



Effect of aging period on the characteristics and coagulation behavior of polyferric chloride and polyferric chloride–polyamine composite coagulant for synthetic dyeing wastewater treatment

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ABSTRACT

In this paper, a new composite inorganic–organic coagulant (PFC–EPI–DMA) was prepared by polyferric chloride (PFC) and epichlorohydrin–dimethylamine (EPI–DMA) under a given EPI–DMA/Fe and OH/Fe molar ratio. In comparison with PFC, the Fe (III) species and zeta potential of PFC–EPI–DMA were measured. Then their coagulation performance and coagulation kinetics for treating synthetic reactive dyeing wastewater were investigated. The results showed that the content of Fe_a and Fe_b in PFC–EPI–DMA and PFC coagulants decreased with increasing aging period. Compared to PFC, PFC–EPI–DMA had higher content of Fe_a but lower content of Fe_b and Fe_c. The zeta potentials of two coagulants decreased with increasing aging period within all tested pH range. For the treatment of reactive red 24, the color removal efficiency treated by PFC–EPI–DMA decreased, while that treated by PFC remained almost constant with increasing aging period. However, the color removal efficiencies of reactive blue 14 treated by two coagulants both decreased with increasing aging period. The results of floc aggregation process confirmed that with increasing aging period, the orders of floc growth rate, ratio and TWV treated by two coagulants were complicated.

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1. Introduction

Coagulation/flocculation is a widely used process in water and wastewater treatment and coagulants play an important role for removing suspended particles and coloring materials [1,2]. Traditional inorganic coagulants, based on aluminum and iron salts, are widely used in water and wastewater treatment process [3–5]. The prehydrolyzed polyaluminum salt coagulants are the most widely used coagulants, and extensive research has been focused on them [4]. Since residual aluminum is believed to be harmful to human and living organisms [6–8], iron-based coagulants have attracted more interest and attention [9–11]. It has been recognized that polyferric species was more effective than conventional monomeric ferric salts [12,13]. However, due to the high dosage of inorganic coagulant, large volume of sludge is produced, which requires high cost for sludge disposal, thus restricting the application of inorganic

coagulants. Compared to inorganic coagulants, organic polymeric coagulants produce less sludge and are less pH dependent during coagulation process [14]. Though they have been used as coagulant aids in water and wastewater treatment for several decades, they are used alone as primary coagulants in recent years. However, high cost limited their application in water treatment.

For overcoming the limitation mentioned above and increasing the coagulation efficiency, research has been focused on the application of dual-coagulants. In the traditional method of dual-coagulant systems, inorganic coagulant and organic coagulant are usually added into water or wastewater, separately [15,16]. The dual-coagulant systems need two reagent addition systems which will increase the cost of water treatment. Therefore, a new method was developed, in which inorganic coagulant was premixed with organic coagulant before they were added to the water treated. This new dual-coagulant is called composite inorganic–organic coagulant. In recent years, there has been intensive research on composite coagulant [17–19].

In this paper, a novel composite inorganic–organic coagulant (PFC–EPI–DMA) was prepared by polyferric chloride (PFC) and epichlorohydrin–dimethylamine (EPI–DMA). PFC contains a range of pre-formed Fe (III) hydrolysis species of high positive charge [20], which is mostly affected by the basicity, the aging temperature and time [10]. The basicity, defined as the ratio of the moles

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of base added and/or bounded to the moles of Fe^{3+} ($[\text{OH}^-]/[\text{Fe}^{3+}]$), and the aging temperature can be controlled during manufacturing. However, the Fe (III) species distribution was affected by aging period, which meant the coagulation performance and kinetics of PFC was influenced by aging period. EPI–DMA is a synthetic organic polymeric coagulant, which has been used in water and wastewater treatment processes. They are effective in wide pH range, easy to handle, and immediately soluble in aqueous solution [21]. Since PFC and EPI–DMA were premixed to produce PFC–EPI–DMA composite coagulant, the Fe (III) species distribution and coagulation performance of PFC–EPI–DMA were also affected by aging period. However, there is very limited research on the effect of aging period on characteristics and coagulation performance of polyferric coagulants, and particularly, there is no available literature concerning the relationship between aging period and the coagulation performance of polyferric–organic composite coagulant. The objective of this work is to investigate the effect of aging period on the characteristics of composite coagulant PFC–EPI–DMA and PFC, including the Fe (III) species and zeta potential variation. Moreover, to evaluate coagulation performance, coagulation experiments were conducted for the treatment of synthetic reactive blue and reactive red dyeing wastewater. Finally, the floc aggregation process was investigated with the Photometric Dispersion Analyser (PDA 2000).

2. Materials and methods

2.1. Preparation of PFC and PFC–EPI–DMA

PFC was prepared using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (A.R.) and Na_2CO_3 (A.R.) in our laboratory. Firstly, FeCl_3 solution with a concentration of 7% (w/w) was prepared by dissolving $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in distilled water. Then, the solution was mixed with Na_2CO_3 powder (C.P.) by stirring at room temperature to reach the desired $[\text{OH}^-]/[\text{Fe}]$ ratio (B) value. Finally, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ (A.R.), as a stabilizer, was added to the solution ($[\text{Na}_2\text{HPO}_4]/[\text{Fe}] = 0.08$). PFC with 1 d, 10 d and 30 d aging period was denoted as PFC₁, PFC₁₀ and PFC₃₀, respectively. The target PFC had the following characteristics: $w(\text{Fe}) = 7\%$; $B = 0.5$; $\text{pH} = 0.6–0.75$.

EPI–DMA was also prepared in our laboratory. The initial reactive temperature was 30 °C. Firstly, dimethylamine (33%, C.P.) was added to a 250 mL glass reactor equipped with a temperature controller and a mechanical stirrer. Then epichlorohydrin (A.R.) at a selected weight was gradually added by dropping into the reactor under constant stirring. After that, 1,2-diaminoethane at a chosen weight percentage in the mixture was added into the reactor under stirring. And then, the reactive temperature was raised slowly to 60–75 °C. After 7 h reaction, the polyamine polymers were obtained. The polyamine had the following characteristics: $\eta = 850 \text{ mPa s}$ (intrinsic viscosity); cationicity = 3.5 mmol/g.

For the preparation of composite coagulant PFC–EPI–DMA, EPI–DMA with a measured amount was added to PFC solution under thorough stirring at room temperature. The aging temperature of PFC–EPI–DMA was 20 ± 1 °C. PFC–EPI–DMA with 1 d, 10 d and 30 d aging period was denoted as PFC–E₁, PFC–E₁₀ and PFC–E₃₀, respectively. The target PFC–EPI–DMA solution had the following characteristics: $w(E) = 7.0\%$ (the weight percentage of EPI–EMA); $\text{pH} = 0.7–0.8$; $\rho = 1.22 \text{ g/cm}^3$; turbidity = 5.9–6.2 NTU (with 30 d aging period).

2.2. Measurement of coagulant characterization

The Fe (III) species distribution in PFC and PFC–EPI–DMA solutions was measured by a timed complexation spectroscopy method involving reactions of Fe with Ferron (8-hydroxy-7-iodoquinoline-

5-sulphonic acid) [22]. Visible light absorbance was measured as a function of time at a wavelength of 600 nm (for Fe) to quantify the amount of Fe complex formed. The reactions of Fe (III) monomeric species with Ferron were completed in 1 min (denoted as Fe_a), and the reactions of Fe (III) polymeric species (denoted as Fe_b) with Ferron finished in the next 3 h, and the unreactive Fe (III) species after 3 h was considered to be Fe (III) colloidal and precipitated species (denoted as Fe_c).

The zeta potential of PFC–EPI–DMA at dosage of 100 mg/L (as Fe) was measured by the JS94H Micro-Electrophoretic Mobility Detector, and comparison was made with PFC [23]. During experiments, pH of the coagulant solutions was adjusted by adding HCl (1 mol/L) or NaOH (1 mol/L). After 5 min of gentle stirring, the samples were analyzed and the data were recorded.

2.3. Jar test procedures

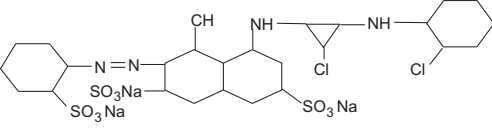
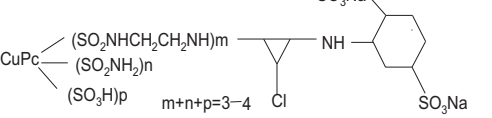
Reactive dyes are the most commonly used dyestuffs in textile industry. Hence, reactive blue (K–GL) and reactive red (K–2BP) which were characterized by different types were chosen for investigation. The dyes were obtained from Jinan No. 2 Textile Dyeing Mill, China. Their color index (CI) numbers are reactive blue 14 and reactive red 24, respectively. The synthetic dye wastewater was prepared by dissolving 0.5 g of dye in 10 L tap water. The CI number, type, molecular structure and the wavelength of maximum absorbance of two dyes are shown in Table 1. The synthetic reactive blue wastewater samples had the following characteristics: $\text{pH} = 8.00 \pm 0.01$; maximum absorbance = 0.500–0.515; turbidity = 6.80–7.70 NTU. The synthetic reactive red wastewater samples had the following characteristics: $\text{pH} = 8.06 \pm 0.01$; maximum absorbance = 0.885–0.900; turbidity = 0.90–1.13 NTU.

Coagulation experiments were carried out by using a conventional Jar-test apparatus (the DC-506 Laboratory Stirrer) at room temperature (19–21 °C). Appropriate amounts of coagulants were injected into the wastewater samples (500 mL). The dosages of coagulants were calculated by the quantity of their effective component, i.e. PFC by Fe, and PFC–EPI–DMA by Fe plus the weight of EPI–DMA. After dosing of coagulants, the wastewater samples were stirred fast at 120 rpm paddle speed for 2.5 min. Then the samples were stirred at the paddle velocity of 40 rpm for 12 min, followed by sedimentation for 20 min. After that, supernatant samples were withdrawn for analyzing color removal efficiency, which was calculated by comparing the absorbance value for the treated wastewater sample to the absorbance value for the original synthetic dye wastewater. Distilled water served as a reference.

2.4. Coagulation kinetics

The formation of floc during coagulation–flocculation process can be monitored by Photometric Dispersion Analyzer (PDA 2000; Rank Brothers Ltd.). During the coagulation periods, the suspension was continuously sampled by peristaltic pump (LEAD-1, Baoding Longer Precision Pump Co. Ltd., China) and monitored by a PDA 2000 to obtain data. The detailed theory of PDA 2000 has been reported in some published literatures [24,25]. The curves as shown in Fig. 1 were plotted using the typical ratio obtained from the experiments and can be divided into three specific regions: lag region, growth region and steady-state region. The ratio values were related to the mean concentration and the size of dispersed particles. In this study, three parameters were calculated to analyze the data collected by PDA 2000 during the coagulation–flocculation process. These parameters included a floc growth rate of the growth region, a time-weighted average steady-state ratio value and a time-weighted ratio variance (TWV) of the steady-state ratio value. The slope of the growth region is an indicator of the rate at which flocs developed. The floc growth rate which is denoted as the linear

Table 1
Dye characteristics.

Name	CI	Type	Molecular structure	Wavelength (nm)
Reactive red 24 (K-2BP)	R.R. 24	Azo		550
Reactive blue 14 (K-GL)	R.B. 14	Phthalocyanine		598

portion can be calculated as:

$$\text{floc growth rate} = \frac{\Delta \text{ratio}}{\Delta \text{time}} \quad (1)$$

The time-weighted average steady-state ratio value (denoted as Ratio), which indicates the floc size in the steady-state region, can be computed as:

$$\text{Ratio} = \frac{\sum_{i=1}^N (\text{ratio}_i \cdot \text{time}_i)}{\sum_{i=1}^N \text{time}_i} \quad (2)$$

The time-weighted ratio variance of the steady-state ratio value (denoted as TWV), which indicates the difference of floc size in steady-state region, was calculated as:

Time-weighted variance (TWV)

$$= \frac{\sqrt{(\sum_{i=1}^N [(\text{ratio}_i - \text{Ratio})^2 \text{time}_i]) / (\sum_{i=1}^N \text{time}_i)}}{\text{Ratio}} \times 100\% \quad (3)$$

3. Results and discussion

3.1. Characterization of coagulants

3.1.1. Measurement of Fe (III) species distribution in coagulants

Prior to the method applied to determining Fe (III) species distribution in PFC–EPI–DMA, it was necessary to study whether the presence of EPI–DMA had any effect on the method. The study

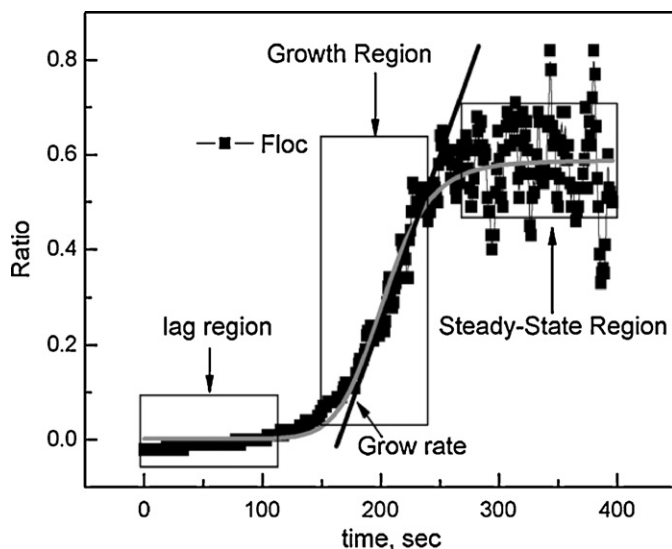


Fig. 1. The typical ratio distribution curve as a function of coagulation time.

was tested with EPI–DMA at different concentrations by reacting with Ferron reagent. The absorbance of the samples at 600 nm, in which the concentration of EPI–DMA was 0, 2, 4, 6, 8 and 10 mg/L, was 0.003, 0.004, 0.003, 0.003 and 0.004, respectively. The results showed that EPI–DMA did not react with Ferron reagent.

The results of the Fe (III) species distribution in PFC–EPI–DMA and PFC coagulants with different aging periods are shown in Table 2. It was observed that with the increase of aging period, the content of both Fe_a and Fe_b in PFC–EPI–DMA and PFC coagulants decreased, whereas the content of Fe_c in both coagulants increased. It was also found that the content of Fe_a in PFC–EPI–DMA was higher than that in PFC, whereas the content of Fe_b and Fe_c in PFC–EPI–DMA was lower than those in PFC, which means that EPI–DMA affected the Fe (III) species distribution of the coagulants.

PFC contains a range of pre-polymerised Fe species, which result from hydrolysis reactions that occurred [26]. A simplified scheme of these reactions is shown in Fig. 2. Different Fe (III) species transformed each other until the chemical equilibriums were reached in polyferric solution, and the chemical equilibriums of these species depended on the concentration of OH^- in the solution [27]. Due to the water molecules being progressively replaced by hydroxyl ions, the degree of polymerizing in polyferric solutions increased, thus the content of Fe_a decreased in PFC–EPI–DMA and PFC solutions with increasing aging period. The equilibrium of H^+ and OH^- ions would be broken and then induce the Fe (III) hydrolysis process to proceed from left to right when EPI–DMA was added to the PFC solution, as the pH of EPI–DMA was higher than that of PFC. Hence, theoretically speaking, the content of Fe_a species would decrease and the content Fe_b would increase. However, the result was not consistent with the phenomenon obtained in this study. This result indicated that other mechanisms might occur in PFC–EPI–DMA, such as the formation of complex compounds between Fe species and EPI–DMA, which increased the content of Fe_a species and decreased the content of Fe_b species. This phenomenon was neither in agreement with a previous study, in which the formation of complex compounds between Fe species and PAA reduced the Fe_a species [19]. This can be explained by different chemical structures and the type of charge between EPI–DMA and PAA.

Table 2

The distribution of Fe species of PFC–EPI–DMA and PFC with aging period.

Aging period (d)	PFC–EPI–DMA			PFC		
	Fe_a (%)	Fe_b (%)	Fe_c (%)	Fe_a (%)	Fe_b (%)	Fe_c (%)
1	75.67	5.72	18.61	62.79	9.60	27.60
10	64.23	3.81	31.96	55.95	3.84	41.04
30	56.61	0	43.39	49.35	0	50.65

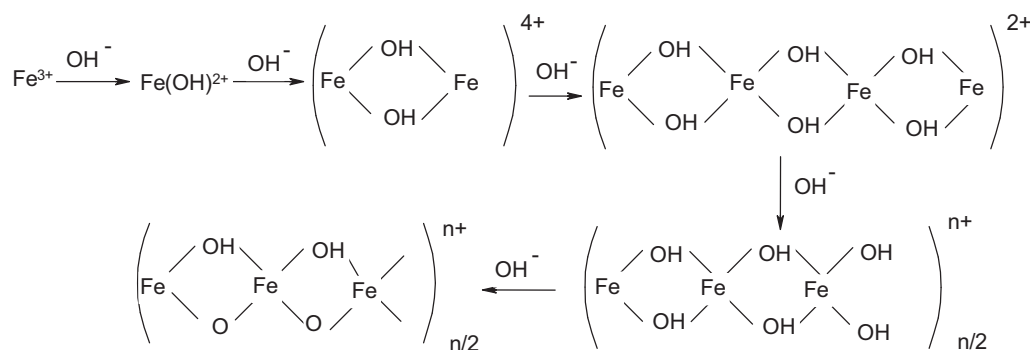


Fig. 2. The hydrolysis–polymerisation process of Fe (III) species.

3.1.2. Variation of zeta potential of PFC and PFC–EPI–DMA with pH and aging

The relationship among the zeta potential of coagulants, pH and aging time is shown in Fig. 3. It was found that zeta potentials of both PFC and PFC–EPI–DMA decreased with increasing pH. The zeta potentials of PFC–EPI–DMA were all above zero under test pH range from 3.0 to 10.5, whereas the zeta potential of PFC became negative under alkaline conditions. The zeta potential of PFC–EPI–DMA was much higher than that of PFC at the same pH, as EPI–DMA was a high positively charged organic polymer. The zeta potentials of both coagulants decreased with the increase of aging period in all pH range. Hu et al. suggested that Fe (III) polymers and colloids transformed to $\text{Fe}(\text{OH})_3$ and lost positive charge more easily than other Fe (III) species with the increase of pH [28]. As the content of Fe_c of both coagulants increased with increasing aging period, coagulants would lose positive charge. Therefore, the zeta potentials of PFC and PFC–EPI–DMA decreased with aging period within the whole pH range.

3.2. Color removal efficiency for synthetic dye wastewater treatment

In this study, color removal efficiencies of two synthetic dyeing wastewater treated by PFC and PFC–EPI–DMA with different aging periods are shown in Fig. 4. It can be seen that the color removal efficiency of both coagulants for synthetic wastewaters treatment increased with the increase of coagulant dosage. For R.R. 24 treatment, the color removal efficiencies using PFC were all below 15% within the dosage range. PFC–EPI–DMA achieved much higher color removal efficiency than PFC and could remove about 90% of color at the dosage of 120 mg/L. As shown in Fig. 4b, for the treatment of the

R.B. 14 solution, the color removal efficiency by PFC–EPI–DMA was higher than that by PFC at the same dosage. PFC–E₁ could remove 98.15% of R.B. 14, whereas PFC₁ could remove 91.67% at a dosage of 36 mg/L.

The efficiency of dye removal greatly depends on the solubility and chemical structures of the dyes as well as the characteristic of the coagulant. Dyes with high solubility cannot be removed effectively by coagulants. Differences of dyes solubility are attributed to the different chemical structures of dyes. Reactive dyes have $-\text{SO}_3^-$, $-\text{COO}^-$ and $-\text{OH}^-$ groups which increase the solubility of the dyes [29]. Owing to their high solubility, reactive dyes cannot be easily absorbed by PFC hydrolysate. Hence, the color removal efficiency of reactive dye was low when treated by PFC.

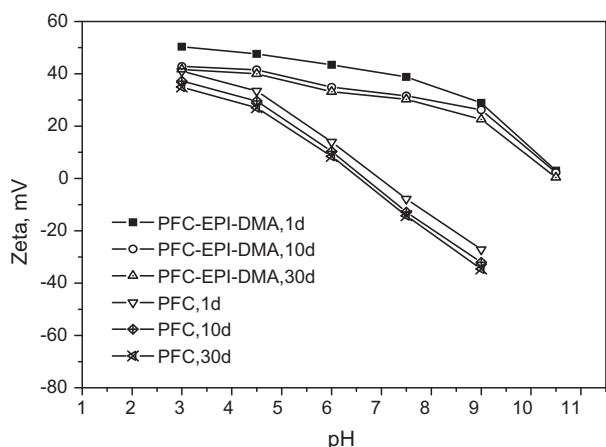


Fig. 3. Zeta potential variations of PFC and PFC–EPI–DMA with aging period.

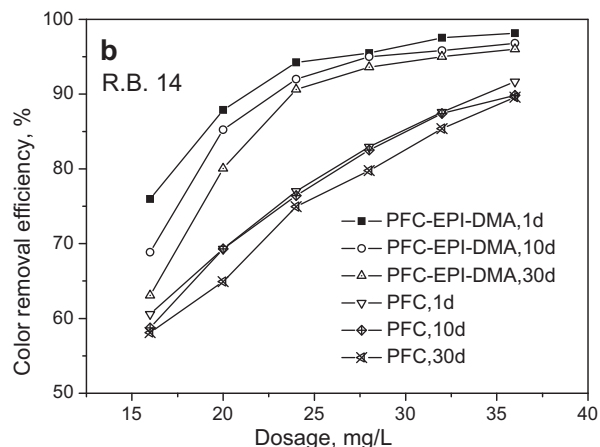
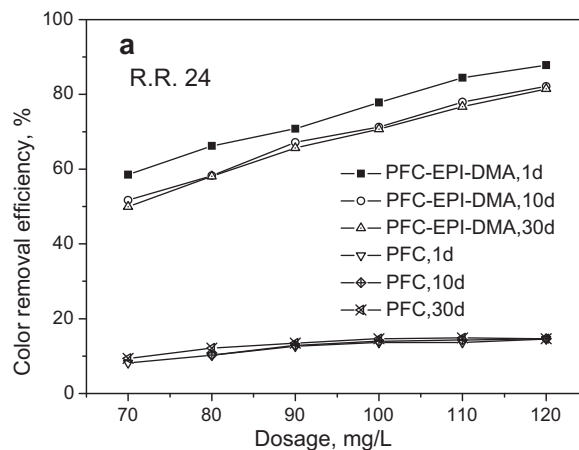


Fig. 4. Effect of aging period of coagulants on the color removal efficiency.

Table 3

Zeta potentials of coagulated flocs as a function of coagulant dose for the removal of R.R. 24.

Zeta potential (mV)	Dosage (mg/L)					
	70	80	90	100	110	120
PFC–EPI–DMA	–6.28	–5.89	–5.33	–4.44	–3.35	–2.27
PFC	–13.87	–13.11	–9.26	–5.90	–4.59	–3.17

The results in Fig. 4 showed that the color removal efficiency of R.B. 14 was higher than that of R.R. 24 even at the much lower dosage of coagulants. This can be explained by the differences in molecular structure of dyes. As shown in Table 1, the number of sulphonic acid (SO_3^-) group in R.B. 14 was not smaller than that in R.R. 24, and the molecular weight of R.B. 14 was heavier than that of R.R. 24. Hence, R.B. 14 can settle from water more easily as it is heavier compared to R.R. 24. Thus, R.B. 14 can be removed more effectively than R.R. 24 by using coagulation process. Ahmad and Puasa reported that the removal of Reactive Black 5 with four SO_3^- group and molecular weight of 991.82 was higher than that of Reactive Orange 16 with two SO_3^- group and molecular weight of 617.54, which presented the same explanation on dye molecular structure as the result obtained in this study [26].

The effect of aging period on dyes removal efficiency was also shown in Fig. 4. For R.R. 24 treatment, the color removal efficiency treated by PFC–EPI–DMA decreased, whereas that treated by PFC remained almost constant with the increase of aging period. As shown in Fig. 4b, the color removal efficiencies of R.B. 14 treated by two coagulants both decreased with increasing aging period of coagulants. Hu et al. reported that Fe (III) polymer and Fe (III) colloids could only adsorb the contaminant and their coagulation efficiency was the lowest in all types of Fe (III) hydrolysis species [28], which indicated that the efficiency of Fe (III) coagulants decreased as the content of Fe_c increased. Based on the phenomenon mentioned above, the content of Fe_c of PFC and PFC–EPI–DMA increased with increasing aging of coagulants; therefore, the color removal efficiencies should decrease as aging period increased. However, the color removal efficiency for treating R.R. 24 solution using PFC was not consistent with the findings of Hu et al. [28]. The reason may be that the removal efficiency of PFC for treating R.R. 24 was very low and then the difference in color removal was not obvious with increasing aging period.

The zeta potentials as a function of coagulant dose for the removal of R.R. 24 and R.B. 14 are shown in Tables 3 and 4. For two synthetic dyeing wastewaters treated by PFC and PFC–EPI–DMA, the zeta potential increased with the increase of coagulant dosage and was below zero within the tested dosage range. Compared with PFC, PFC–EPI–DMA gave higher zeta potential and thus much stronger charge neutralization, which lead to more effective performance for the removal of R.R. 24 and R.B. 14. Pefferkorn suggested that if charge neutralization is the only path for coagulation, the zeta potential should be in excellent correlation with the coagulant dosage and optimal efficiency is achieved when zeta potential is close to zero [30]. According to this theory, the relation of zeta potentials of PFC and PFC–EPI–DMA for the treatment of R.R. 24 and R.B. 14 with coagulant dosage was calculated and showed a good linear relationship with correlation coefficient of 0.96 and

Table 4

Zeta potentials of coagulated flocs as a function of coagulant dose for the removal of R.B. 14.

Zeta potential (mV)	Dosage (mg/L)					
	16	20	24	28	32	36
PFC–EPI–DMA	–21.56	–20.34	–19.96	–19.38	–17.86	–15.96
PFC	–21.89	–21.17	–20.79	–20.25	–20.15	–19.62

above. For the treatment of R.R. 24 by PFC–EPI–DMA and PFC, the zeta potentials were close to zero at the dosage of 120 mg/L, whereas the color removal efficiencies were not optimal. As the data demonstrated, it was suggested that charge neutralization was the dominant mechanism and adsorption/bridging mechanism was also evident (but to a much lower extent) for the treatment of R.R. 24 by PFC–EPI–DMA and PFC. It was also noted that zeta potentials of R.B. 14 flocs treated by PFC and PFC–EPI–DMA were much lower than isoelectric point even at the dosage of 36 mg/L, which suggested that different mechanisms other than charge neutralization were occurred, such as adsorption/bridging mechanism.

3.3. Coagulation kinetics

In the treatment of dyes solutions, floc growth rate, Ratio and TWV of PFC and PFC–EPI–DMA as a function of coagulant dosage are demonstrated in Figs. 5 and 6, respectively. For R.R. 24 treated by PFC₁, floc growth rate increased within the dosage range 70–90 mg/L, but decreased when the dosage was higher than 90 mg/L. Nevertheless, floc growth rates treated by PFC₁₀ and PFC₃₀ decreased within all the tested dosage range. When the dosage was less than 100 mg/L, PFC₁ got the highest floc growth rate followed by PFC₃₀ and PFC₁₀. However, within the dosage range 110–120 mg/L, PFC₁₀ got the highest floc growth rate followed by PFC₁ and PFC₃₀. Within all the tested dosage range, both Ratio and TWV decreased at low dosage, but increased at high dosage. Ratio values with various aging periods were in the order: PFC₁ > PFC₃₀ > PFC₁₀. However, the order of TWV was: PFC₁₀ > PFC₃₀ > PFC₁. Based on the data mentioned above, the orders of these parameters were not consistent with the order of R.R. 24 removal treated by PFC.

For the treatment of R.R. 24 by PFC–EPI–DMA, both floc growth rate and TWV with various aging periods were in the following order: PFC–E₁₀ > PFC–E₁ > PFC–E₃₀, which was not in good agreement with the order of color removal. The order of Ratio values was complicated within the tested dosage range. However, Ratio values were almost between 0.25 and 0.34, which indicated that there was a slight difference in Ratio values. As previous study suggested, there were many factors affecting coagulation efficiency besides floc size, such as the velocity of floc aggregation, the floc density, the floc shape and the sedimentation, etc. [31]. As floc growth rate increased, coagulants would take less time to aggregate, which may increase coagulation performance. However, a higher TWV implied a wider range of floc size which may reduce the performance of sedimentation. As data demonstrated, both floc growth rate and TWV treated by PFC–E₁₀ was higher than those by PFC–E₁. Considering the effect of both floc growth rate and TWV, the color removal performance by PFC–E₁ was slightly higher than that by PFC–E₁₀ in this study.

Compared to the treatment of R.R. 24 by two coagulants, both floc growth rate and Ratio treated by PFC–EPI–DMA were higher than those by PFC when the dosage was not less than 100 mg/L. Ratio values represent the floc size in the steady-state region. A larger Ratio indicated larger aggregate size and better separation by subsequent sedimentation [32]. Meanwhile, increasing floc growth rate can also increase coagulation efficiency. Therefore, considering the effect of Ratio value and floc growth rate, the color removal performance of PFC–EPI–DMA was higher than that of PFC. It was also observed that TWV of PFC–EPI–DMA was higher than that of PFC within the tested dosage range, which indicated that a wider range of floc size existed when PFC–EPI–DMA was used. TWV can also be used to explain the coagulation mechanism. In previous relevant study, it was suggested that the flocs formed under sweep and bridging mechanism tended to have open structure and possibly with a wider distribution of floc size, whereas flocs formed under charge neutralization mechanism were more condensed with a

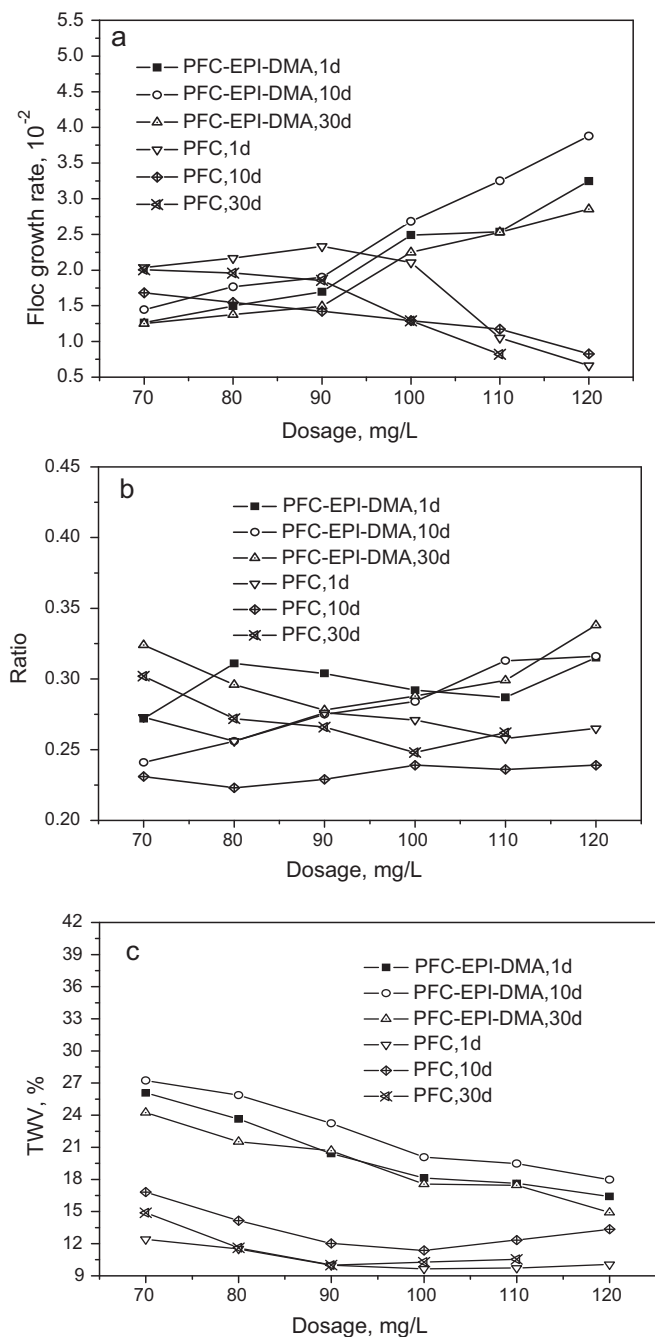


Fig. 5. Coagulation kinetics in R.R. 24 treatment.

narrower distribution of floc size [33]. For the treatment of R.R. 24 by PFC–EPI–DMA, charge neutralization occurred and thus insoluble flocs were formed. Then insoluble particles were adsorbed onto the available sites of polymer chains. Consequently, the size of the formed flocs was different, depending on several parameters, such as particle concentration, size of polymer chain, etc. Therefore, the produced flocs tended to have open structure and with a wide range of floc size under different mechanisms. On the other hand, the main mechanism in the treatment of R.R. 24 by PFC was charge neutralization and thus the formed flocs had less variance in the distribution of floc size.

The impact of dosage and aging period on the three parameters for the treatment of R.B. 14 is shown in Fig. 6. When PFC was used, floc growth rate increased with increasing dosage. However, floc growth rates were generally the same under the condition of

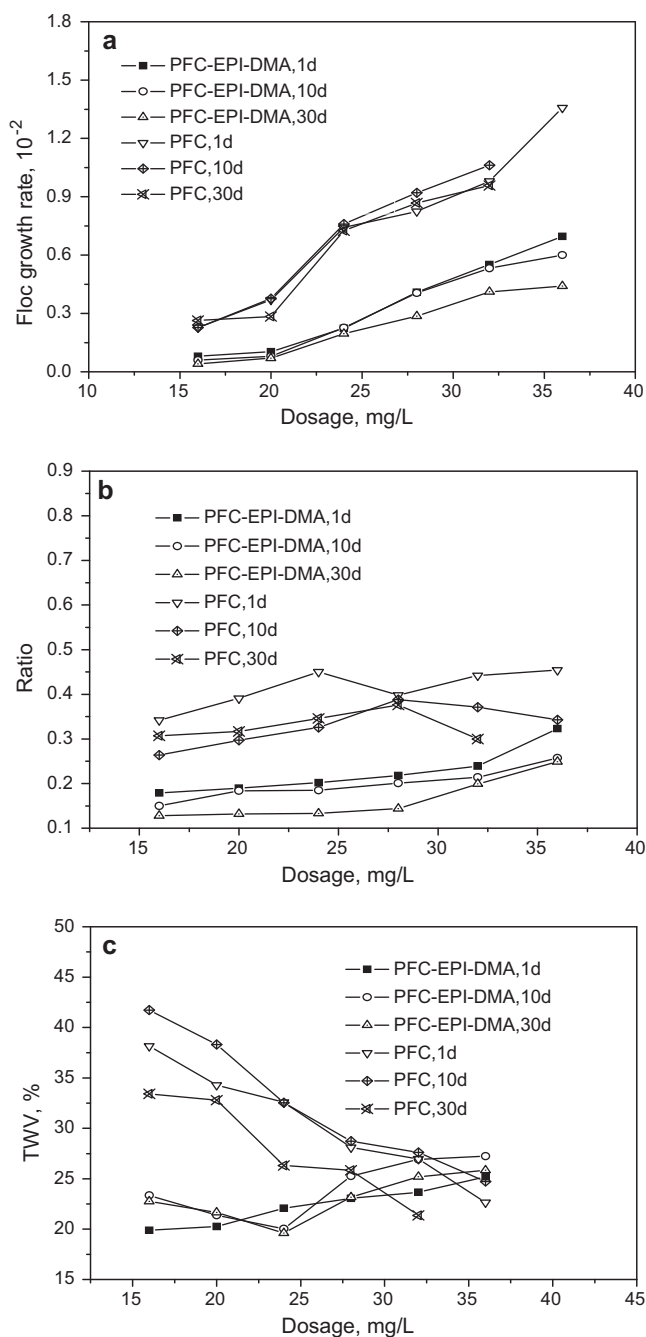


Fig. 6. Coagulation kinetics in R.B. 14 treatment.

different aging periods. PFC₁ got the highest Ratio values followed by PFC₃₀ and PFC₁₀ in the dosage range of 16–24 mg/L. It was also observed that there was a little difference in Ratio between PFC₁₀ and PFC₃₀. However, Ratio values treated by PFC decreased with the increase of aging period in the dosage range of 28–36 mg/L, which indicated that the R.B. 14 removal by PFC decreased with the increase of aging period. As revealed in Fig. 6c, TWV decreased with the increase of dosage, which meant that tighter and more uniform flocs were formed as the dosage increased. With different aging periods of PFC, TWV values were in the following order: PFC₁₀ > PFC₁ > PFC₃₀, which was not consistent with the order of the R.B. 14 removal by PFC.

For the treatment of R.B. 14 by PFC–EPI–DMA, both floc growth rate and Ratio increased with increasing dosage, which indicated that it took less time for coagulants to aggregate larger flocs and

thus better color removal efficiency was obtained with the increase of dosage. Nevertheless, both floc growth rate and Ratio decreased with increasing aging period of PFC–EPI–DMA, which indicated that it took more time to aggregate smaller flocs and then color removal efficiency decreased as aging period increased. For R.R. 24 treated by PFC–E₁, TWV increased with the increase of dosage. However, TWV of PFC–E₁₀ and PFC–E₃₀ decreased within the dosage range 16–24 mg/L, but increased when the dosage was higher than 24 mg/L. Within the tested dosage range except 24 mg/L, TWV value by PFC–E₁₀ was the highest followed those by PFC–E₃₀ and PFC–E₁.

For the treatment of R.B. 14 solution, the three parameters of PFC–EPI–DMA were generally lower than those of PFC. Compared with PFC, lower floc growth rate and Ratio value of PFC–EPI–DMA indicated that it took more time to aggregate smaller flocs and thus worse color removal efficiency was obtained, which was not consistent with the result of R.B. 14 removal efficiency obtained above. However, TWV of PFC–EPI–DMA was almost lower than that of PFC, which implied that a narrower range of floc size existed in the R.B. 14 treatment by PFC–EPI–DMA and thus the performance of sedimentation may be enhanced. As mentioned above, TWV can also be used to interpret the coagulation mechanism. A wider range of floc size formed by PFC may represent that PFC removed R.B. 14 by different mechanisms. As other researchers have observed, PFC contains a range of pre-formed Fe (III) hydrolysis species which may affect the behaviors in coagulation [34]. Fe (III) monomer can remove particles by charge neutralization. Fe (III) polymer can adsorb particles via their negatively charged surface by bridging. Fe(OH)₃ and Fe(OH)₄[−] remove particles by bridging and sweeping. Consequently, various coagulation mechanisms occurred when PFC was used. Hence, floc size by PFC was in a wider range which indicated that PFC removed R.B. 14 by charge neutralization and adsorption/bridging. On the other hand, a narrower range of floc size occurred when treated by PFC–EPI–DMA, which indicated that tighter and more condensed flocs were produced by PFC–EPI–DMA. Charge neutralization was the predominant mechanism at the low dosage of coagulant. A previous study suggested that flocs formed under charge neutralization mechanism were more condensed with a narrower distribution of floc size than those formed under sweep and bridging mechanism [33]. Because of the high cationicity of EPI–DMA, the charge neutralization ability of PFC–EPI–DMA was higher than that of PFC, which indicated that the distribution of floc size by PFC–EPI–DMA was narrower than that by PFC for the removal of R.B. 14.

4. Conclusions

- (1) In PFC–EPI–DMA and PFC coagulants, the content of both Fe_a and Fe_b decreased, whereas the content of Fe_c increased with increasing aging period. Compared to PFC, PFC–EPI–DMA had higher content of Fe_a but lower content of Fe_b and Fe_c at the same aging period.
- (2) The zeta potential of PFC–EPI–DMA was much higher than that of PFC at the same pH. As the increase of aging period, the zeta potentials of PFC–EPI–DMA and PFC decreased within the tested pH range.
- (3) Compared to R.R. 24, R.B. 14 could be more easily removed by coagulation. For R.R. 24 treatment, the color removal efficiency treated by PFC–EPI–DMA decreased, whereas that treated by PFC was almost the same with the increase of aging period. For both PFC–EPI–DMA and PFC, the color removal efficiency for the treatment of R.B. 14 solution decreased with increasing aging period. For the treatment of R.R. 24 and R.B. 14 by PFC–EPI–DMA and PFC, charge neutralization mechanism was the dominant mechanism and adsorption/bridging mechanism was also evident.

- (4) For the treatment of R.R. 24, both floc growth rate and Ratio of PFC–EPI–DMA were higher than those of PFC when the dosage was not less than 100 mg/L. Within the tested dosage range, TWV of PFC–EPI–DMA was higher than that of PFC. As aging period increased, the orders of floc growth rate, Ratio and TWV treated by two coagulants were not consistent with the orders of their color removal performances.
- (5) For the treatment of R.B. 14, floc growth rate, Ratio and TWV of PFC–EPI–DMA were generally lower than those of PFC. For the treatment of PFC, floc growth rates were almost the same with the increase of aging period. The impact of aging period on Ratio differed within different dosage ranges. And TWV values were in the following order: PFC₁₀ > PFC₁ > PFC₃₀. Both floc growth rate and Ratio treated by PFC–EPI–DMA decreased as aging period increased. However, TWV values were almost in the following order: PFC–E₁₀ > PFC–E₃₀ > PFC–E₁.

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