Effect of viscosity, basicity and organic content of composite flocculant on the decolorization performance and mechanism for reactive dyeing wastewater

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Abstract

A coagulation/flocculation process using the composite flocculant polyaluminum chloride-epichlorohydrin dimethylamine (PAC-EPI-DMA) was employed for the treatment of an anionic azo dye (Reactive Brilliant Red K-2BP dye). The effect of viscosity (η), basicity (B = [OH]/[Al]) and organic content (W_P) on the flocculation performance as well as the mechanism of PAC-EPI-DMA flocculant were investigated. The η was the key factor affecting the dye removal efficiency of PAC-EPI-DMA. PAC-EPI-DMA with an intermediate η (2400 mPa·sec) gave higher decolorization efficiency by adsorption bridging and charge neutralization due to the co-effect of PAC and EPI-DMA polymers. The W_P of the composite flocculant was a minor important factor for the flocculation. The adsorption bridging of PAC-EPI-DMA with η of 300 or 4300 mPa·sec played an important role with the increase of W_P, whereas the charge neutralization of them was weaker with the increase of W_P. There was interaction between W_P and B on the removal of reactive dye. The composite flocculant with intermediate viscosity and organic content was effective for the treatment of reactive dyeing wastewater, which could achieve high reactive dye removal efficiency with low organic dosage.

Key words: composite flocculant; reactive dye removal; flocculation mechanism; decolorization efficiency

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Introduction

The water contamination resulted from the discharge of textile wastewater containing reactive azo dye has become an issue of major concern. This wastewater generally exhibits bad characteristics for the environment, such as strong color, high toxicity and poor biodegradability. A number of treatment techniques has been applied in treating textile wastewater, including: (a) coagulation/flocculation (Szygula et al., 2009; Wei et al., 2009; Fang et al., 2010); (b) adsorption on activated carbon or other adsorbents (Nigam et al., 2000; Kavitha and Namasivayam, 2008; Li et al., 2010); (c) biodegradation (Chang et al., 2001; Kurosumi et al., 2008); (d) membrane filtration (Marcucci et al., 2002; Purkait et al., 2004; Criscuoli et al., 2008); (e) oxidation (Kurbus et al., 2003; Xu et al., 2005; Yasar et al., 2007); (f) photocatalysis degradation (Tang and Chen, 2004; Harrelkas et al., 2008). Among these processes, coagulation/flocculation is one of the most popular techniques for the treatment of textile wastewater.

The decolorization of textile wastewater mainly depends on the type of dye included and the structure of the flocculant used. As reported by Georgiou et al. (2003)

and Kim et al. (2004), inorganic coagulants such as ferric chloride, lime and ferrous sulfate, were not effective for the treatment of reactive dye solution. Recently, the application of cationic polymeric flocculants for the removal of reactive dye is getting more concern. High decolorization efficiency for the reactive dye can be achieved by cationic polymeric flocculant at a certain dosage, such as polyamine flocculant (Yue et al., 2008), P (AM-DMC) flocculant (Shen et al., 2006) and polydiallyldimethylammoniumchloride flocculant (Kang, 2007). Considering the relatively high preparation cost of polymeric flocculant, research on novel flocculant has been investigated in recent years. The combination of inorganic coagulant and organic flocculant was shown to be effective for the removal of reactive dye (Gao et al., 2007).

In this study, composite flocculant polyaluminum chloride-epichlorohydrin dimethylamine (PAC-EPI-DMA) was used to obtain high dye removal efficiency with low dosage of organic flocculant. The objective of this work was to investigate the flocculation performance and the mechanism of PAC-EPI-DMA in treating reactive dyeing wastewater. The effect of viscosity (η), basicity (B= [OH]/[Al]) and organic content (W_P) on the flocculation performance and the mechanism of PAC-EPI-DMA with

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different characteristics were also investigated.

1 Materials and methods

1.1 Synthesis of composite flocculant

According to the method described in our previous work (Wang et al., 2009), three EPI-DMA polymers with different η values (300, 2400 and 4300 mPa·sec) were synthesized. Then, the inorganic component PAC with different B values (0.5, 1.0, 1.5) was prepared by mixing AlCl$_3$·6H$_2$O (reagent grade) ($C_{Al_{total}}$ = 2.0 mol/L) with different amounts of Na$_2$CO$_3$ (reagent grade) powder in distilled water. Finally, the composite flocculant PAC-EPI-DMA with different W_P (5%, 10% and 20%) was prepared by mixing these two prepared polymers in distilled water.

The concentration of Al$_{total}$ into the composite flocculant was 10 g/L. During the flocculation process, the dosage of the composite flocculant was calculated as the concentration of Al$_{total}$ (mg/L).

Zeta potential of EPI-DMA and PAC-EPI-DMA was measured with a Zetasizer 3000HSa (Malvern Instruments, UK).

1.2 Test water

The synthetic dyeing solution was prepared by dissolving 0.1 g of Reactive Brilliant Red K-2BP (RBR, Jinan No. 2 Textile Dyeing Mill, China) in 1 L deionized water. The pH of raw test water was 8.45, which was close to the strongly alkaline characteristics of real textile effluents. The maximum absorbance of original RBR dye solution was 2.43 at λ_{max} (538 nm).

1.3 Flocculation experiments

To investigate the effects of η, B and W_P on the flocculation performance of composite flocculants, orthogonal array of L$_9$ (3^4) type was used (Table 1). The orthogonal test included nine sets of flocculation experiments. Flocculation experiment was carried out in 100 mg/L of synthetic Reactive Red dyeing solution. A jar test was composed of a rapid mixing for 3 min at 120 r/min, a slow mixing for 12 min at 40 r/min and a settling process for 20 min.

The absorbance of supernatant was measured with a spectrophotometer (UV-754, Shanghai Analytical Instrument Factory, China) at λ_{max} and zeta potential of flocs was determined using micro-electrophoresis analyzer (JS94H, Shanghai Zhongchen Digital Technology Equipment Co., Ltd., China).

Table 1   Factors and levels of orthogonal experiments

Factor	η (mPa·sec)	B	W_P (%)
Level 1	300	0.5	5
Level 2	2400	1.0	10
Level 3	4300	1.5	20

η: viscosity; B: basicity of PAC; W_P: organic content.

2 Results and discussion

2.1 Effects of η, B and W_P on the flocculation performance of PAC-EPI-DMA

The analysis of orthogonal experimental data is shown in Table 2. In removing dye from wastewater, the highest dye removal efficiency (R_{max}) and the corresponding flocculant dosage ($D_{optimum}$) are the main characteristics to determine the flocculation performance of flocculants. The η value of the organic polymer EPI-DMA with the highest constant range (C_r) 9.5% for R_{max} and 7.3 for $D_{optimum}$ was the most important factor affecting the PAC-EPI-DMA flocculation performance for RBR dye. The B value of PAC was a minor important factor for R_{max} because of a higher constant C_r, 4.1%. The changes of W_P of organic component lead to the lowest constant C_r of 2.8% among the three factors, which meant W_P was the least important factor for R_{max} in treating RBR dyeing wastewater. However, the constant C_r of these three factors for $D_{optimum}$ was $\eta > W_P > B$. This result indicated that W_P had more significant influence on the dye removal than B if considering $D_{optimum}$. To determine the flocculation performance of PAC-EPI-DMA for RBR dye, the η of EPI-DMA was the key factor. The effect of the other two factors (B and W_P) on the flocculation performance of the composite flocculant also needs to be investigated because of their high relative C_r for R_{max} and $D_{optimum}$.

To obtain the highest dye removal efficiency, the optimum levels were η = 2400 mPa·sec, B = 0.5 and W_P = 10% for the composite flocculant. The composite flocculant with η = 2400 mPa·sec, B = 1.0 and W_P = 5% lead to the lowest $D_{optimum}$, and consequently resulted in the lowest cost for the removal of RBR dye.

2.2 Zeta potential of PAC-EPI-DMA

The charge neutralization potential of flocculants was investigated by measuring the zeta potential of PAC-EPI-DMA flocculants. The results presented in Table 3 showed a clearly relationship between zeta potential and W_P of PAC-EPI-DMA. The zeta potential of the composite flocculants with η = 300 mPa·sec increased with increasing W_P, and a same trend was observed for the composite flocculants with η of 2400 and 4300 mPa·sec. The results indicated that the zeta potential of the composite flocculant was improved by increasing the organic content into the composite flocculant. This is due to the high positive electrical charge of the organic polymer EPI-DMA. At a same W_P, zeta potential of these three series of composite flocculants followed an increasing order: PAC-EPI-DMA with η = 4300 mPa·sec < PAC-EPI-DMA with η = 300 mPa·sec < PAC-EPI-DMA with η = 2400 mPa·sec. This result can be explained by the order of the zeta potential of EPI-DMA used, EPI-DMA with η = 4300 mPa·sec (7.5 mV) < EPI-DMA with η = 300 mPa·sec (9.0 mV) < EPI-DMA with η = 2400 mPa·sec (13.3 mV).

Table 2 Design of orthogonal L_9 (3^4) experiments and analysis of the data

Exp. no.	Level			Error	Result		
	η	B	W_P		R_{max} [a] (%)	$D_{optimum}$ [b] (mg/L)	D_{range} [c] (mg/L)
1	1	1	1	1	97.5	8	6–9
2	1	2	2	2	95.8	9	6–9
3	1	3	3	3	95.9	8	6–9
4	2	1	2	3	97.5	5	4–8
5	2	2	3	1	96.9	6	5–9
6	2	3	1	2	97.7	6	4–7
7	3	1	3	2	91.1	14	–
8	3	2	1	3	81.2	11	10–12 [d]
9	3	3	2	1	91.4	14	–
Analysis of the orthogonal data							
R_{max}							
T_1	289.2	286.1	276.4	285.8			
T_2	292.1	273.9	284.7	284.6			
T_3	263.7	285	283.9	274.6			
K_1	96.4	95.4	92.1	95.3			
K_2	97.4	91.3	94.9	94.9			
K_3	87.9	95	94.6	91.5			
C_r	9.5	4.1	2.8	3.8			
$D_{optimum}$							
T_1	25	27	25	28			
T_2	17	26	28	29			
T_3	39	28	28	24			
K_1	8.3	9	8.3	9.3			
K_2	5.7	8.7	9.3	9.7			
K_3	13	9.3	9.3	8			
C_r	7.3	0.6	1	1.7			

T: sum of each level, K: average of each level, $C_r = K_{max} - K_{min}$.
[a] The highest dye removal efficiency; [b] the optimum dosage where the highest dye removal efficiency was obtained; [c] the effective flocculation dosage range where the dye removal efficiency was higher than 90%; [d] the dye removal efficiency was around 80% within this dosage range.

Table 3 Zeta potential of flocculants used in this study

PAC-EPI-DMA $\eta = 300$ mPa·sec		Zeta potential (mV)	PAC-EPI-DMA $\eta = 2400$ mPa·sec		Zeta potential (mV)	PAC-EPI-DMA $\eta = 4300$ mPa·sec		Zeta potential (mV)
B	W_P		B	W_P		B	W_P	
0.5	5%	13.9	1.5	5%	16.9	1.0	5%	12.0
1.0	10%	17.7	0.5	10%	22.1	1.5	10%	13.2
1.5	20%	25.2	1.0	20%	28.4	0.5	20%	21.6

2.3 Flocculation behavior of PAC-EPI-DMA ($\eta = 300$ mPa·sec)

Flocculation experiments were conducted using composite flocculants ($\eta = 300$ mPa·sec) in treating synthetic RBR dyeing wastewater. Based on the linear relationship between dye concentration and absorbance value at λ_{max}, the dye removal efficiency R (%) of flocculant was calculated by the following equation:

$$R = \frac{A_0 - A}{A_0} \times 100\% \qquad (1)$$

where, A_0 and A are the absorbance values of raw dyeing solution and the supernatant samples, respectively.

As shown in Fig. 1a within the low dosage range, the dye removal efficiency of the three composite flocculants increased gradually with increasing flocculant dosage, and the removal efficiencies obtained by PAC-EPI-DMA ($B = 0.5$, $W_P = 5\%$) and PAC-EPI-DMA ($B = 1.5$, $W_P = 20\%$) were similar. By contrast, PAC-EPI-DMA ($B = 1.0$, $W_P = 10\%$) gave a higher dye removal efficiency. With increasing flocculant dosage up to 6 mg/L, all the dye removal curves associated with these three composite flocculants reached a plateau at Al_{total} 6 mg/L and above, and the dye removal efficiency was around 95%. For the three composite flocculants, a decrease in dye removal was not observed.

The variation of zeta potential of the floc as a function of flocculant dosage is shown in Fig. 1b. Three composite flocculants gave similar zeta potential trends: increase with increasing flocculant dosage, while the differences in charge neutralization ability of three flocculants were observed. The charge neutralization ability exhibited an increasing order: PAC-EPI-DMA ($B = 1.5$, $W_P = 20\%$) < PAC-EPI-DMA ($B = 1.0$, $W_P = 10\%$) < PAC-EPI-DMA ($B = 0.5$, $W_P = 5\%$). However, the flocculant dosage required to reach the isoelectric point of locculants followed the increasing order: PAC-EPI-DMA ($B = 0.5$, $W_P = 5\%$) < PAC-EPI-DMA ($B = 1.0$, $W_P = 10\%$) < PAC-EPI-DMA ($B = 1.5$, $W_P = 20\%$), and the corresponding dosages were 3.9, 5.6 and 6.5 mg/L, respectively.

During the flocculation process of PAC-EPI-DMA with $\eta = 300$ mPa·sec in treating RBR dye, particle restabilization (dye removal reduction with an increasing dosage) did not occur within the investigated dosage range. Moreover, the maximum dye removal efficiency was not appeared
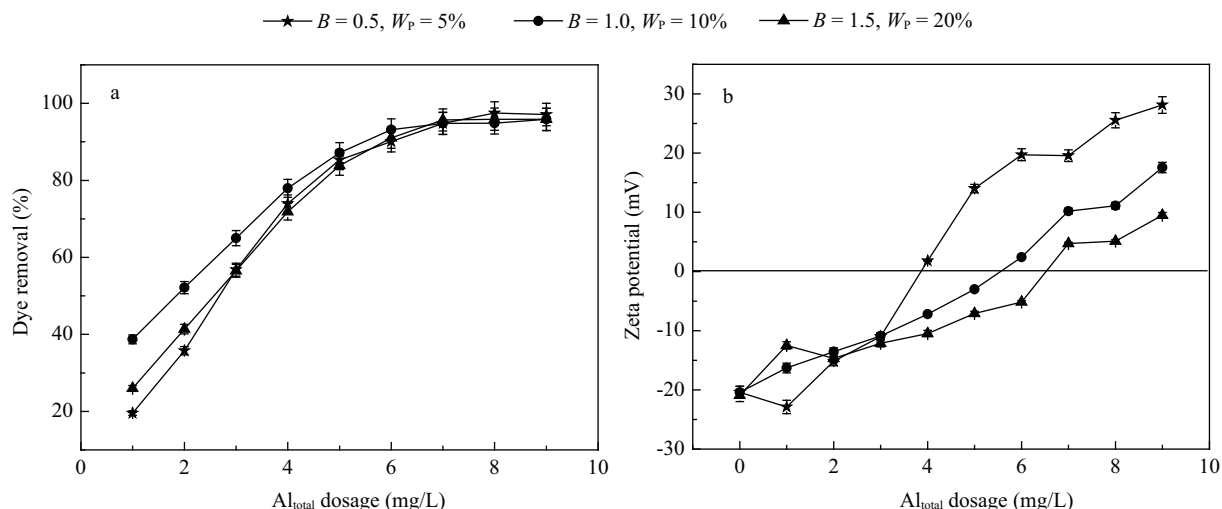
Fig. 1 Flocculation performance of PAC-EPI-DMA with η = 300 mPa·sec. (a) dye removal efficiency; (b) zeta potential.

when the zeta potential values of these three flocculants were near the isoelectric point, and removal efficiency increased as the dosage further increased. The results indicated that charge neutralization was not the dominant mechanism for RBR removal.

When the dosage was lower than 6 mg/L, PAC-EPI-DMA with W_P = 10% gave higher dye removal efficiency than the other two flocculants (Fig. 1a). It is easy to understand for PAC-EPI-DMA with W_P = 20%, because its charge neutralization was the weakest among these three composite flocculants. However, PAC-EPI-DMA with the lowest W_P (5%) gave similar dye removal efficiency with PAC-EPI-DMA with the highest W_P (20%), although the charge neutralization of the former was the strongest. It is known that the mechanism for the removal of anionic dyes by cationic polymeric flocculants can be described by two mechanisms, which are adsorption bridging and charge neutralization (Gao et al., 2007). The results indicated that the adsorption bridging ability of the flocculant played an important role especially in the initial pre-phase of floccu-lation, and the higher the W_P, the stronger the adsorption bridging ability for the removal of RBR. When PAC-EPI-DMA was added to RBR dye solutions containing $-SO_3^-$ and $-OH$ groups, three possible components contributed to the flocculation of dye molecules and aggregation of flocs. These components included two single polymers PAC and EPI-DMA, and an extended conformation of EPI-DMA chains due to the interaction between the hydroxyl group $-OH$ of PAC polymer and the positively charged quaternary amine R_4N^+ of EPI-DMA polymer. The two single polymers can neutralize the negative charge on RBR dye molecule by reacting with the reactive groups, and consequently, result in the formation of insoluble complex dye + PAC or dye + EPI-DMA. The strong adsorption bridging ability of EPI-DMA also played an important role for the removal of RBR dye. Moreover, the adsorption bridging ability of the composite flocculant was improved due to the formation of the conformation with long chains. Therefore, the adsorption bridging ability of PAC-EPI-DMA was strong with high W_P.

It can be concluded that adsorption bridging was the

dominant mechanism of PAC-EPI-DMA with η = 300 mPa·sec, and played an important role in the initial pre-phase of the flocculation if the W_P of the flocculant was high.

2.4 Flocculation behavior of PAC-EPI-DMA (η = 2400 mPa·sec)

As shown in Fig. 2 at η = 2400 mPa·sec with the flocculant dosage lower than 6 mg/L, the three composite flocculants gave similar dye removal efficiency. The dye removal efficiency increased dramatically with an increas-ing dosage. Almost 100% removal was achieved at Al_{total} of 5 mg/L. When the dosage was higher than 6 mg/L, the differences on the dye removal efficiency of flocculants were appeared. The dye removal efficiency of PAC-EPI-DMA (B = 1.0, W_P = 20%) remained constant as the dosage further increased. By contrast, for the other two flocculants, a gradual decrease of dye removal efficiency was observed, which resulted from the restabilization of particles in solution. PAC-EPI-DMA (B = 1.5, W_P = 5%) gave the most serious restabilization with over dosage, because the flocculant gave the strongest charge neutral-ization (Fig. 2b), and then the sites on particle surface were saturated by PAC-EPI-DMA with high positive charge.

As shown in Fig. 2b, all the zeta potential of flocculants increased with increasing flocculant dosage and shifted into the positive region at a certain dosage. PAC-EPI-DMA (B = 1.5, W_P = 5%) gave higher zeta potential, and therefore stronger charge neutralization for the removal of RBR. The dosage of PAC-EPI-DMA (B = 1.5, W_P = 5%) required to attain the isoelectric point was 2.8 mg/L, much lower than those of the other two flocculants. However, the particle restabilization occurred above 6 mg/L for RBR removal by PAC-EPI-DMA (B = 1.5, W_P = 5%) (Fig. 2a). The result suggested that both charge neutralization and adsorption bridging were the flocculation mechanisms of PAC-EPI-DMA (B = 1.5, W_P = 5%) for RBR removal.

In the case of PAC-EPI-DMA (B = 0.5, W_P = 10%), less serious particle restabilization was observed above 6 mg/L, whereas the reverse of the zeta potential occurred when the dosage was larger than 4.5 mg/L. It can be
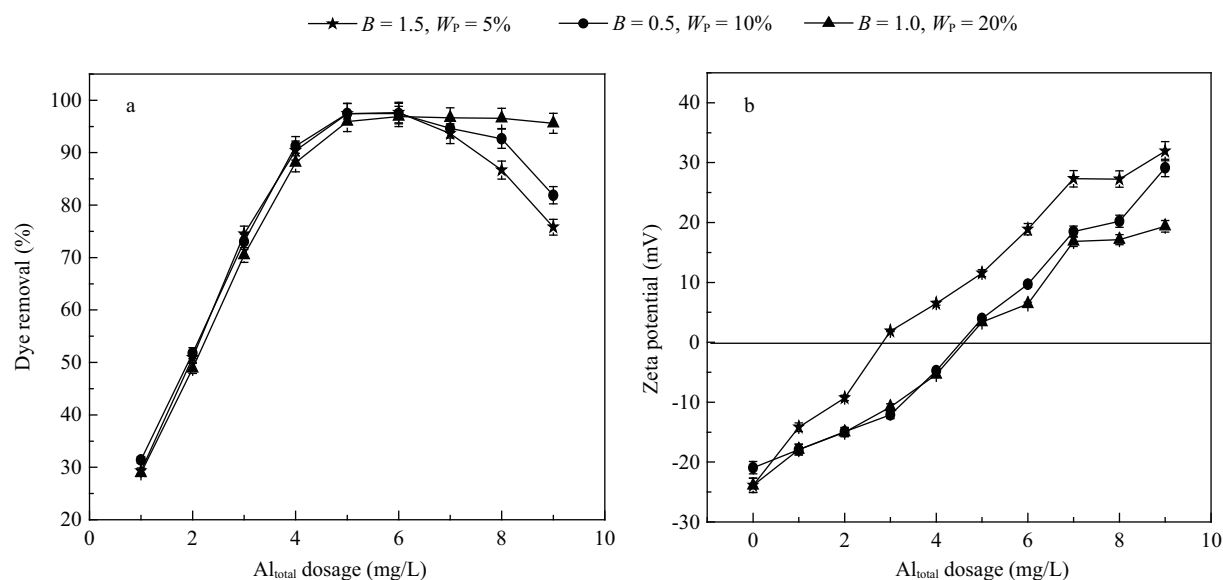
Fig. 2   Flocculation performance of PAC-EPI-DMA with η = 2400 mPa·sec. (a) dye removal efficiency; (b) zeta potential.

concluded that adsorption bridging of PAC-EPI-DMA (B = 0.5, W_P = 10%) played a more important role than charge neutralization in the flocculation of RBR. As shown in Fig. 2b, the zeta potential of PAC-EPI-DMA (B = 1.0, W_P = 20%) was quite similar with that of PAC-EPI-DMA (B = 0.5, W_P = 10%) at 5 mg/L and below, and slightly lower than that of the latter as the dosage further increased. The dye removal efficiency of PAC-EPI-DMA (B = 1.0, W_P = 20%) reached a plateau after the maximum removal efficiency was achieved, although the zeta potential remained increasing with increasing dosage. This result indicated that charge patch and adsorption bridging were the flocculation mechanism for the removal of RBR dye by PAC-EPI-DMA (B = 1.0, W_P = 20%), and the latter was the dominant.

In general, a higher zeta potential leads to a higher charge neutralization potential for a flocculant. From Table 3, it can be seen that the higher W_P was, the higher the zeta potential of the composite flocculant was. Therefore, charge neutralization potential should increase with increasing W_P. However, the zeta potential results in Fig. 2b indicated that the charge neutralization ability of the composite flocculant was weak when W_P was high. Similar zeta potential results were observed in Fig. 1b. The results suggested that the flocculant with high charge neutralization potential did not necessarily exhibit strong charge neutralization ability. This can be explained as follows. When PAC-EPI-DMA with the highest W_P was dosed to the RBR dye solution, most of dye molecules dispersed in solution were adsorbed on the sites on the chains of the cationic polymer and the conformation contributed EPI-DMA. Consequently, charge neutralization mechanism was unlikely to play a major part for the removal of RBR dye by the composite flocculant. By contrast, PAC-EPI-DMA with a lower W_P gave weaker adsorption bridging ability. Thus, the charge neutralization of PAC-EPI-DMA with a certain η value followed the order: PAC-EPI-DMA (W_P = 5%) > PAC-EPI-DMA (W_P = 10%) > PAC-EPI-DMA (W_P = 20%).

It can be concluded that both adsorption bridging and charge neutralization were the flocculation mechanisms of PAC-EPI-DMA with η = 2400 mPa·sec, and the former was more important in treating RBR dye as the W_P of the flocculant increased.

2.5 Flocculation behavior of PAC-EPI-DMA (η = 4300 mPa·sec)

The flocculation behavior of the composite flocculants with η = 4300 mPa·sec was investigated within a broad dosage range from 1 to 14 mg/L as Al$_{total}$. The variations of RBR dye removal efficiency and zeta potential with flocculant dosage are illustrated in Fig. 3. Compared with PAC-EPI-DMA (η = 300 mPa·sec) and PAC-EPI-DMA (η = 2400 mPa·sec), the dye removal efficiency of PAC-EPI-DMA (η = 4300 mPa·sec) increased slowly with an increase in flocculant dosage, and the lowest removal efficiency was achieved at each dosage. This is because the dye removal performance of the composite flocculant PAC-EPI-DMA greatly depends on the viscosity of EPI-DMA polymer, which was supported by the data in Table 2. The EPI-DMA polymer with high viscosity was a long-chain polyelectrolyte with many active sites (quaternary ammonium groups), and exhibited strong adsorption to the negative particles. After the addition of the polymer with too high viscosity, excessive aggregates would be adsorbed on the surface of dye molecules, and then would weaken the surface charge density of the aggregates. The repulsion force between aggregates also increased. Moreover, a higher η value of EPI-DMA polymer lead to a lower pervasion capability of the polymer, and consequently resulted in weaker charge neutralization and adsorption bridging ability of the flocculant. In addition, zeta potential values of PAC-EPI-DMA (η = 4300 mPa·sec) were the lowest compared to those of the other two flocculants (Table 3), indicating the weakest charge neutralization ability. Therefore, PAC-EPI-DMA (η = 4300 mPa·sec) gave the worst dye removal efficiency. As to PAC-EPI-DMA (η = 2400 mPa·sec), the best removal efficiency was
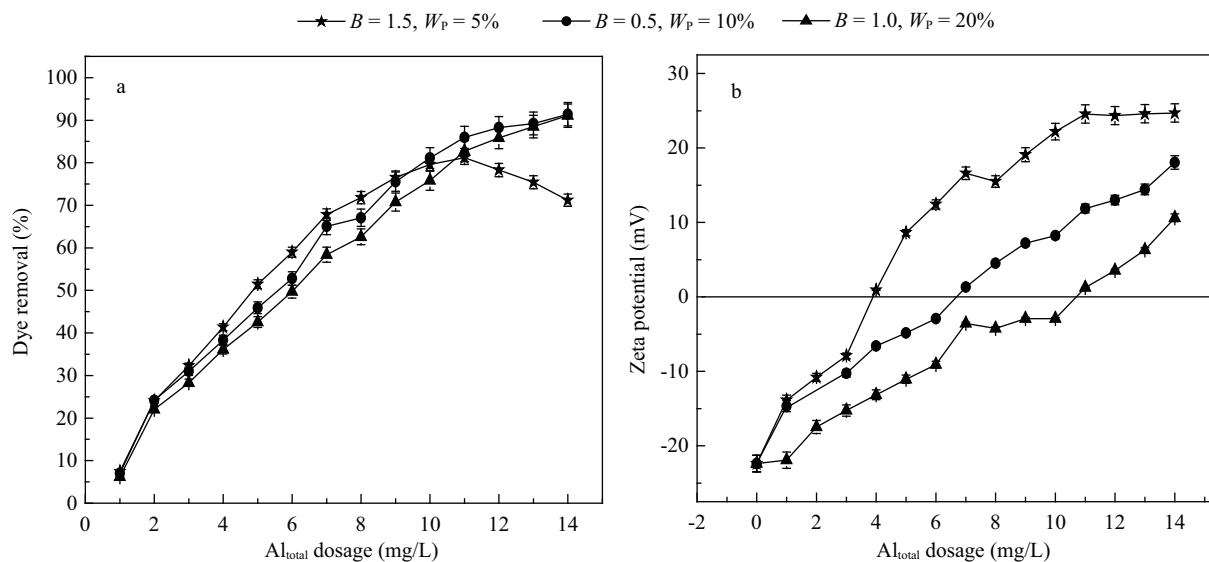
Fig. 3   Flocculation performance of PAC-EPI-DMA with η = 4300 mPa·sec. (a) dye removal efficiency; (b) zeta potential.

achieved because of its good pervasion capability and high zeta potential. Overall, the three composite flocculants with η = 2400 mPa·sec performed better than PAC-EPI-DMA with η = 300 mPa·sec and η= 4300 mPa·sec for the removal of RBR.

As shown in Fig. 3a, with the dosage below 9 mg/L, the flocculation efficiency of these three composite flocculants was: PAC-EPI-DMA (B = 1.0, W_P = 5%) > PAC-EPI-DMA (B = 1.5, W_P = 10%) > PAC-EPI-DMA (B = 0.5, W_P = 20%). As the dosage further increased, the dye removal efficiency of the two flocculants except PAC-EPI-DMA (B = 1.0, W_P = 5%) increased slightly and the differences between them tended to diminish with an increase in dosage, and near 90% of dye removal was achieved at a dosage of 13 mg/L. It was noted that the particle restabilization phenomenon was not observed for these two flocculants even the dosage increased to 14 mg/L. In the case of PAC-EPI-DMA (B = 1.0, W_P = 5%), particle restabilization was observed after the maximum removal efficiency (81.2%) was achieved at a dosage of 11 mg/L.

The zeta potential curves associated three composite flocculants were depicted in Fig. 3b. The zeta potential of PAC-EPI-DMA (B = 1.0, W_P = 5%) increased sharply within low dosage range, and then reached the isoelectric point at 3.9 mg/L of Al_{total} dosage. The other two composite flocculants exhibited a gradual increase in zeta potential within the dosage range investigated. It was also found that the charge neutralization ability of these three flocculants followed an increasing order: PAC-EPI-DMA (B = 1.0, W_P = 5%) < PAC-EPI-DMA (B = 1.5, W_P = 10%) < PAC-EPI-DMA (B = 0.5, W_P = 20%). The dosage required to reach the isoelectric point of PAC-EPI-DMA (B = 1.5, W_P = 10%) and PAC-EPI-DMA (B = 0.5, W_P = 20%) were 6.7 mg/L and 10.8 mg/L, respectively.

It was noted that the dye removal efficiency of PAC-EPI-DMA with high W_P (10% and 20%) kept increasing even after about 90% of dye removal was achieved, and the zeta potential was already high positive. This result suggested that charge neutralization was not the dominant

flocculation mechanism of PAC-EPI-DMA with high W_P in treating RBR dye. As to PAC-EPI-DMA (B = 1.0, W_P = 5%), the maximum dye removal efficiency was obtained when the zeta potential was higher than the isoelectric point, although restabilization was observed as the dosage further increased. This result indicated that PAC-EPI-DMA (B = 1.0, W_P = 5%) was likely to work by charge neutralization and adsorption bridging.

Similar with the composite flocculants with η = 300 mPa·sec, adsorption bridging was the dominant mechanism of PAC-EPI-DMA with η = 4300 mPa·sec, but the lower the W_P of the flocculant was, the more important the charge neutralization was.

2.6 pH of RBR dyeing wastewater after the flocculation

In this study, the initial pH value of raw reactive dyeing wastewater was 8.45, without additional pH adjustment. The final pH curves associated with the composite flocculants were obtained after the flocculation for RBR dye, and the variations of final pH as a function of flocculant dosage are shown in Fig. 4. It can be found that the pH values decreased with the increase of flocculant dosage. The flocculation performance of EPI-DMA flocculant was independent on the pH of RBR dye solution. Therefore, the reduction in the pH of dye solution was attributed to the flocculation behavior of PAC into the composite flocculant. At a high initial pH, the amorphous hydroxide formed by the hydrolysis of Al increased with an increase in flocculant dosage, and thus the reduction in pH was observed with an increase in dosage.

It is noted that the degree of reduction in pH value was different for different flocculants. For PAC-EPI-DMA with a certain η, the pH value decreased with the decrease of W_P at the same dosage. As discussed above, the sweep bridging of the amorphous hydroxide played an important role under alkaline conditions, which lead to the decrease of pH. The result indicated that the sweep bridging of PAC played a more important role for the removal of RBR dye with the decrease of W_P.
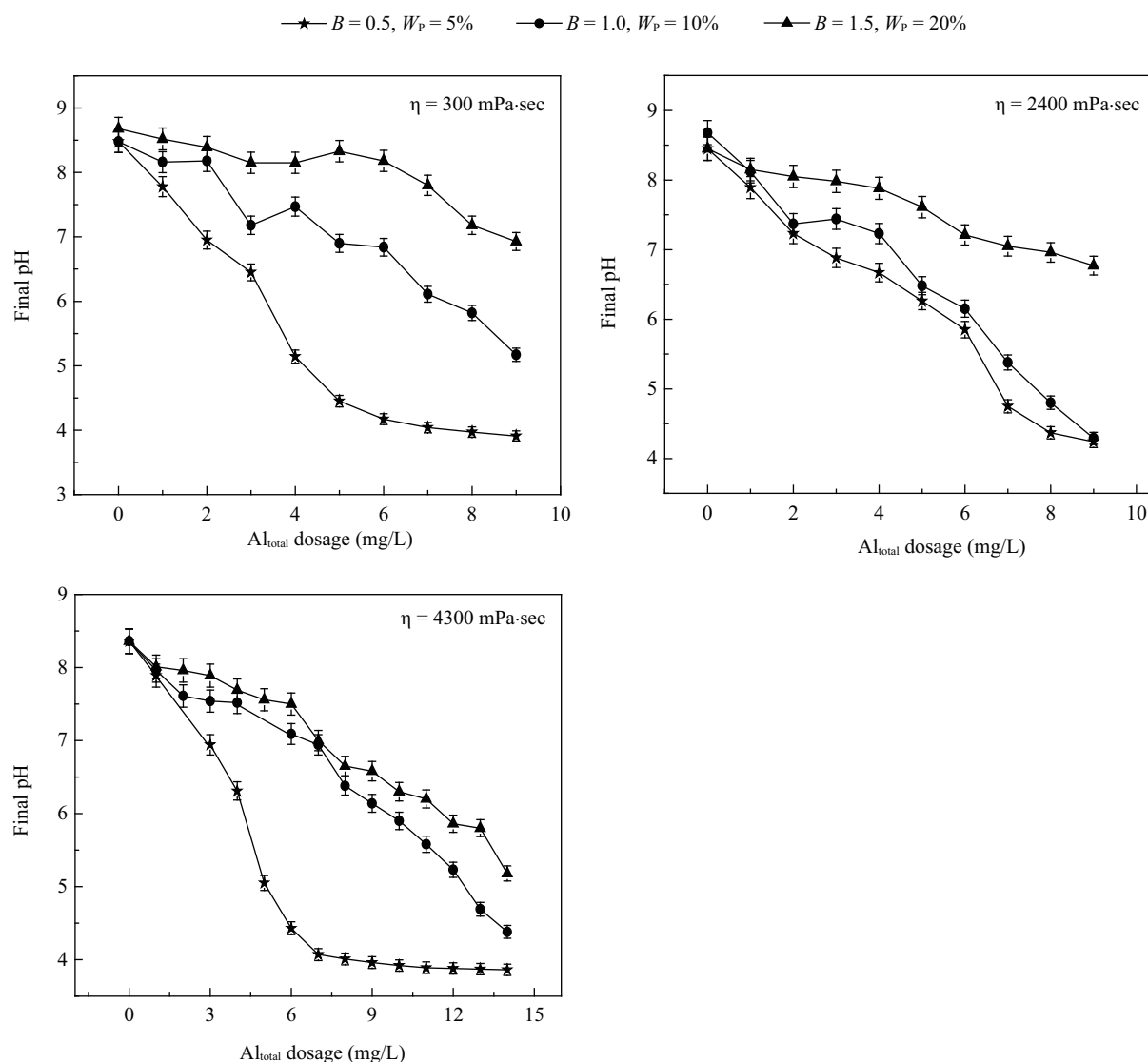
Fig. 4 Variations of pH of RBR dyeing wastewater versus the dosage of PAC-EPI-DMA.

3 Conclusions

The composite flocculant PAC-EPI-DMA was highly effective for the removal of anionic azo dye from synthetic dyeing wastewater. The dye removal performance of these composite flocculants with different characteristics mainly depended on the viscosity of organic EPI-DMA component and the organic content. Compared with other composite flocculants, PAC-EPI-DMA with intermediate η (2400 mPa·sec) gave a higher reactive dye removal at lower dosage, and also gave a broader effective flocculation dosage range. Both charge neutralization and adsorption bridging were responsible for the removal of RBR by PAC-EPI-DMA with η = 2400 mPa·sec. With the increase of W_P, adsorption bridging played a more important role than charge neutralization for the removal of RBR.

For PAC-EPI-DMA with a low or high η, adsorption bridging was the dominant flocculation mechanism, and became stronger with increasing W_P. For PAC-EPI-DMA with certain η, its charge neutralization ability was stronger with decreasing W_P.

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