structures of the dyes. Reactive dyes have $-SO_3^-$, $-COO^-$ and $-OH^-$ groups, which increase the solubility of the dyes (Uddin *et al.* 2003). Owing to their high solubility, reactive dyes cannot be easily removed by PAFC hydrolysate which led to the lower decolorization efficiency.

Zeta potential is a controlling parameter for the charge neutralization of coagulant and it can be generally applied to interpret the variation trend of coagulation efficiency (Wang *et al.* 2007). From Figure 1(b), it can be concluded that the zeta potentials of PAFC and PAFC-EPI-ETA presented an increasing tendency as the dosage increased and were less than zero within the whole coagulant dosages studied. Compared with PAFC, PAFC-EPI-ETA has higher zeta potential, which led to much stronger charge neutralization and higher color removal efficiency. In addition, flocs with high zeta potential were formed at a low P value within all examined coagulant dosages. The results can be explained by the following reasons. The molecules of compounds in the dyeing wastewater had a negative charge on their surfaces because of the sulfonic acid groups (Uddin *et al.* 2003). Thus, the higher the positive charge on the surface of coagulant molecules, the better the color removal efficiency. Therefore, PAFC-EPI-ETA at P = 1:1 can provide more charge adsorption sites for removing reactive red dye compared with those at P = 2:1 and 4:1.

Pefferkorn reported that if charge neutralization is the only mechanism in the coagulation process, a good linear relationship between zeta potential and coagulant dosage should be obtained and optimal removal efficiency is achieved at zeta potential close to zero (Pefferkorn 2006). From Figure 1(b), the zeta potential of PAFC and PAFC-EPI-ETA showed excellent correlation with dosage and the correlation coefficients were above 0.96, suggesting charge neutralization was one of the dominant mechanisms. For PAFC, zeta potentials of flocs were much lower than zero even at the dosage of 100 mg/L, which indicated that adsorption/bridging mechanisms occurred. For PAFC-EPI-ETA, the zeta potentials were close to the isoelectric point at the dosage of 100 mg/L, whereas decolorization efficiency was not optimal, indicating charge neutralization and adsorption/bridging mechanism played important roles in the reaction.

Decolorization performance of composite coagulants under different pHs

During coagulation, pH plays an important role in determining coagulation efficiency (Yang et al. 2010). During wastewater treatment with composite coagulants, an optimum pH range should be obtained to achieve maximum flocculation efficiency (Xu et al. 2010a). During reactive red wastewater treatment, the color removal efficiency and zeta potential of flocs were examined at various pHs (3, 4, 5, 6.5, 7.5, 9 and 10.5) and the results are shown in Figure 2.

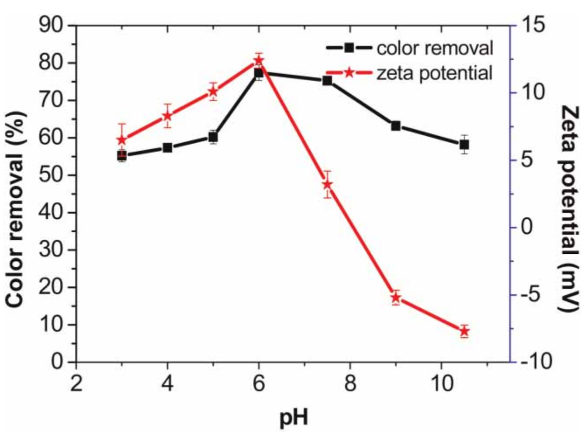

Figure 2 | Color removal efficiency and zeta potentials of flocs by PAFC-EPI-ETA with P = 1:1 under different pHs.

The coagulant dosage of PAFC-EPI-ETA was 100 mg (Fe + Al + EPI-ETA)/L. PAFC-EPI-ETA with P = 1:1 was selected to treat the synthetic wastewater.

As shown in Figure 2, the decolorization efficiency increased from 55 to 75% as the initial pH increased from 3 to 6, whereas when further increasing the initial pH from 6 to 10.5, the color removal efficiency decreased. The zeta potential of the formed flocs possessed a similar trend to that of the color removal efficiency. Under acidic and neutral conditions, zeta potential was higher than that under the alkaline condition. The dyeing compounds usually have negative charges on their surfaces (Gao et al. 2011). Therefore, the reactive red dyes could be effectively removed by PAFC-EPI-ETA due to their high positive charges under weakly acidic and neutral pHs. The charge neutralization mechanism is also one main driving force for reactive red removal. Under strongly acidic conditions, the color can be effectively removed by the charge neutralization of Fe(III) and Al(III) hydroxide with high positive potential. As the solution pH increased, the hydrolysis of iron salts was promoted, and the positive charge on the surface of Fe(III) and Al(III) hydroxide and the charge neutralization declined. When pH increased to weakly acid or neutral, the dye was removed through both charge neutralization and the adsorption of Fe(III) and Al(III) hydroxide. As pH increased to alkaline condition, the formation of negatively charged Fe(III) and Al(III) hydroxide improved the electrostatic repulsion between flocculants and dye compound molecules. The results indicated that pH of the dyeing wastewater should be properly controlled so as to achieve a higher removal efficiency.

Floc characterization of the composite coagulants

The influence of (Fe + Al) to EPI-ETA mass ratio (P) on floc characteristics of PAFC-EPI-ETA was examined at dosage of 20–100 mg/L. The changes of ratio, growth rate and TWV values of flocs with the dosages and P values are shown in Figure 3.

Regardless of P value of PAFC-EPI-ETA, both ratio and growth rate increased when the dosage increased from 20 to 100 mg/L, which implied that less time was taken for coagulants to aggregate and form larger flocs, and thus better color removal efficiency was obtained with the increasing dosage. When PAFC-EPI-ETA with P = 1:1 was used, TWV decreased within the dosage range. For PAFC-EPI-ETA with P = 2:1 and P = 4:1, TWV increased within the dosage range 20–60 mg/L, but decreased when the dosage was higher than 60 mg/L.

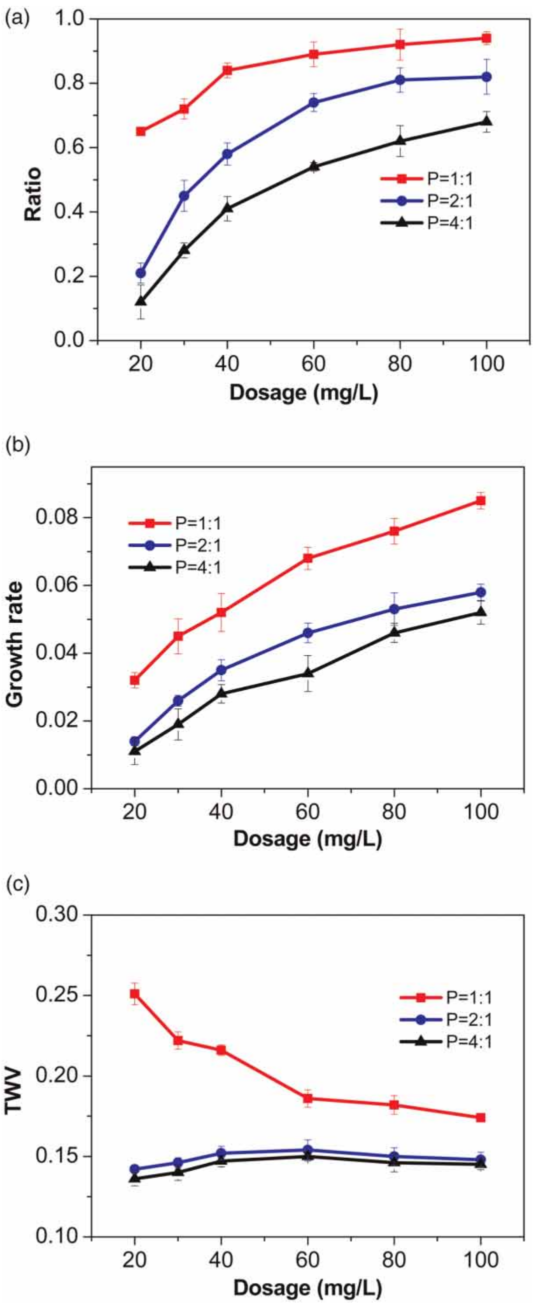

Figure 3 | Floc characteristics ((a) ratio; (b) growth rate; and (c) TWV) using PAFC-EPI-ETA with different P values.

From Figure 3, it was found that ratio, growth rate and TWV increased with decreasing P values at the same coagulant dosage, which was in good agreement with the changes in color removal. The results signified that PAFC-EPI-ETA with a low PAFC content (a high EPI-ETA content) achieved a high ratio and fast growth rate of flocs at the same coagulant dosage during reactive dye removal. Higher ratio implies larger aggregate size and better separation efficiency of subsequent solid–liquid separation (Gao *et al.* 2011). Faster growth rate indicates that less time is taken for coagulants to aggregate, which may improve coagulation performance. When EPI-ETA content of the composite coagulant increases, the particles and colloids may have a greater amount of open polymer loops for bridging adjacent particles, resulting in promoting the formation of large and easily settleable flocs through the bridging mechanism. Moreover, PAFC-EPI-ETA with higher EPI-ETA content has a high positive charge and strong charge neutralization potential, and can effectively neutralize the negative charge on the dye molecular surface. This could lead to the enhancement of particle collision efficiency and promote the formation of flocs with large size and high growth rate.

However, a high TWV suggests that a wide distribution of floc size existed. This may reduce the sedimentation performance. As Figure 3 demonstrates, TWV was in the following order: $P = 1:1 > P = 2:1 > P = 4:1$. Considering the effect of both floc growth rate and TWV, the color removal efficiency was higher by PAFC-EPI-ETA with a high EPI-ETA content in this study. In addition, TWV can also be used to interpret the coagulation mechanism. The flocs formed under the sweeping/bridging mechanism have open structure with a wider range of floc size (Hopkins & Ducoste 2003). For the removal of dye by PAFC-EPI-ETA, insoluble flocs were formed when charge neutralization occurred. Then, the produced insoluble particles were adsorbed onto the available sites of polymer chains by bridging/sweeping. Consequently, under different mechanisms, the flocs have open structure with a range of floc size.

CONCLUSION

Various PAFC-EPI-ETA composite coagulants with different (Fe + Al) to EPI-ETA mass ratios and different pHs were comparatively investigated in terms of coagulation performance and floc characteristics for the dyeing wastewater treatment. The main conclusions are summarized as follows:

1. The organic EPI-ETA component in PAFC-EPI-ETA significantly improved the decolorization efficiencies, and composite flocculant with higher P was more effective in removing dye molecules.
2. pH would affect the color removal efficiency by changing the molecular structures of coagulants' hydrolysis product. Neutral or weakly acidic wastewater condition ($pH = 6.0$–7.0) was favorable to improve the decolorization efficiency for PAFC-EPI-ETA in the treatment of dye wastewater.

3. Flocs with relatively larger floc size, faster growth rate and wider size distribution were obtained for PAFC-EPI-ETA with high (Fe + Al)/EPI-ETA mass ratios.

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