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Preparation and optimization of inorganic-organic composite coagulant for enhancing treatment of textile wastewater

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ABSTRACT

Inorganic-organic composite coagulants have good application prospects in textile wastewater treatment due to their favorable properties. However, a comprehensive optimization of these composites is still desired for environmental and economical purposes. To provide a valid comparison of typical inorganic/organic composite coagulants and to optimize the coagulation efficiency for textile wastewater treatment, in this paper, four different kinds of typical inorganic-organic composite coagulants were prepared and tested for their efficiencies of treating textile wastewater. As a result, a starch-based composite PAFGS (polyaluminum ferric chloride-grafted starch with acrylamide and dimethyl diallyl ammonium chloride) achieved the best efficiency. The Al/Fe molar ratio and the basicity of PAFGS were further optimized. The results showed that reactive dye blue KN-R removal efficiency of the optimized PAFGS could reach 97.2% at an Al + Fe dosage of 2.4 mmol/L. Large positive charges of the inorganic component and a branchy structure of the organic polymer were significant to improve the reactive dye removal of the composites. PAFGS also exhibited strong abilities of removing turbidity and dissolved organic matters from textile wastewater. Moreover, the composite coagulant significantly reduced chemical dosage compared with conventional coagulation/flocculation. The optimized PAFGS proved promising in textile wastewater treatment as a starch-based material with little environmental risk and high performance.

Keywords: Composite coagulants; Textile wastewater; Optimization; Starch graft copolymerization

1. Introduction

Textile wastewater is a typical industrial wastewater characterized with large volume and complex constituents [1–3]. Among available processes for textile wastewater treatment, coagulation is widely applied due to its cost effectiveness [4]. Recently, inorganic-organic composite coagulants are reported to have better coagulation performances in wastewater treatment than individual coagulants because of the synergistic effect of their components [5]. For instance, the mixing of inorganic Al species and organic polyelectrolyte in one polymeric matrix can induce hydrogen bonding and enhance bridging effect [6]. Using composites can also simplify dosing facilities compared with conventional separated coagulation/flocculation process [7]. Therefore, inorganic-organic composite coagulants have good application prospects in textile wastewater treatment. However, a comparison and optimization of these composite coagulants is required before their applications to optimize the coagulation efficiency and to reduce chemical dosage and sludge production [8].

A variety of inorganic and organic components have been used to prepare composite coagulants. Inorganic components are generally metallic salts, and the most common ones are polymeric Al and Fe salts [9], such as polyaluminum chloride (PAC). As pre-hydrolyzed coagulants, polymeric coagulants are more effective and less pH sensitive than simple inorganic salts [10]. Moreover, Al and Fe salts have strong abilities of decolorization [9]. As for organic components, the most commonly used ones are polyacrylamide (PAM). Another typical polymer is cationic poly-dimethyl

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diallyl ammonium chloride (PDM) [11]. Natural polymers such as modified chitosan and starch are often applied as eco-friendly organic components [12,13]. However, although various inorganic-organic composite coagulants have been prepared from these components, a valid comparison of the composites was unavailable. The unified preparation parameters and application conditions of these composites in different literatures provide limited comparability [14].

The aim of the study is to provide a valid comparison of inorganic-organic composite coagulants and to optimize the coagulation efficiency for textile wastewater treatment. Four organic polymers, PAM, PDM, the copolymer of acrylamide (AM), and diallyl dimethyl ammonium chloride (PAD), and grafted starch with AM and diallyl dimethyl ammonium chloride monomers (GS) were composited with inorganic polyaluminum ferric chloride (PAFC), respectively, in the study. PAFC was chosen previously as the inorganic component because it proved to be highly effective with both the advantages of polymeric Al and Fe salts [15]. The chosen four organic polymers can represent both synthetic and natural polymers. These inorganic and organic ingredients are all common and accessible materials, which are convenient for their applications. The composites were compared and applied to treat textile wastewater-containing reactive dyes. The best performer of the composites was selected out and further optimized for its important preparation parameters including Al/Fe molar ratio and basicity (i.e. OH/(Al + Fe)).

2. Materials and methods

2.1. Materials

Dyeing auxiliaries for the synthesis of textile wastewater were obtained directly from Kunfeng Textile Co., Ltd., Jiangsu, China, including degreaser, penetrant, detergent, anti-creasing agent, levelling agent, and soaping agent. Other chemicals were analytical reagents and obtained from National Pharmaceutical Group Corporation, Beijing, China, including PAM (non-ionic), PDM, PAD, potato starch, PAFC, NaOH, $FeCl_3$, and $AlCl_3$. The molecular weights of the organic polymers are shown in Table 1. All chemicals were used without further purification.

2.2. Synthesis and characteristics of grafted starch

The grafted starch was synthesized by starch copolymerization with AM and diallyl dimethyl ammonium chloride (DMDAAC) monomers. A method using $KMnO_4$, HIO_4, and H_2SO_4 as initiators was adopted. The method achieved a favorable efficiency of grafting AM onto starch and had been described in detail earlier [16]. AM and DMDAAC were both added in the graft reaction under 70°C, with an AM/DMDAAC weight ratio of 1:1 and a monomer/starch weight ratio of 2:1. The grafting of AM and DMDAAC monomers onto the starch backbone was intended to increase the molecular weight and cationic degree of the polymer. By pre-experiments, one graft copolymer with best properties was selected, which had a cationic degree of 1.46 meq/g and a viscosity of 3.0 mPa s (0.8 g/L aqueous solution). Morphology was then tested by Scanning Electronic Microscope (SEM) (JSM-6460LV, JEOL, Japan).

Table 1
Molecular weights of organic polymers

Polymer	Molecular weight (kDa)
PAM	~10,000
PDM	100–200
PAD	~5,000
Potato starch	~14

2.3. Preparation of PAFC and composite coagulants

To prepare PAFC, NaOH solution (1 mol/L) was added dropwise to a mixture of $AlCl_3$ and $FeCl_3$ solution at 1 mL/min controlled by a peristaltic pump (BT100S-1, Leadfluid, China). The mixture was constantly stirred under 50°C until it became clarified. Then PAFC was aged for 24 h under ambient temperature to stabilize its polymeric species. For optimization, the effects of its Al/Fe molar ratio and basicity on the coagulation performance were studied. The experimental variables and values of PAFC are shown in Table 2.

Composite coagulants were prepared by similar procedures as above. Organic components PAM, PDM, PAD, and GS aqueous solutions were added dropwise to PAFC solutions to form composite coagulants PAFAM, PAFDM, PAFAD, and PAFGS (polyaluminum ferric chloride-grafted starch with AM and dimethyl diallyl ammonium chloride), respectively. Four inorganic-organic composite coagulants were prepared. Each of these final solutions had organic polymers of 0.2 g/L and Al + Fe of 0.1 mol/L.

2.4. Preparation of textile wastewater

Two kinds of textile wastewater were applied in the study. They were single-dye solutions (100 mg/L) and synthetic textile wastewater. The types and characteristics of dyes used in the study are shown in Table 3. Reactive dyes are highly soluble dyes. Reactive brilliant blue KN-R is more difficult to be removed due to its higher solubility than other reactive dyes. Therefore, KN-R was mainly applied for the comparison and optimization of composites, in order to better distinguish the properties of composites. Disperse dyes are insoluble in water; therefore, they were used to test the coagulant efficiency of removing turbidity from water. The composition of synthetic textile wastewater is shown in Table 4. Involving

Table 2
Experimental variables and values for optimization of PAFC

Variables	Basicity (i.e. OH/(Al + Fe))	Al/Fe molar ratio
Values	0.5	9:1
	1.0	9:1
	1.5	10:0 (i.e. PAC)
		9:1
		7:3
		5:5
	2.0	9:1
	2.5	9:1

Table 3
Main characteristics of dyes used in the study

Dyes	Structural type	Water solubility (g/L)	Molecular weight (Da)	Number of sulfonic groups
Reactive red X-3B	Azo	80 (20°C)	615.33	2
Reactive brilliant blue KN-R	Anthraquinone	100 (20°C)	626.53	2
Reactive yellow M-3RE	Azo	100 (50°C)	880.17	3
Reactive dark blue M-2GE	Bis-azo	80 (50°C)	1,205.35	5
Reactive green KE-4B	Bis-azo	65 (50°C)	1,418.91	6
Disperse blue 2BLN	Anthraquinone	2×10^{-4} (25°C)	304.7	0
Disperse yellow E-3G	Heterocyclic	8×10^{-4} (25°C)	289.2	0

typical inorganic and organic pollutants from the overall textile processing, the composition is a comprehensive embodiment of the characteristics of textile wastewater [3].

2.5. Tests for coagulation performances

A multiple stirrer (MY3000-6M, Meiyu Co. Ltd., China) was used to conduct coagulation tests. Five hundred milliliters of raw wastewater was added to each jar. After addition of the composite coagulants, the mixture was stirred at 120 rpm for 1 min, then 80 rpm for 5 min, followed by 30 rpm for 15 min, and finally settled for 30 min. Turbidity was tested by a turbidimeter of surface scattered light (2100Q, HACH, USA). The dye removal efficiency was tested by UV spectrophotometry (DR5000, HACH, USA). Chemical oxygen demand (COD) was tested according to the Standard Methods for the Examination of Water and Wastewater [17].

2.6. Investigation of inorganic species distribution

Al and Fe polymeric species distributions were investigated by Ferron complexation timed spectrophotometry (DR5000, HACH, USA) [18]. Three species can be identified based on the different complex reaction rates between Ferron agent and different species. Species reacted with Ferron in 1 min were denoted as M_a (mononuclear species, e.g. $Al(OH)^{2+}$, $Fe(OH)_2^+$) and those over the next 3 h were M_b (mainly multinuclear species, e.g. $[Fe_2(OH)_2]^{4+}$, $[Al_8(OH)_{20}]^{4+}$). Unreactive species in 3 h were uncharged and precipitated species as M_c (e.g. $Al(OH)_3$) [19].

3. Results and discussion

3.1. Comparison of composite coagulants

The reactive dye KN-R removal efficiencies of the four different composite coagulants were compared. The results showed that PAFGS achieved the highest dye removal efficiency among the four composite coagulants (Fig. 1). The dye removal efficiencies of PAFDM and PAFAD were moderate and undistinguishable, while PAFC-PAM had a distinctly lower removal efficiency.

The preparation parameters of PAFCs in these composites were identical. Moreover, the inorganic species distributions

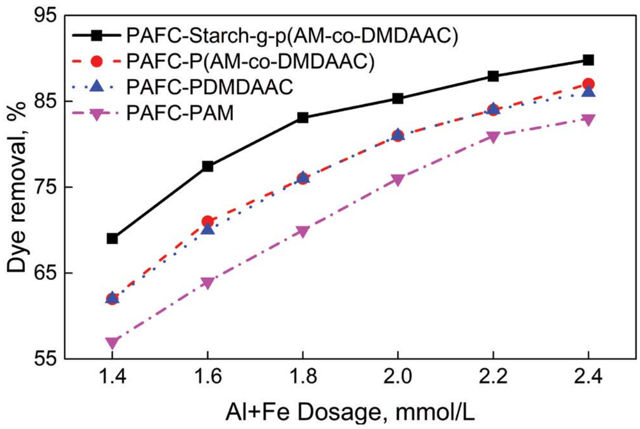

Fig. 1. Dye KN-R removal of different composite coagulants. Preparation parameters: Al/Fe = 9:1, basicity = 1.5.

Table 4
Composition of synthetic textile wastewater

Chemicals added	Concentration (mg/L)	Chemicals added	Concentration (mg/L)
Degreaser	40	Reactive red X-3B	30
Penetrant	40	Reactive brilliant blue KN-R	30
Detergent	40	Reactive yellow M-3RE	30
Anti-creasing agent	40	Reactive dark blue M-2GE	30
Levelling agent	100	Reactive green KE-4B	30
Soaping agent	40	NaOH	35
Na_2SO_4	1,200	$(NaPO_3)_6$	50
Na_2CO_3	50	$Na_3C_6H_5O_7$ Sodium citrate	10

given in Table 5 showed that the proportions of the species were not varied significantly in differet composite coagulants. This indicated that combination of PAFC with the four organic components had similar consequences on the species distribution. Therefore, the different performances of these composites in Fig. 1 were mainly attributed to their organic components.

The SEM images in Fig. 2 show that the grafted starch copolymer has a multibranched structure (Fig. 2(a)). The graft of extrinsic long chains onto the starch backbone contributed to a porous and cross-linking structure of the copolymer [20]. However, PAM has a linear structure (Fig. 2(b)). In fact, PDM and PAD also have linear structures. The branchy grafted starch had a larger surface area and fractal dimension than these linear polymers, enhancing the ability of aggregating particles and bridging effects [21,22]. Therefore, the favorable morphology of the grafted starch contributed to the better performance of PAFGS.

The dye removal efficiencies of PAFDM and PAFAD were difficult to distinguish as shown in Fig. 1. However, PAFDM led to higher residual turbidity of the supernatants than PAFAD, as shown in Fig. 3. This indicated a weaker settling ability of PAFDM. This phenomenon could be attributed to the lower molecular weight of PDM. Due to the strong mutual repulsion between cationic monomers, PDM has a relatively low degree of polymerization, and thus a low molecular weight (100–200 kDa), which is known as a restriction to its solid-liquid separation ability [21].

While PAFAM had a favorable settling ability (Fig. 3) because of the extremely high molecular weight of PAM (10,000 kDa), PAFAM was distinctly less efficient in dye removal than the other three composite coagulants (Fig. 1).

Table 5
Inorganic species distribution of different composite coagulants

Composite coagulants	M_a %	M_b %	M_c %
PAFGS	88.8	0.9	10.3
PAFAM	89.0	2.0	8.9
PAFDM	92.4	1.1	6.4
PAFAD	90.1	2.3	7.6

Preparation parameters: Al/Fe = 9:1, basicity = 1.5.

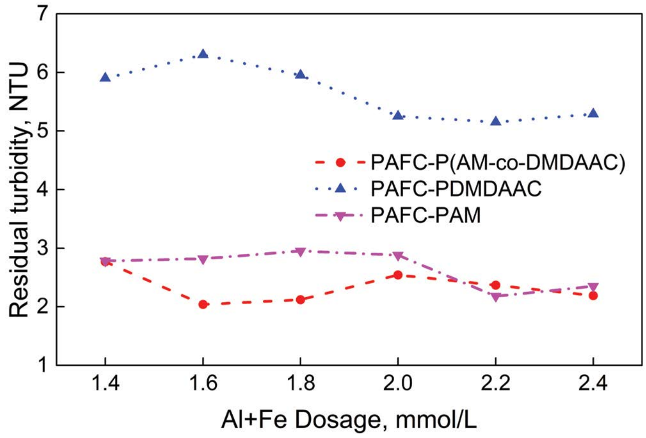

Fig. 3. Residual turbidity of supernatants using composite coagulants to treat KN-R solutions.

The inferior dye removal efficiency of PAFAM was attributed to the fact that non-ionic PAM carried no cationic charges like the other organic polymers. Since reactive blue KN-R is highly soluble and anionic due to its sulfonic groups (Table 1), the ionic adsorption of anionic dyes onto the cationic polymer would play an important role in the dye removal process [23]. More importantly, though, the result implied that when organic polymers were used to treat highly hydrophilic dissolved organic matters (DOM) such as reactive dyes, the significance of their molecular weights should not be overrated.

PAFAD exhibited both good settling ability (Fig. 3) and dye removal efficiency (Fig. 1) because it has the combined advantages of high molecular weight and cationic charges. Therefore, the superiority of these four composite coagulants for reactive dye KN-R removal was finally presented as follows: PAFGS > PAFAD > PAFDM > PAFAM. Considering further the good biodegradability of the grafted starch, PAFGS could be a promising composite coagulant for textile wastewater treatment.

3.2. Optimization of PAFGS

PAFGS was selected out and its inorganic component PAFC was optimized to further enhance its coagulation

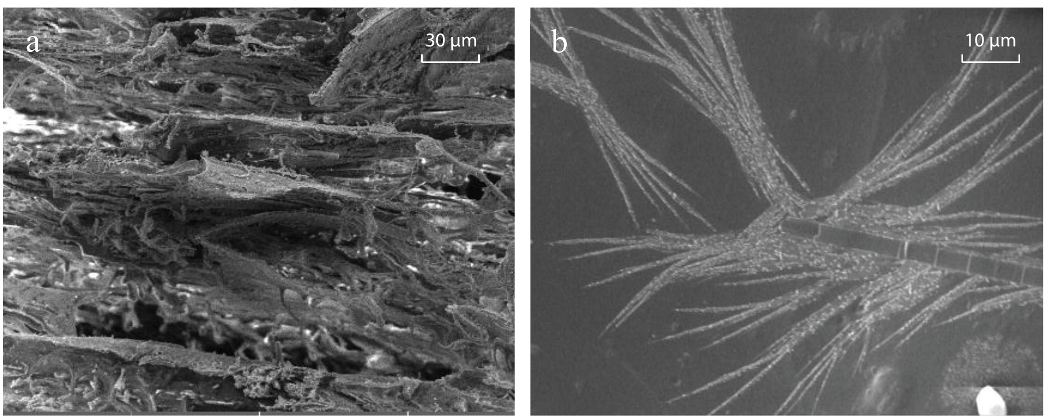

Fig. 2. SEM images of the grafted starch (a) and PAM (b).

ability. Al/Fe molar ratio and basicity are the most important preparation parameters because they significantly influence the polymeric species distribution of PAFC and thus affect the coagulation performance [15].

The effects of basicity on dye removal efficiency and polymeric species distribution are exhibited in Fig. 4. With the increase of basicity from 0.5 to 2.5, dye removal efficiency of PAFGS was decreased, which was also accompanied by the decrease of M_a species and the increase of M_b and M_c species.

The effect of basicity on the polymeric species distribution was consistent with other studies. The polymerization degree of metallic salts increased with the addition of hydroxyls, causing species to transform from M_a to M_b and then to M_c [24]. M_b was mainly formed when basicity increased from 0.5 to 2.0, and then M_c was mainly formed when basicity increased from 2.0 to 2.5. Meanwhile, as basicity increased to 2.5, a significant decrease of dye removal efficiency was observed, while the other four curves (basicity from 0.5 to 2.0) were relatively close (Fig. 4). There was therefore a clear cause-and-effect relationship between the increase of M_c and the decline of removal efficiency. Therefore, M_c species and its net-sweeping function proved ineffective in reactive dye removal, while positively charged M_a and M_b species were main functional species.

Though higher total amounts of M_a and M_b contributed to better coagulation performance, however, the dye removal efficiency was negatively correlated with the content of M_b (Fig. 4). This was inconsistent with the conclusions from other studies that the major effective species in coagulation was M_b [12]. For instance, Gao et al. found that PAC-PDM with a basicity of 1.5 achieved the best efficiency for oil field wastewater treatment as the M_b content reached the highest [12]. This inconsistency could be attributed to the fact that the reactive dyes are highly hydrophilic substances different from conventional colloidal coagulation objects [25]. This indicated that compared with colloid removal, reactive dye removal was more closely related to the total amount of charges (i.e. M_a + M_b) and had less to do with the degree of polymerization of the inorganic components. The optimization of different coagulants for treating different objects could yield different results, and thus, specified and targeted optimization was necessary [14]. Consequently, the optimized basicity of PAFGS for reactive blue KN-R removal was found to be 0.5.

Al/Fe molar ratio of PAFGS was then optimized. The effects of Al/Fe molar ratio on the coagulation performance and species distribution were tested and shown in Fig. 5. The dye removal efficiency increased with the increase of Al/Fe, up to 92.7% when there was completely no Fe in the inorganic component (i.e., PAC). The increasing Al content increased the total amount of positively charged species in PAFGS, thereby increasing the dye removal efficiency. This was in agreement with the previous discussion. However, the dye removal efficiency was no more negatively correlated with the content of M_b, but a reverse phenomenon was observed. This confirmed that neither M_a nor M_b alone was dominant in reactive dye removal, while the total amount of positive charges was decisive.

The addition of Fe increased the relative proportion of M_c species (Fig. 5(b)). This was because Fe(III) had a stronger ionization potential and a greater inclination to polymerize with hydroxyls than Al [25]. The results indicated that the polymeric species of Al played a more important role than Fe species in reactive dye removal. However, although the increase of Fe reduced the dye removal efficiency, the residual turbidity of the supernatants increased largely without the addition of Fe (Fig. 5(a)). This suggested that moderate addition of Fe was necessary to improve the settling ability of the composite coagulant. This was because flocs formed by Fe species were more compact and easier to settle down than those by Al species [26]. Besides, changing Al/Fe from 10:0 to 9:1, the dye removal efficiency was not declined significantly. Therefore, Al/Fe molar ratio at 9:1 proved to be the optimal level.

Finally, the optimized PAFGS had a basicity of 0.5 and Al/Fe molar ratio of 9:1. To test the validity of the optimization, the coagulation performances of the optimized laboratory-made PAFCs were compared with those of commercial PAFCs, as shown in Fig. 6. The dye removal efficiencies of the optimized PAFCs were significantly improved compared with the commercial ones. Therefore, the optimization of PAFC was rewarding and necessary for the composite coagulant to be applied in textile wastewater treatment. Besides, the dye removal efficiency of laboratory-made PAFC was lower than the composite coagulant, which was due to

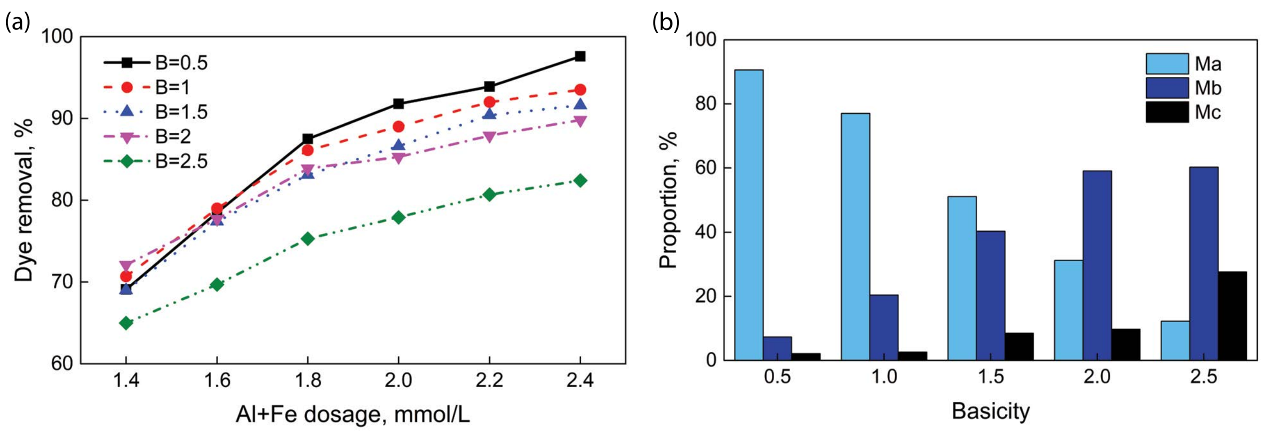

Fig. 4. The effects of basicity of PAFGS on KN-R removal efficiency (a) and its polymeric species distribution (b). Al/Fe = 9:1.

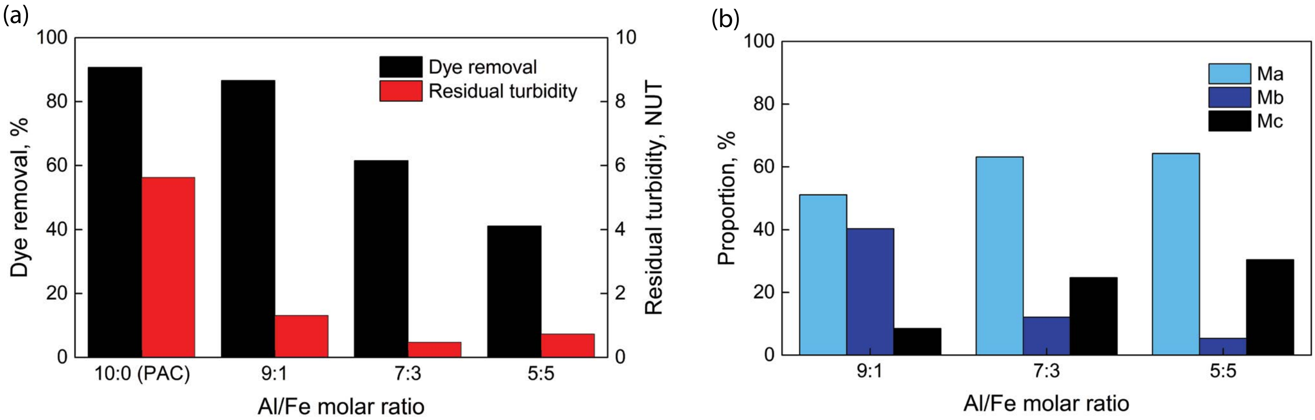

Fig. 5. The effects of Al/Fe molar ratio on KN-R removal (a) and species distribution of PAFGS (b). Dosage: Al + Fe = 2.0 mmol/L. Basicity = 1.5.

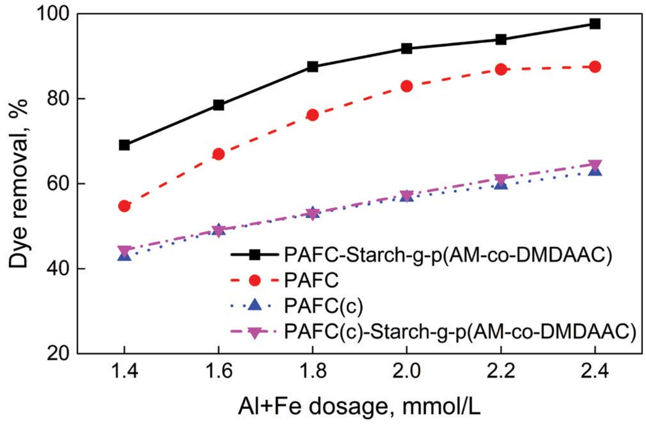

Fig. 6. Comparison of the optimized laboratory-made PAFC with commercial PAFC (CPAFC) and the composite (CPAFGS) for KN-R removal.

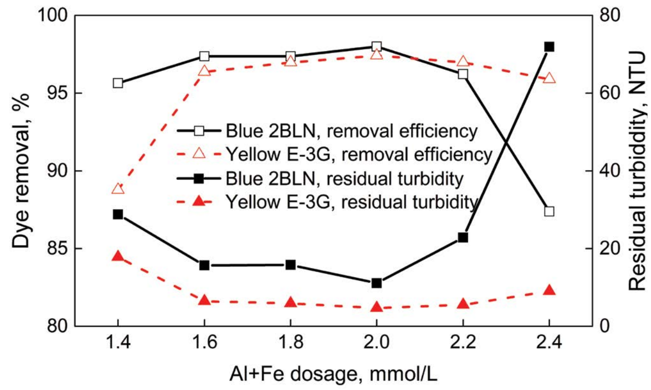

Fig. 7. Disperse dye 2BLN and E-3G removal of the optimized PAFGS.

the lack of bridging effect and cationic charges of the organic polymer. This indicated the importance of cationic polymers in reactive dye removal. After the optimization of PAFC, the reactive dye removal efficiency by PAFGS could reach up to 97.2% when Al + Fe dosage was 2.4 mmol/L.

3.3. Performances treating other dyes and synthetic textile wastewater

Disperse dyes, other reactive dyes than blue KN-R solutions, and synthetic textile wastewater were used as raw wastewater in order to further test the coagulation ability of the composite. Fig. 7 exhibits disperse blue 2BLN and disperse yellow E-3G removal of the optimized PAFGS. The result showed that the composite coagulant had high removal efficiencies above 95% for both disperse dyes. However, at high Al + Fe dosage of 2.4 mmol/L, its performance for blue 2BLN removal exhibited a significant decrease, but the performance for yellow E-3G removal maintained stable. The unstable effect in 2BLN removal was due to the restabilized flocs with excessive charges on their surfaces. This phenomenon was common in other researches [10]. However, high dosage is neither desired nor necessary in practice. Using the composite coagulant, a high removal efficiency was achieved at a very low Al + Fe dosage of 1.6 mmol/L. As disperse dyes mostly form suspensions due to the lack of hydrophilic groups (Table 1), the effectiveness of removing disperse dyes indicated a good ability of the composite coagulant to remove turbidity from wastewater.

Disperse dyes and reactive dyes are both largely used in textile processes, while the latter are more difficult to be removed by coagulation due to their higher solubilities. Fig. 8 shows that the composite coagulant had high removal efficiencies for other typical reactive dyes than blue KN-R. These dyes are azo or bis-azo dyes, while blue KN-R is anthraquinone dye (Table 1). The results therefore indicated that the optimized composite coagulant was suitable to treat different dyes with varied structural types. Besides, the green KE-4B removal efficiency was found to be higher than the other dyes. This was attributed to its lower solubility, which was consistent with other studies suggesting that color removal of coagulation decreased with the increase of dye solubility [27]. However, since ionic adsorption played such an important role in the removing process, the higher number of anionic groups in green KE-4B than other dyes (Table 1) would also contribute to its higher removal through

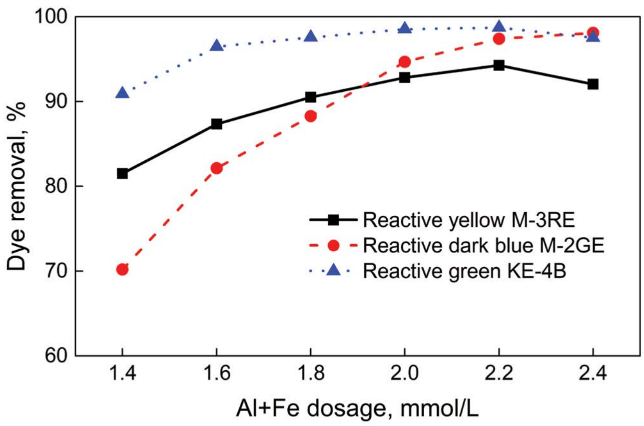

Fig. 8. Reactive dye removal efficiencies of the optimized PAFGS.

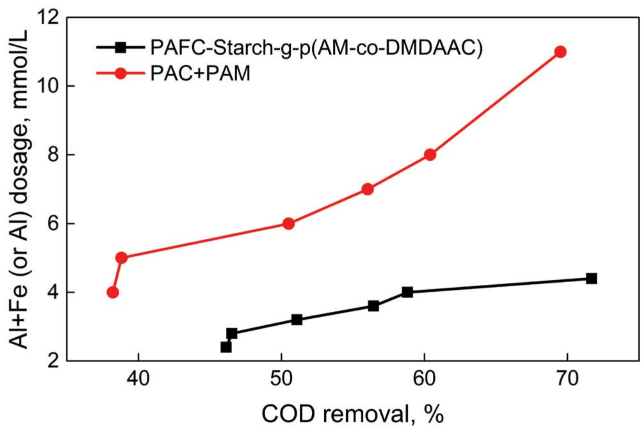

Fig. 9. Comparison of PAFGS with conventional coagulation-flocculation process using PAC and PAM to treat synthetic textile wastewater.

stronger ionic interactions with the coagulants. Showing good ability to remove various highly soluble reactive dyes, the optimized PAFGS has the potential to successfully treat DOM, the removing of which has been a longstanding problem in coagulation.

In addition to dyes, textile wastewater has many other organic and inorganic pollutants. The COD removal efficiency of PAFGS for synthetic textile wastewater treatment was compared with conventional coagulation-flocculation method (Fig. 9). In a separate coagulation-flocculation process, PAC was added first as coagulant and PAM (5 mg/L) was followed as coagulant aid. It was found that necessary Al + Fe dosage of the composite coagulant was significantly less than the Al dosage of PAC to achieve the same COD removal efficiency. Especially, only 4.4 mmol/L Al + Fe dosage was required to achieve 70% COD removal when using the composite coagulant, while it needed 11 mmol/L Al for the conventional method to achieve the same removal level. This showed that PAFGS could significantly lower the dosage of inorganic salts. Moreover, since Al was not recommended to be used largely due to its long-term toxicity [28, 29], PAFGS could be a promising substitution for common Al-based coagulant as it could significantly lower Al dosage and meanwhile maintain a high performance.

4. Conclusions

Four inorganic-organic composite coagulants PAFGS, PAFAM, PAFDM, and PAFAD were compared for textile wastewater treatment. PAFGS was selected out as the best-performed composite coagulant. After optimization, the basicity and the Al/Fe molar ratio of PAFGS were determined at 0.5 and 9, respectively. The composite exhibited strong abilities to remove color, turbidity, and DOM from textile wastewater. It was suggested that during reactive dye removal processes, large positive charges of inorganic component and a branchy structure of organic component were essential. PAFGS was an effective coagulant with high biodegradability, which could significantly lower chemical dosage, sludge amount, and also the risk of the sludge to the environment.

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