

The characterization and flocculation efficiency of composite flocculant iron salts–polydimethyldiallylammonium chloride

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Abstract

In this study, new composite flocculants were prepared from iron salts and polydimethyldiallylammonium chloride (PDMDAAC). The Fe(III) species and zeta potential of the composite poly-ferric chloride (PFC) and PDMDAAC flocculant (PFC–PDMDAAC) and PFC were measured by a timed complexation spectroscopy method and the Malvern Zetasizer 3000, respectively. The results showed that when PDMDAAC fraction (W_p) was 7.0%, PFC–PDMDAAC contained the smallest content of Fe_c and had the highest zeta potential. The flocculation efficiency of PFC–PDMDAAC and the composite $FeCl_3$ and PDMDAAC flocculant ($FeCl_3$ –PDMDAAC) for treating actual surface water or wastewater samples was compared with that of $FeCl_3$, PFC and PDMDAAC. The results showed that for surface water from Yellow River, PFC–PDMDAAC produced the highest flocculation efficiency, while for papermaking intermediate wastewater, the flocculation efficiency of $FeCl_3$ –PDMDAAC was the highest.

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Keywords: Composite flocculant; Poly-ferric chloride; Fe(III) species; Zeta potential; Flocculation efficiency

1. Introduction

Coagulation/flocculation is a widely used process for particle removal in water and wastewater treatment. In recent years, various flocculant categories have been developed including inorganic flocculants, organic flocculants and composite flocculants. Because of their superior efficiency compared with traditional inorganic flocculants, and lower cost compared with organic flocculants, composite flocculants have been extensively studied and applied to water and wastewater treatment systems today [1]. The main method for preparing composite flocculants is adding other additive components to inorganic flocculants [2]. The goals of this method are to enhance the aggregating power of flocculants by increase the ratio of effective component and positive electric charge of flocculants. The first commercial composite flocculants [1] used colloidal silicates to combine cationic flocculants. Composites with anionic silicates show improved flocculation and aggregation [3], but their merits are partly offset by the reduced charge neutralizing ability of the original cationic inorganic polymer flocculants [4]. In principle, composing cationic inorganic flocculants with

cationic organic flocculants should be more effective in dealing with negatively charged contaminants, such as clay, dye, humic acid. In the traditional method of using inorganic–organic composite flocculants, inorganic flocculant and organic flocculant are added to wastewater, separately [14]. This traditional inorganic–organic composite flocculant needs two flocculant addition systems which will increase the cost of water treatment. So, new method of using composite flocculant, in which inorganic coagulant is premixed with organic coagulant before the coagulant is used to treat water, has been developed [15]. However, very limited work has been reported on the characterization and flocculation behavior of new inorganic–organic composite flocculants.

In this study, new composite flocculants, which was composed from iron salts and polydimethyldiallylammonium chloride (PDMDAAC), were investigated. Iron salts is not like aluminum coagulants to be harmful to human and living organisms, therefore, iron salts has gained much attention as the flocculants choice to destabilize colloidal and suspend solids. The iron salts are categorized in mono- and poly-ferric salts. When mono-ferric salts such as $FeCl_3$ is added directly into raw water, Fe(III) ions hydrolyze rapidly, producing a range of Fe(III) species which play an essential role in flocculation [16]. Poly-ferric salts are a series of pre-hydrolysable flocculants, which can be controlled to a specific hydrolysable

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degree during manufacturing. Poly-ferric chloride (PFC) is a relatively new polymeric coagulant, which contains a range of pre-formed hydrolyzed Fe(III) species with high positive charge and medium to large molecular weights [5]. PFC has been shown to be more efficient than the traditional ferric flocculants for removing turbidity, algae, color and natural organic matter at the certain conditions [6]. Moreover, PFC is also less corrosive than FeCl_3 [7]. Because of these advantages, PFC has been extensively studied and applied to water treatment systems in recent years. PDMDAAC, used either alone or in combination with ployaluminum chloride, has been reported to be effective in the flocculation of suspended particles, dyes, and oil in water [8,9].

The objectives of this study are to investigate the characteristics of composite ferric flocculants, including the Fe(III) species and zeta potential variation; to test the flocculation efficiency of composite ferric flocculants in comparison with FeCl_3 , PFC, PDMDAAC and the traditional ferric composite flocculants.

2. Materials and methods

2.1. Materials

The PFC used in this study was prepared in our laboratory. Stock FeCl_3 solutions of 7–9% by weight were prepared by dissolving $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (A.R.) in distilled water. Then, the FeCl_3 solutions were slowly mixed with chemically pure Na_2CO_3 powder to obtain the PFC solutions with desired $[\text{OH}^-]/[\text{Fe}]$ (B) values. Na_2HPO_4 (A.R.) was added to the PFC solution as a stabilizer ($[\text{Na}_2\text{HPO}_4]/[\text{Fe}] = 0.04$).

PDMDAAC was obtained directly from Bin Zhou Chemical Company, Shandong, China. A measured amount of PDMDAAC was injected into the stock solution of FeCl_3 and PFC with strong stirring to prepare the composite mono-ferric flocculants (FeCl_3 -PDMDAAC) and the composite poly-ferric flocculants (PFC-PDMDAAC), respectively. Three percentages (3.5%, 7.0% and 14%) of PDMDAAC by weight (W_p) in the flocculants were adopted. The characteristics of PFC, PFC-PDMDAAC and FeCl_3 -PDMDAAC are shown in Table 1.

2.2. Determination of Fe(III) speciation in PFC and PFC-PDMDAAC

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

iodoquinoline-5-sulphonic acid). This procedure has been used previously [10,11] to identify the nature of the Al or Fe flocculant species. Visible light absorbance is measured as a function of time at a wavelength of 600 nm (for Fe) to quantify the amount of metal complex formed. The Fe(III) species reacting with Ferron in 1 min is considered to be Fe(III) monomeric species (denoted as Fe_a), and the Fe(III) species reacting with Ferron over the next 3 h is considered to be Fe(III) polymeric species (denoted as Fe_b), and the unreactive Fe(III) species in 3 h is considered to be Fe(III) colloidal and precipitated species (denoted as Fe_c).

2.3. Determination of zeta potential

The Malvern Zetasizer 3000 was used to measure zeta potential of PFC and PFC-PDMDAAC. Experiments were performed at flocculant dosage of 5 mg/L as Fe. And pH of the flocculant 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.

2.4. Flocculation test procedures

All flocculation experiments were conducted in 1.0 L Plexi glass beakers using a conventional Jar-test apparatus (DC-506 Laboratory Stirrer). 500 mL water were dosed with different flocculants. The solutions were stirred rapidly at 120 rpm for 3 min during flocculant addition, and followed by slow stirring at 40 rpm for 12 min and sedimentation for 12 min. After sedimentation, supernatant samples were taken from a point of 3 cm below the water surface of the beaker for analysis. The dosages of different flocculants were calculated by the quantity of their effective component, i.e. PFC by Fe_2O_3 , PDMDAAC by its dry weight, and PFC-PDMDAAC by Fe_2O_3 plus the dry weight of PDMDAAC.

3. Results and discussion

3.1. Characterization of flocculants

FeCl_3 plays flocculation function in water after hydrolyzing to a range of Fe(III) species. This process is unable to control during dilution under the prevailing raw water conditions and in competition with other reactions. Therefore, characterization of pure FeCl_3 and FeCl_3 -PDMDAAC were not important for determining flocculation efficiency. Therefore, characterization of FeCl_3 and FeCl_3 -PDMDAAC was not measured in this study.

3.1.1. Chemical speciation of PFC and PFC-PDMDAAC

Fe-Ferron method was originally developed to investigate the speciation of pure iron salt solutions. Before the method was applied to the determination of iron species in PFC-PDMDAAC, it was necessary to study the effect of PDMDAAC on the method. The test was performed using five samples prepared with 20 mL Ferron reagent, PDMDAAC with viscosity (η) of 1.02 dL/g and distilled water in a 50 mL volumetric flask. The absorbance of the samples at 600 nm, in which the concentration of PDMDAAC was 0, 2, 4, 6, 8 and 10.0 mg/L, was 0.051, 0.050, 0.048,

Table 1
Characteristic of PFC, PFC-PDMDAAC and FeCl_3 -PDMDAAC

No.	Flocculant	W_p	$W_{\text{Fe}_2\text{O}_3}$	B	pH
1	PFC	0	7.12	1.0	0.80
2	PFC-PDMDAAC	3.5	6.91	1.0	0.82
3	PFC-PDMDAAC	7.0	6.62	1.0	0.83
4	PFC-PDMDAAC	14.0	6.12	1.0	0.86
5	FeCl_3 -PDMDAAC	3.5	7.16	–	0.36
6	FeCl_3 -PDMDAAC	7.0	6.89	–	0.37
7	FeCl_3 -PDMDAAC	14.0	6.44	–	0.39

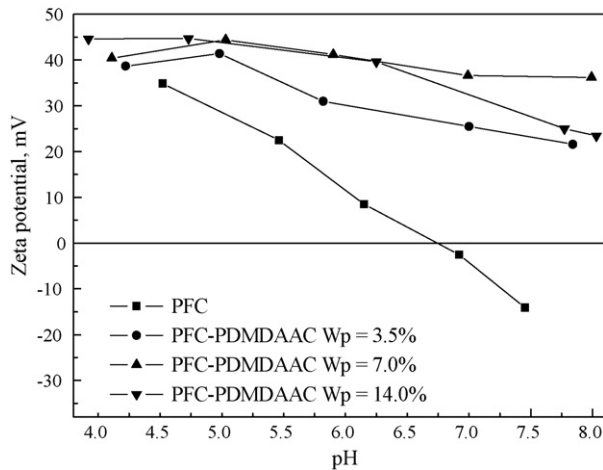


Fig. 2. Variations of the zeta potential of PFC–PDMDAAC and PFC with the change of pH.

of PFC–PDMDAAC at $W_p = 14.0\%$ was the highest among all three percentages. At $pH > 5.0$, the zeta potential of PFC–PDMDAAC at $W_p = 7.0\%$ was the highest among all the three percentages.

The species in PFC–PDMDAAC at $W_p = 14.0\%$ were predominantly polymers and colloids, Fe_c (Fig. 1). $Fe(III)$ polymers and colloids more easily transform to $Fe(OH)_3$ and lose positive charge with increasing pH than others $Fe(III)$ species [13]. When the pH of flocculant solution increases, the $Fe(III)$ species in PFC–PDMDAAC at $W_p = 14.0\%$ turn to $Fe(OH)_3$, and then would lose positive charge. Therefore the zeta potential of PFC–PDMDAAC at $W_p = 14.0\%$ is lower than that of PFC–PDMDAAC at $W_p = 7.0\%$ when $pH > 5.0$.

3.2. Flocculation efficiency

Flocculation tests were performed using actual surface water or wastewater samples, and the effectiveness of composite ferric flocculants was compared with that of $FeCl_3$, PFC, PDMDAAC and the traditional ferric composite flocculants (Fig. 3).

3.2.1. Application of composite flocculants to treat surface water from Yellow River

Yellow River is the second largest river in China and is a very important water source for drinking, agriculture and industry beside the river. High-suspended solids (SS) and high turbidity characterize the raw water in the river. Test water was taken from the Jinan section of the river. The pH, water temperature, turbidity, COD_{Mn} and UV-254 of the sample were 8.12, 18.0 °C, 776 NTU, 6.23 mg/L and 0.311, respectively.

The results of treating the water of Yellow River by coagulants are shown in Fig. 4. The advantages of composite flocculants for treating the water of Yellow River are very evident. For example, the lowest residual turbidity, COD_{Mn} and UV-254 of PFC–PDMDAAC treatment is 1.15–NTU, 2.02 mg/L and 0.051 at the dosage of 3 mg/L, respectively, but the lowest residual turbidity, COD_{Mn} and UV-254 of PDMDAAC treatment is 2.36 NTU, 3.15 mg/L and 0.121 at the dosage of 3 mg/L, respec-

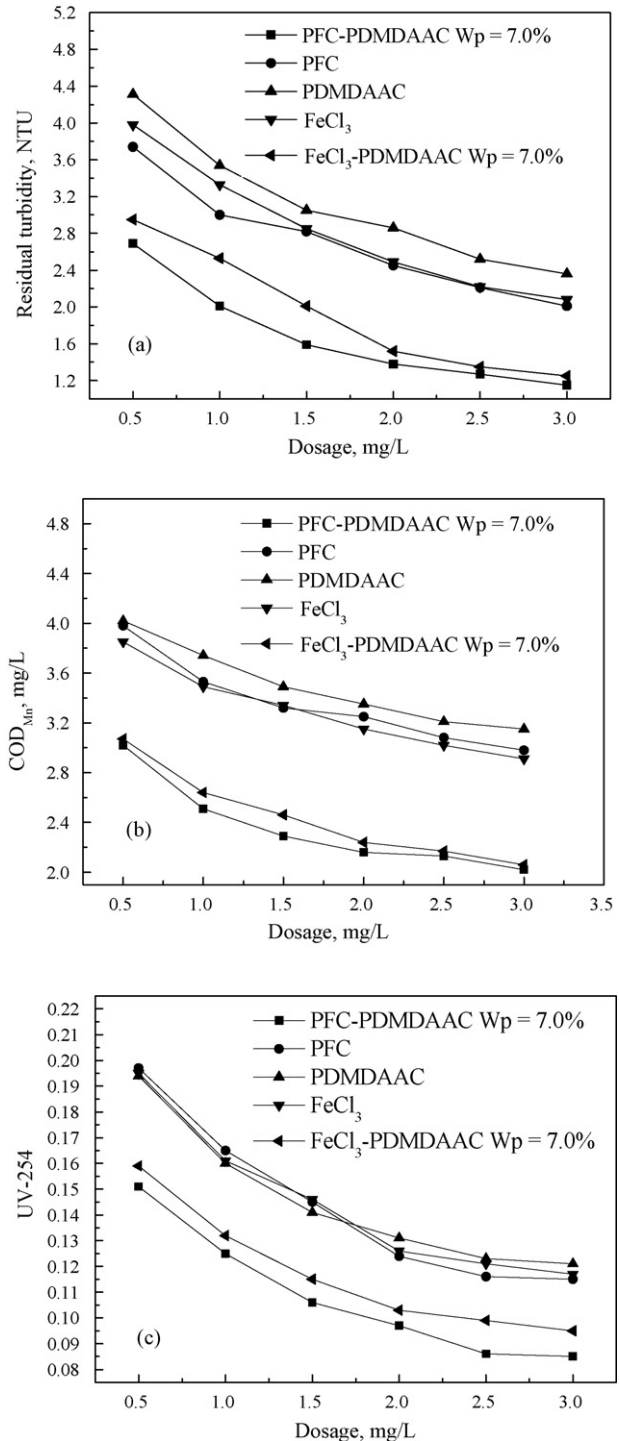


Fig. 3. (a–c) Variation of flocculation efficiency for water from Yellow River.

tively. These results indicate that the flocculation efficiency can be improved by the composite of inorganic ferric flocculants and PDMDAAC. For composite flocculants, the efficiency of PFC–PDMDAAC is higher than that of $FeCl_3$ –PDMDAAC. Therefore, PFC–PDMDAAC was chosen for further investigation of the flocculation efficiency of composite flocculants.

Because PDMDAAC are used traditionally with Fe flocculants or Al flocculants as flocculants aids which is separately added, in this study, the flocculation efficiency of

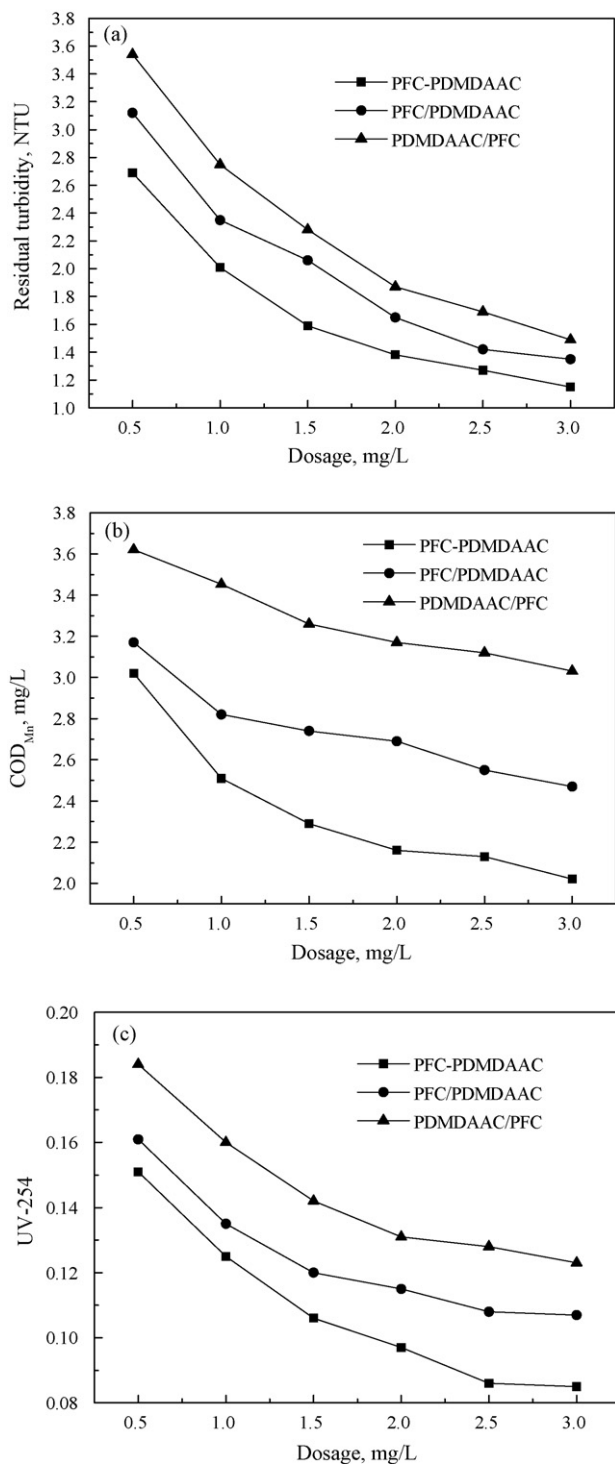


Fig. 4. (a–c) Comparison of PFC–PDMDAAC with the traditional ferric composite flocculants.

PFC–PDMDAAC ($W_p = 7.0\%$) was compared with that of the traditional ferric composite flocculants at equivalent dosages. Two different traditional ferric composite flocculants were chosen for comparing with PFC–PDMDAAC. The first traditional ferric composite flocculant was denoted as PFC/PDMDAAC. The flocculant procedure was that PFC with different dosages was first added to wastewater, and after 1 min, PDMDAAC, at a dosage of 14% of that of PFC, was added. The second

traditional ferric composite flocculant was denoted as PDM-DAAC/PFC. This flocculant procedure was the same as that of PFC/PDMDAAC except that the sequence of addition of PFC and PDMDAAC was reversed. The results are shown in Fig. 5. It can be seen that PFC–PDMDAAC is more efficient in removing contamination than PFC/PDMDAAC and PDM-DAAC/PFC. The results mentioned above indicate that PFC can cooperate with PDMDAAC in the PFC–PDMDAAC to remove contamination.

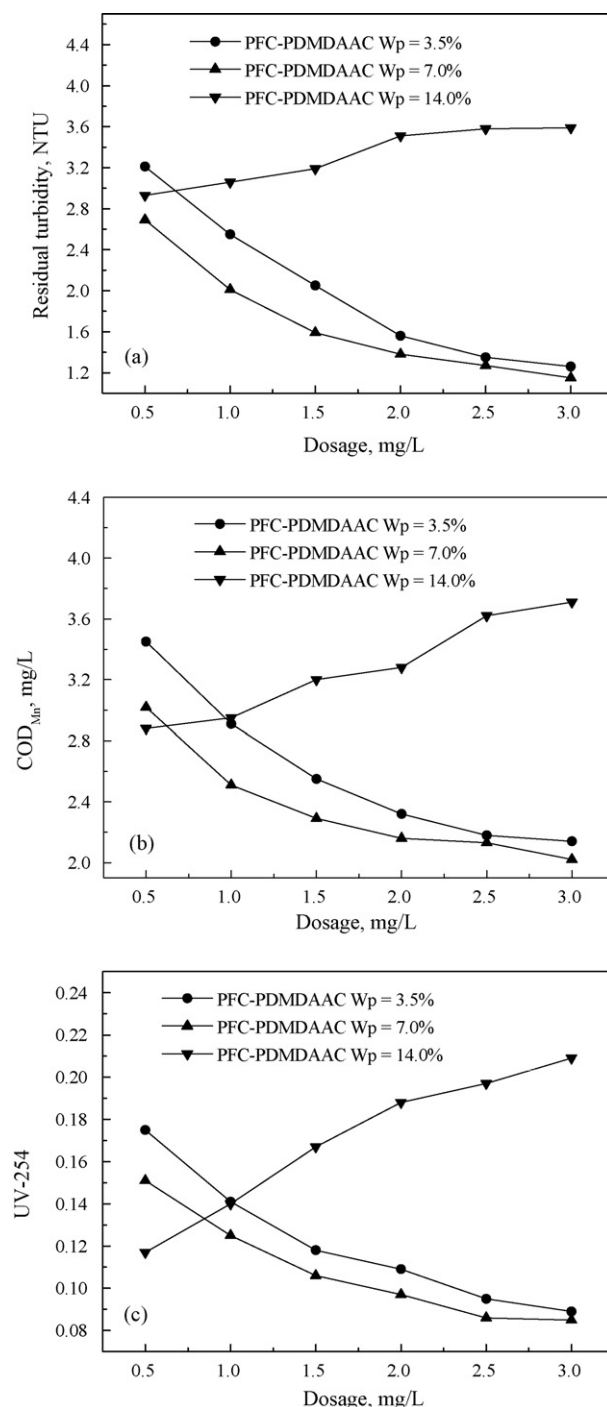


Fig. 5. (a–c) Effect of PDMDAAC fraction (W_p) on flocculation efficiency for water from Yellow River of PFC–PDMDAAC.

Fig. 5 shows the effect of W_p on flocculation efficiency by PFC–PDMDAAC. It can be seen that the optimum W_p is 7.0% for treating surface water of Yellow River. This can be explained by results in Figs. 1 and 2. At $W_p=7.0\%$, PFC–PDMDAAC contains the smallest content of Fe_c and has the highest zeta potential value, which gives very strong charge neutralization for negative-charged colloidal particles in waters. This indicates that PFC–PDMDAAC at $W_p=7.0\%$ contains the highest content of effective Fe(III) species and the highest charge neutralization ability, so it gives a good coagulating results. The flocculation efficiency of PFC–PDMDAAC with $W_p=14.0\%$ increases with the increase of dosage, which may be due to that the optimal dosage of PFC–PDMDAAC with $W_p=14.0\%$ is lower than 0.5 mg/L.

3.2.2. Application of composite flocculants to treat papermaking intermediate wastewater

Paper making industry generally discharges large volumes of wastewater, which contains high concentration of organic matter, non-biodegradable matter, and toxic substances etc. Papermaking intermediate wastewater to be tested was obtained from the Chenming Paper Making Company, Shandong Province, China, and its COD and pH are 2205 mg/L and 10.34, respectively.

COD removal for papermaking intermediate wastewater as a function of coagulant dosage is shown in Fig. 6. It can be seen that the efficiency of composite flocculants was superior to those achieved with individual flocculants. And treatment of papermaking intermediate wastewater by $FeCl_3$ –PDMDAAC yielded the highest flocculation efficiency. $FeCl_3$ –PDMDAAC can remove 57.2% of COD at a dosage of 160 mg/L, and further increase in dosage produce a slight increase in removal efficiency. For further investigation, $FeCl_3$ –PDMDAAC was selected as flocculant to carry out the experiments of the flocculation efficiency.

Two different traditionally used separate additions of $FeCl_3$ and PDMDAAC were chosen for comparing with $FeCl_3$ –PDMDAAC ($W_p=7.0\%$) at equivalent dosages. These tra-

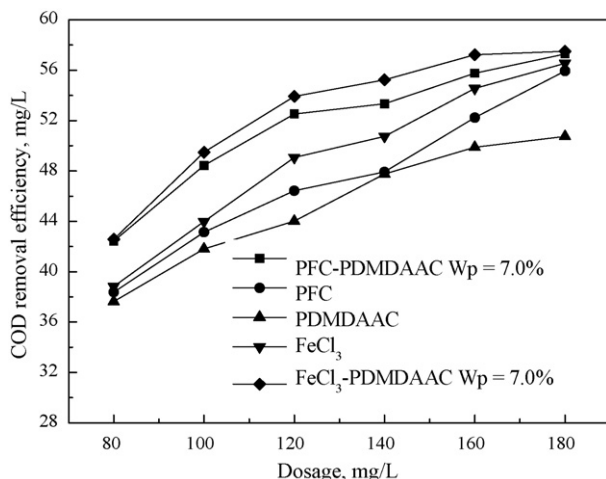


Fig. 6. Variation of flocculation efficiency for papermaking intermediate wastewater.

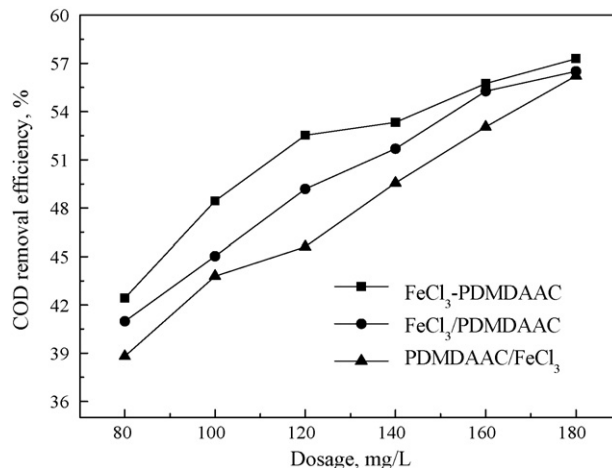


Fig. 7. Comparison of $FeCl_3$ –PDMDAAC with the traditional ferric composite flocculants.

ditional flocculant procedures were the same as that of PFC/PDMDAAC and PDMDAAC/PFC except that PFC was replaced by $FeCl_3$, and were denoted as $FeCl_3$ /PDMDAAC and PDMDAAC/ $FeCl_3$. The results are shown in Fig. 7. It can be seen that $FeCl_3$ –PDMDAAC is more efficient in removing contamination than $FeCl_3$ /PDMDAAC and PDMDAAC/ $FeCl_3$. This reconfirms that inorganic component can cooperate with organic component in the composite flocculant to remove contamination.

Fig. 8 shows the effect of W_p of $FeCl_3$ –PDMDAAC on COD removal efficiency. It can be seen that W_p has significant impact on the COD removal efficiency. For $W_p=3.5\%$ and 7.0% , the COD removal efficiency of $FeCl_3$ –PDMDAAC increased with the dosage, while for $W_p=14.0\%$, the maximum COD removal rate was 56.4% at a dosage of 160 mg/L and further increase in the $FeCl_3$ –PDMDAAC dosage produces worse removal efficiency. When dosage is lower than 160 mg/L, the COD removal efficiency increases with increasing W_p , while when dosage is higher than 160 mg/L, the optimum W_p is 7.0% for treating papermaking intermediate wastewater, and the COD removal

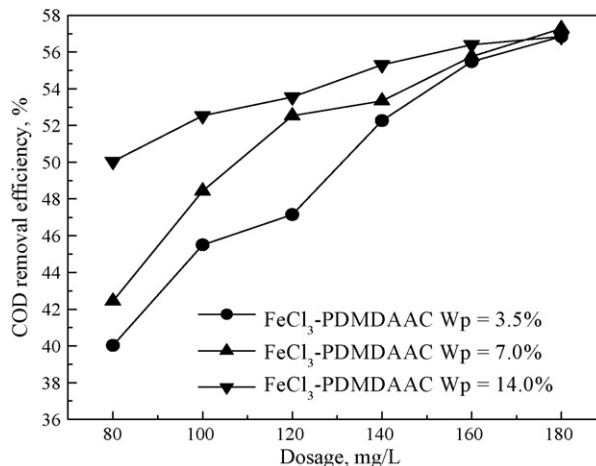


Fig. 8. Effect of PDMDAAC fraction (W_p) on flocculation efficiency for papermaking intermediate wastewater using $FeCl_3$ –PDMDAAC.

efficiency of FeCl_3 -PDMDAAC with $W_p = 7.0\%$ is the highest in this study.

4. Conclusion

Fe(III) chemical speciation PFC-PDMDAAC is significantly different from that in PFC. When the fraction of PDMDAAC is lower than 7.0%, the content of Fe_c in PFC-PDMDAAC is lower than that of PFC. And when W_p is 14.0%, the species in PFC-PDMDAAC are predominantly polymers with high molecular weight and colloids.

PFC-PDMDAAC has significantly higher positive charge compared to PFC, and the fraction of PDMDAAC influences zeta potential of PFC-PDMDAAC. At $\text{pH} < 5.0$, zeta potential of PFC-PDMDAAC at $W_p = 14.0\%$ was the highest among all three percentages. When $\text{pH} > 5.0$, zeta potential of PFC-PDMDAAC at $W_p = 7.0\%$ was the highest among all three percentages.

The results of flocculation tests indicated that PFC-PDMDAAC is more effective than PFC and PDMDAAC. Residual turbidity, COD_{Mn} and UV-254 of the Yellow River sample treated by PFC-PDMDAAC ($W_p = 7.0\%$) at the dosage of 3 mg/L are 1.15 NTU, 2.02 mg/L and 0.085, respectively. And the maximum COD removal efficiency of FeCl_3 -PDMDAAC ($W_p = 7.0\%$) for treating papermaking intermediate wastewater can approach 57.3%.

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