

## Application of a novel coagulant in reservoir water treatment in Qingdao

Shenglei Sun<sup>a,\*</sup>, Honghua Liu<sup>b</sup>, Jianwei Zhang<sup>a,d,\*</sup>, Wei Wang<sup>c</sup>, Peilong Xu<sup>a,e</sup>,  
Xiaohua Zhu<sup>d</sup>, Youjie Wang<sup>a</sup>, Shengli Wan<sup>a</sup>

<sup>a</sup>Institute of Balsalt Fiber in Eco-Application, School of Environmental Science and Engineering, Qingdao University, Qingdao 266071, China, Tel. +8618553511338; emails: sunshenglei@qdu.edu.cn (S. Sun), Tel. +8618661864970; email: sdqdzjw@qdu.edu.cn (J. Zhang), Tel. +8618561813518; email: xpl@qdu.edu.cn (P. Xu), Tel. +86053285953269; email: Yyjwang19011@163.com (Y. Wang), Tel. +86053285953269; email: williamli2000@163.com (S. Wan)

<sup>b</sup>Key Laboratory of Urban Geology and Underground Space Resources Shandong Provincial Bureau of Geology and Mineral Resources, Geo-Engineering Investigation Institute of Qingdao, Qingdao 266100, China, Tel. +8613396483697; email: 264635873@qq.com (H. Liu)

<sup>c</sup>Department of Pathology, The Affiliated Hospital of Qingdao University, Qingdao 266071, China, Tel. +8613168799876; email: 419249449@qq.com (W. Wang)

<sup>d</sup>Key Laboratory of Eco-geochemistry, Ministry of Natural Resources; National Research Center for Geoanalysis, Beijing 100037, China, Tel. +8615066106589; email: zglzby@163.com (X. Zhu)

<sup>e</sup>State Key Laboratory of Bio-Fibers and Eco Textiles, Qingdao University, Qingdao, 266071, China

Received 23 May 2022; Accepted 7 December 2022

### ABSTRACT

Epichlorohydrin-dimethylamine (DAM-ECHs) of different viscosity were acquired by adjusting the mass fraction of cross-linker and applied as assistant of polyferric chloride (PFC, basicity = 1.0) on treatment of humic acid polluted reservoir water in a hybrid coagulation–ultrafiltration process (C-UF). The coagulation effects of PFC combined with DAM-ECHs was compared and the ideal dosing methods were selected to conduct the ultrafiltration treatment. Thus, the impacts of DAM-ECHs co-operate with PFC on membrane fouling of regenerated cellulose (RC) membrane in C-UF were evaluated. Experimental outcome disclosed that application of DAM-ECH<sub>3</sub> was more effective on turbidity and HA elimination than the other two DAM-ECHs, especially at low PFC dosage. This phenomenon was owing to highest cationic degree (viscosity) among three DAM-ECHs. The enhance effect of DAM-ECHs became obsolete when the dosage exceeded 1.0 mg/L. Besides floc strength, increase of DAM-ECHs dosage in certain range relatively increased floc size, structure (compactness) and recovery ability, which was proved to be crucial for control of membrane fouling. Specifically, when the mass fraction of ethanediamine was 3.0%, coagulation process formed floc possess largest size, most open structure, and superior recoverability, which resulted in lowest membrane fouling resistance.

**Keywords:** Epichlorohydrin-dimethylamine; Viscosity; Reservoir water; Coagulation–ultrafiltration; Membrane fouling resistance

### 1. Introduction

Based on our previous researches on the enhance effects of epichlorohydrin-dimethylamine (DAM-ECH) on polyferric chloride (PFC) in humic acid removal, this

study will apply it to practical water treatment [1]. The existing of high HA pollution in Taoyuan River not only result in water colorize, but also jeopardize health of living being of the surrounding area by chelating with toxic heavy metals and inceasing their solubilities in Nuocheng

\* Corresponding authors.

reservoir (Fig. 1), which was one of the ground water resource in Qingdao region [2,3]. Moreover, HA has been recognized as the main precursor of trihalomethanes, which inevitably generated during the disinfection process of portable water [4]. In other words, high level of residual HA in drinking water would increase the liver and bowel cancer risk of the stakeholders [5,6]. Thus, efficiently removal of HA from portable water resources is a vital mission in treatment process.

Presently, multiple processes have been generated and applied in water treatment industry [7,8]. It has been widely recognized that coagulation is an ideal pre-treatment for ultrafiltration (coagulation–ultrafiltration process, C-UF), which can enormously reduce the membrane fouling [9,10]. Moreover, the enhanced effects of DAM-ECH on PFC coagulation performance and the subsequent filtration process have been proved by our previous research [11,12]. Thus, application of DAM-ECH in the process would generate positive result on the whole multiprocess. Specific, on one hand, DAM-ECH can enhance the coagulation performance of PFC; on the other hand, introduction of DAM-ECH may modify the characteristic of generated floc and enhance the membrane performance [13]. However, the impacts of DAM-ECH characteristic on the hybrid process still need to be studied in detail. Thus, in this research, DAM-ECHs were cooperatively applied with polyferric chloride (PFC, basicity of 1.0.) in a coagulation–ultrafiltration multiple system for efficiently obliteration of HA. This research would provide valuable references for application of DAM-ECH in application of water treatment processes.

## 2. Methods and materials

### 2.1. Chemicals

The ferric salt coagulant (PFC) was compounded using  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (approximately 24.5 g) and  $\text{Na}_2\text{CO}_3$  (2.4 g),

which were dissolved completely in ultrapure water, respectively. For second-step, slowly dripping the  $\text{Na}_2\text{CO}_3$  solution into  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  solution.  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  (2.5 g) was imported to keep the PFC product remain stable.

The coagulation aid (DAM-ECHs) were synthesized using three analytical reagents: epichlorohydrin, dimethylamine and ethanediamine. Thereinto, ethanediamine was the cross-linking agent, which dosage were adjusted (footnote 2) during the experiments to determine different viscosities of DAM-ECHs [12]. The viscosities of acquired DAM-ECHs were measured by a NDJ-79 rotary viscosimeter (Jingmi Co., Shanghai, China), which were 260, 540 and 1,020 mPa·s, respectively. The cationic degrees of three DAM-ECHs were surveyed by content of quaternary ammonium salt: overdose sodium tetraphenylborate into 1 g/L DAM-ECH solution, and then back titration with hexadecyl trimethyl ammonium bromide using Thiazol Yellow as indicator, the results were as follows: 4.17 mmol/g (DAM-ECH<sub>1</sub>), 5.23 mmol/g (DAM-ECH<sub>2</sub>) and 5.96 mmol/g (DAM-ECH<sub>3</sub>).

### 2.2. Test samples

The target water was acquired from the confluent area of Taoyuan River and Nuocheng Reservoir during spring time around 20°C, the characteristics of water sample were: turbidity =  $6.5 \pm 1.5$  NTU,  $\text{UV}_{254} = 0.27 \pm 0.12$ ,  $\text{DOC} = 1.80 \pm 0.21$  mg/L,  $\text{pH} = 6.85 \pm 0.15$ .

### 2.3. Design of coagulation experiments and analytical methods

Jar tests were carried out using JJ-4 program-controlled flocculators (Weier Co., Suzhou, China) to optimize the HA elimination of PFC&DAM-ECHs. The indexes of water quality were measured as follows: turbidity (2100P turbidimeter, produced by Hach, USA); zeta potential (Zetasizer, Malvern, UK); DOC (dissolved organic carbon, TOC-2000,



Fig. 1. Location of Taoyuan River and Nuocheng Reservoir.

Metash, China); UV<sub>254</sub> (absorbency degree of ultraviolet at wavelength 254, UV-754, Aoxi Co., China).

The setup of JJ-4 program-controlled flocculators was as follows:

- The stir in phase: the raw reservoir water (1.0 L) was stirred by 200 revolutions/min (rpm) for 0.5 min;
- Then certain dose of PFC was added, followed by another stirring period of 200 rpm for 2 min; when DAM-ECH was involved, it would be dosed 0.5 min after PFC was added. At all events, the total rapid stirring at 200 rpm would last 2 min for coagulant dispersion;
- In this period, stirring speed would be reduced to 40 rpm for floc growth, which lasted for 10 min;
- After the low speed stir period (floc growth period), the stirring would stop for flocs to settle 20 min. At the end of jar test, about 200 mL of supernatant water was withdrawn from each jar as test water sample, and filtered through 0.45 μm fiber membrane before UV<sub>254</sub> and DOC tests.

#### 2.4. Flocs

Floc properties were monitored to evaluate the influences of DAM-ECHs on membrane resistance distribution. Thereinto, strength and recovery abilities were applied to estimate the floc potential on shearing forces. Fractal dimension was calculated to reveal the structure (compactness) of flocs.

##### 2.4.1. Intensity and recovery

Floc strength factor ( $S_f$ ) and recovery factor ( $R_f$ ) generated by the coagulation process was acquired by Eqs. (1) and (2) [14–17].

$$\text{Strength factor}(\%) = \frac{d_2}{d_1} \times 100 \quad (1)$$

$$\text{Recovery factor}(\%) = \frac{d_3 - d_2}{d_1 - d_2} \times 100 \quad (2)$$

where  $d_1$ ,  $d_2$  and  $d_3$  were flocs sizes at the very beginning as coagulants were added, after broken by shear force, and steady period after re-growth, respectively. In detail, greater  $S_f$  manifest higher immunity to shear stress, meanwhile higher  $R_f$  reveals better regenerability.

##### 2.4.2. Floc dimension

Fractal dimension ( $D_f$ ) was calculated by Eq. (3), higher  $D_f$  value means the floc was more compact in structure.

$$I \propto Q^{-D_f} \quad (3)$$

where  $D_f$  was generated using the slope of a plot of  $I$  as a function of  $Q$  on a log–log scale;  $I$  stand for light density;  $Q$  was the scattering vector, defined as:

$$Q = \frac{4\pi n \sin(\theta/2)}{\lambda} \quad (4)$$

where  $n$  was the suspending medium refractive index;  $\theta$  stand for the angle of scattering;  $\lambda$  was the vacuum radiation wavelength.

#### 2.5. Analysis of membrane fouling

In order to further understand the membrane fouling mechanism of the C-UF process, the ultrafiltration process was carried out as a multi-step process with ultra-membrane (CAT. NO. PLHK07610, produced by Millipore). The detailed process was designed and verified by our previous research, to be specific, the total membrane resistance  $R_t$  was composited by the sum of  $R_m$  (the resistance generated by the membrane) and  $R_f$  ( $R_{ef}$  was the external fouling resistance which generated by floc formed cake layer;  $R_{if}$  was resistance inside membrane pores caused by pore blocking. Furthermore,  $R_{ef}$  can be categorized as loosely ( $R_{ef-l}$  can be removed by physical cleaning, such as quick stir or brushing) and strongly ( $R_{ef-s}$  cannot be removed by physical cleaning) external resistance; meanwhile,  $R_{if}$  can be separated into revisable ( $R_{if-r}$  removable by membrane pore cleaning, such as backwashing) and irreversible ( $R_{if-ir}$  immune to backwashing) internal fouling resistance [13].

### 3. Results and discussion

As previously mentioned, coagulation effect of combined coagulants, floc characteristics, membrane resistance were monitored through the whole coagulation–ultrafiltration multi-process. The generated results will be analyzed in this section to optimize the system performance.

#### 3.1. Impacts of DAM-ECHs on coagulation

Effects of DAM-ECHs with different viscosities and cationic degrees combined with PFC on HA removal were investigated. The range of PFC dosage varied from 3 to 15 mg/L, meanwhile DAM-ECH dosages were set to be 0–1.5 mg/L.

##### 3.1.1. Turbidity removal

Generally, 1.0 mg/L of DAM-ECHs ensured the growth rate of turbidity elimination trended to be steady and close to 90% at PFC dosage of 12 mg/L instead of over 15 mg/L (Fig. 2). Moreover, it was obvious that as DAM-ECHs was introduced, the removal rates remarkably increased especially at low PFC dose. This phenomena was because addition of DAM-ECHs brought high concentration of cations and enhanced charge neutralization of PFC with the negatively charged colloidal contaminants in reservoir water, which was proved by zeta potential tendency [18,19]. Thereinto, it was also worth noticing that when PFC dosage was low, PFC&DAM-ECH<sub>3</sub> achieved higher turbidity obliteration than the other DAM-ECHs, which was because DAM-ECH<sub>3</sub> possess highest cationic degree (5.96 mmol/g) among all three DAM-ECHs. Furthermore,

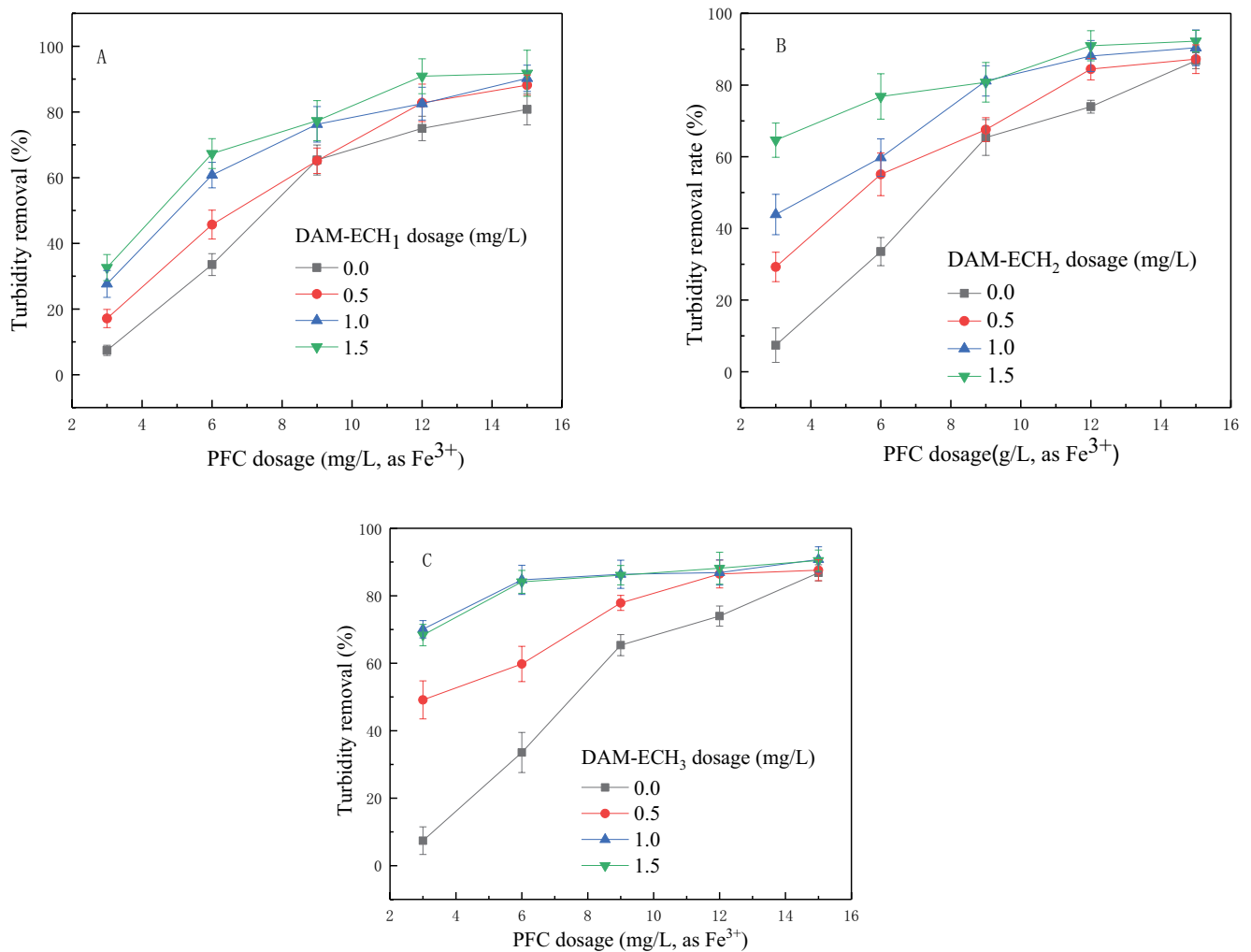


Fig. 2. Turbidity removal rates of PFC with DAM-ECHs as functions of PFC dosage.

it can be observed that the turbidity elimination efficiency tended to be similar when PFC dosage exceeded 12 mg/L and DAM-ECH dosage reached 1.0 mg/L.

### 3.1.2. HA reduction

As mentioned previously, experimental results of UV<sub>254</sub> and DOC elimination in Figs. 3 and 4 revealed the impacts of DAM-ECHs on HA reduction of PFC, which possessed similar variation tendency. Specifically, without addition of DAM-ECHs, UV<sub>254</sub> and DOC clearance rates were rather low in the selected PFC dosage range, particularly for DOC (around 30%). When DAM-ECHs were introduced into the system, UV<sub>254</sub> and DOC removal efficiencies all showed prominent enhancement. In detail, at lowest PFC dosage of 3 mg/L, DAM-ECH<sub>3</sub> achieved highest UV<sub>254</sub> and DOC elimination. Considering the zeta potential in Fig. 5, this result was owing to the highest cationic strength of DAM-ECH<sub>3</sub> among all DAM-ECHs, so that it can charge neutralize more HA colloid even at low dose. Particularly for UV<sub>254</sub>, the wipe off ratio approached to 90% at relatively low PFC dosage of 9 mg/L. However, the rising tendency for both UV<sub>254</sub> and DOC elimination became steady when the PFC

dosage exceeded 12 mg/L, and DAM-ECHs dosage reached 1.0 mg/L. According to the results of zeta potential given in Fig. 5, this was because that there were few negatively charged HA molecules remain in water samples, which was consisted with previous researches [20–22]. Specifically, the HA elimination tended to be negligible when zeta potential approached null point, which demonstrated that in this study, charge neutralization was the dominating mechanism in coagulation process [23].

According to the above results, PFC dosage of 12 mg/L of PFC and DAM-ECHs of 0.5 and 1.0 mg/L were applied to carry out ultrafiltration experiments to demonstrate the dosage and characteristics of DAM-ECHs on ultrafiltration.

## 3.2. Floc properties

To understand the impacts of DAM-ECHs on ultra-membrane performance, floc characteristics of PFC and PFC&DAM-ECHs were analyzed in this section.

### 3.2.1. Floc breakage

The first graph of Fig. 6 revealed the floc size variation of PFC floc during the whole coagulation process. As

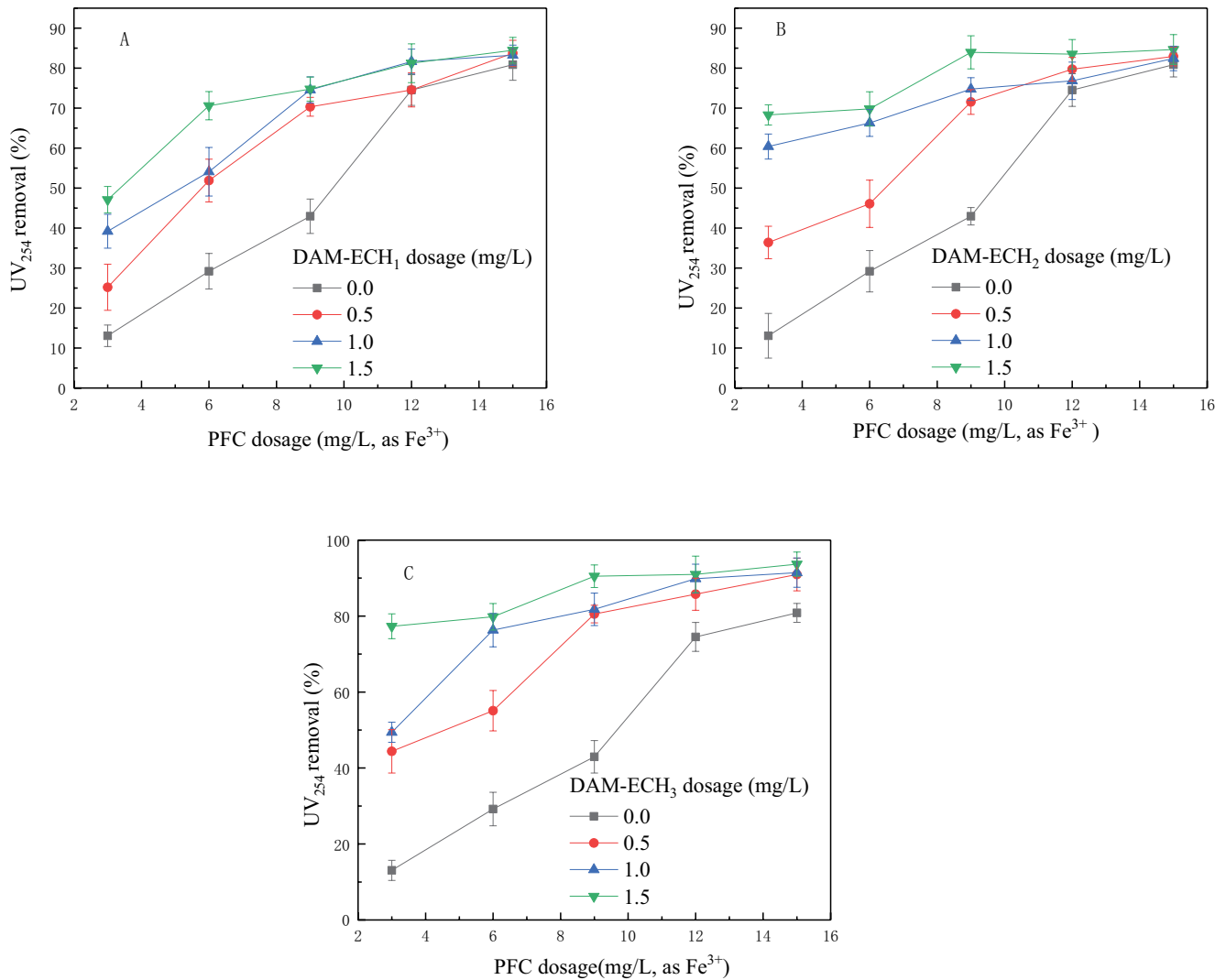


Fig. 3.  $UV_{254}$  removal efficiencies of PFC with DAM-ECHs as functions of PFC dosage.

the coagulant intruded the water sample, there would be a lag period and then floc size dramatically clime up as colloids destabilized by coagulant. After a certain period, the floc size variation trended to be steady, which was owing to the floc growth and breakage achieved balance. Once shear forces invaded the system, there was a violent decline of floc sizes which owing to the breakage of floc. Finally when water sample restore calm, floc size recovered as floc regrowth. However, under all circumstances, the regenerated floc would not regain the original size, which was accordant with results obtained by other researchers [24,25]. Comparing the changing trends of different flocs, it can be concluded that DAM-ECHs remarkably changed the upper and lower limits of floc size under all circumstances, which was because DAM-ECHs enhanced the charge neutralization of coagulation process. Besides, chain-like molecule structure of DAM-ECHs enhanced the bridge and sweep flocculation processes, and formed larger floc than PFC used alone. Thereinto, PFC&DAM-ECH<sub>3</sub> floc possessed highest floc size. Specifically, this result rooted in the highest charge

density and viscosity (higher molecular weight, longer polymer chain) of DAM-ECH<sub>y</sub>, which means it may adsorb and bridge more colloid particles and form larger flocs [26,27]. Moreover, the increase of DAM-ECHs dosage from 0.5 to 1.0 mg/L also relatively enlarged the floc size during the whole process, which consistent with previous work that higher of polymer dosing would evidently raise the amount of captured particles and enlarge floc size [28].

### 3.2.2. Floc resistance and regeneration

In practical water treatment processes, the underwater situation would be complex and floc breakage by shear forces that generated by water flow cannot be avoid. In other words, floc strength and regrowth ability would be critical for adjustment of floc characteristics, which would determine the membrane performance of the multi-process. Thus, in this section, shearing forces were introduced to the C-UF system and floc strength and recovery factors are given in Tables 1 and 2.

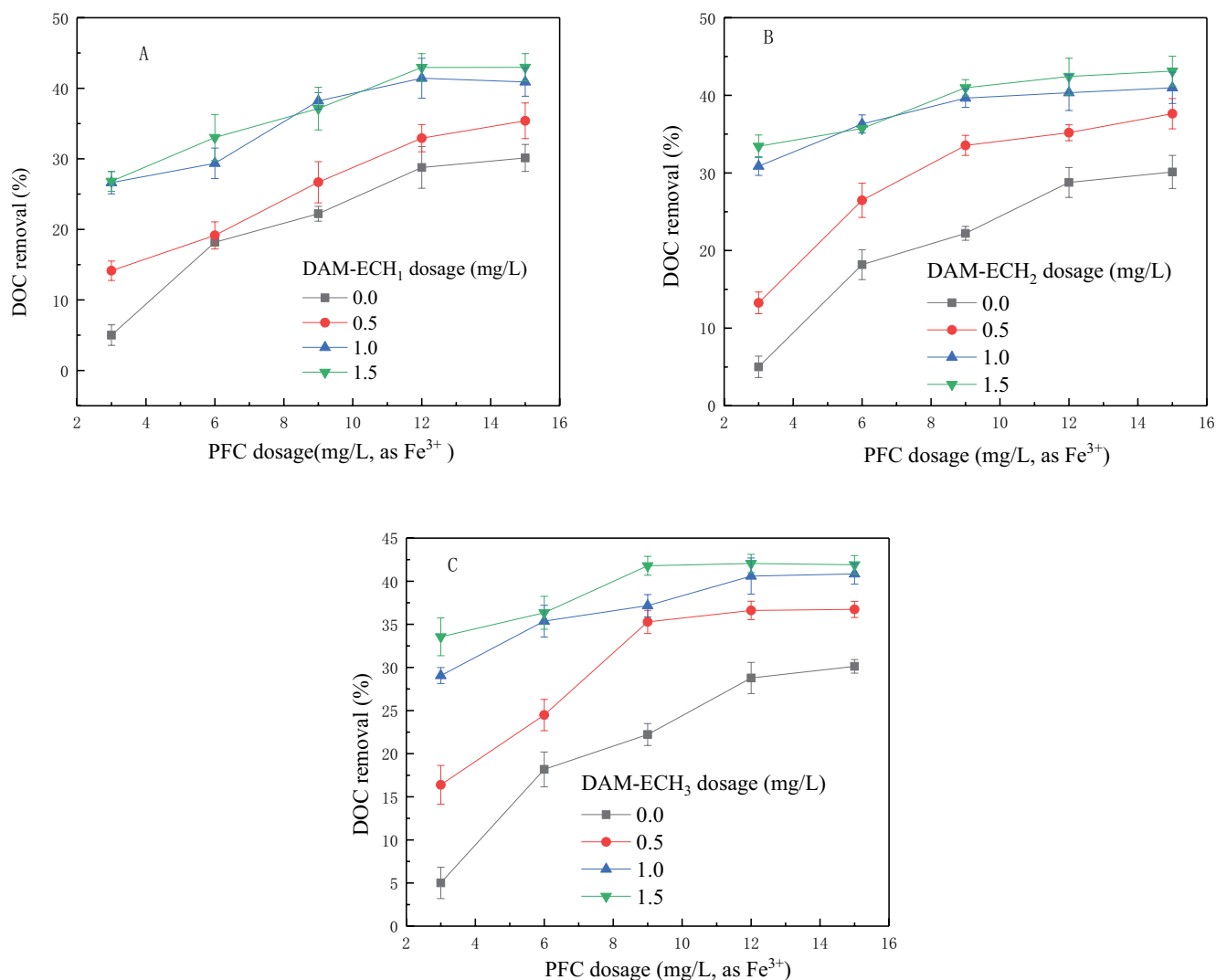


Fig. 4. DOC removal efficiencies of PFC with different coagulant aids as functions of PFC dosage.

According to Table 1, PFC floc processed the highest strength among all flocs due to the smallest size it possesses; meanwhile the addition of DAM-ECHs seemed to reduce the floc strength by enlarging the floc size. It should be mentioned that the strength factors of PFC&DAM-ECHs did not show remarkable decline compared to PFC floc, considering the prominent size enhancement by DAM-ECHs in Fig. 6, especially for DAM-ECH<sub>3</sub>. This was probably on account of the high charge density cationic of DAM-ECHs, which made particles adsorb stronger to their molecule chain and generated larger floc with firm structure [16,28]. Moreover, dosage variation of DAM-ECHs (from 0.5 to 1.0 mg/L) did not remarkably change the strength factor. Finally, strength factors of all floc tended to be similar to each other once the rotation speed reached 400 rpm, indicating that floc immunity to shearing forces had a cap, which means shearing forces should be restricted to keep steady structure of floc.

As for floc recovery ability, it is obvious that with the aid of DAM-ECHs, the factors of PFC&DAM-ECHs floc all increased enormously (twice or more) comparing with

those of PFC floc. It should be mentioned that comparing to strength factor, the increase of DAM-ECHs dosages slightly increased the floc recovery factor. Considering the zeta potential variation at the same time, this was probably because of the enhancement of charge neutralization by increase of cationic concentration with more DAM-ECHs addition. However, as stirring stress attained 400 rpm, recovery factors all showed significant decline. This phenomenon indicated that recovery ability of floc was also limited under certain conditions. When floc was broken into too minor pieces, it became far more difficult to regrow to the original size, which was accordant with existing literatures [29–31].

### 3.2.3. Floc compactness

As described previously, floc fractal dimension ( $D_f$ ) was calculated for evaluation of the floc compactness. Overall, it can be observed in Fig. 7 that the  $D_f$  of floc kept varying in different procedures. At the very beginning that the coagulants were added, the floc started to grow and form porous structure as  $D_f$  kept falling, and tended to be steady;

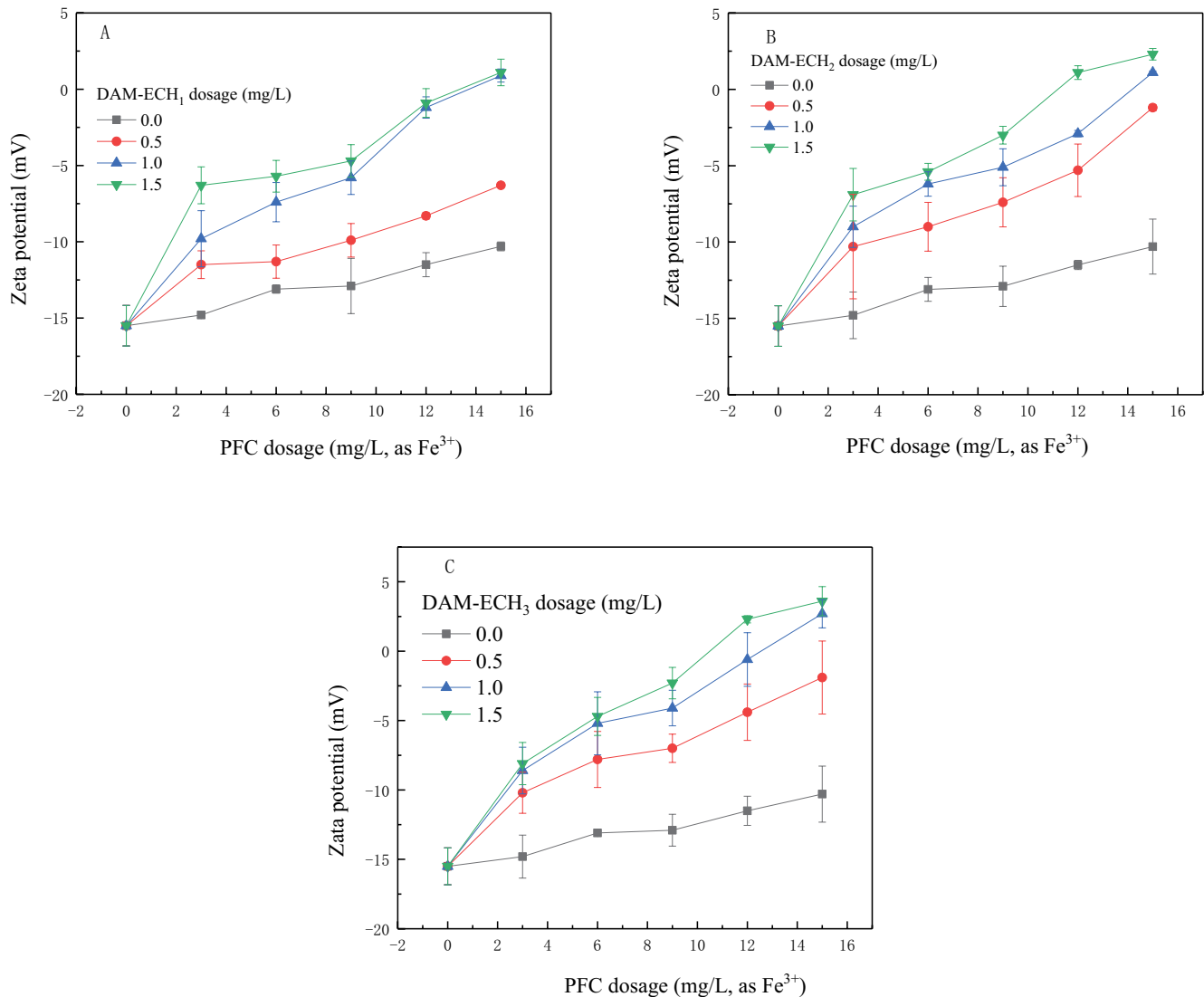


Fig. 5. Zeta potential of coagulated water samples by different dual-coagulants as functions of PFC dosage.

then followed by a sharp growth in the breakage region that floc was broken; finally the  $D_f$  values dropped down again to varied extents during regrowth period, according to shear forces.

Apparently, addition of DAM-ECHs remarkably brought down the floc  $D_f$ , which indicated that the floc was looser in structure. Considering the results of floc size shown in Fig. 6, it can be concluded that the DAM-ECHs made the floc larger in size and looser in structure compared with PFC floc, which was also evidenced by previous studies [32–34]. Experimental results show the compactness of floc during steady period was as follows: PFC > P&D<sub>1</sub>(PFC&DAM-ECH<sub>1</sub>) > P&D<sub>2</sub>(PFC&DAM-ECH<sub>2</sub>) > P&D<sub>3</sub>(PFC&DAM-ECH<sub>3</sub>). As mentioned previously, after a short steady period,  $D_f$  values all grew dramatically as shearing force invaded, the higher shear power, the larger the values became. In other words, higher shear force would break floc into more compact and smaller ones (Fig. 6). In the recovery period,  $D_f$  started to decline as floc size restore, especially for PFC&DAM-ECH<sub>3</sub> floc, which means the floc structure

became more porous as floc recovery comparing with PFC floc. This was because DAM-ECH<sub>3</sub> possessed highest charge density that would enhance charge neutralize and form floc with more. However, as shear force reached 400 rpm,  $D_f$  climbed to the highest level under all coagulation methods; even the shear force was withdrawn, the  $D_f$  values dropped slighter than that under 100 or 200 rpm, which indicates that the porousness of floc would be rather difficult to recover under extreme shearing forces [31].

### 3.3. Membrane performance

The flux variation of different water samples was recorded during the ultrafiltration process to evaluate the membrane fouling situation.

According to Fig. 8, original HA-Kaolin water resulted in highest total membrane fouling compared with the other water samples. Furthermore, each part of the fouling resistance caused by HA-Kaolin water sample were also remarkably heavier than the other water samples. It can be observed

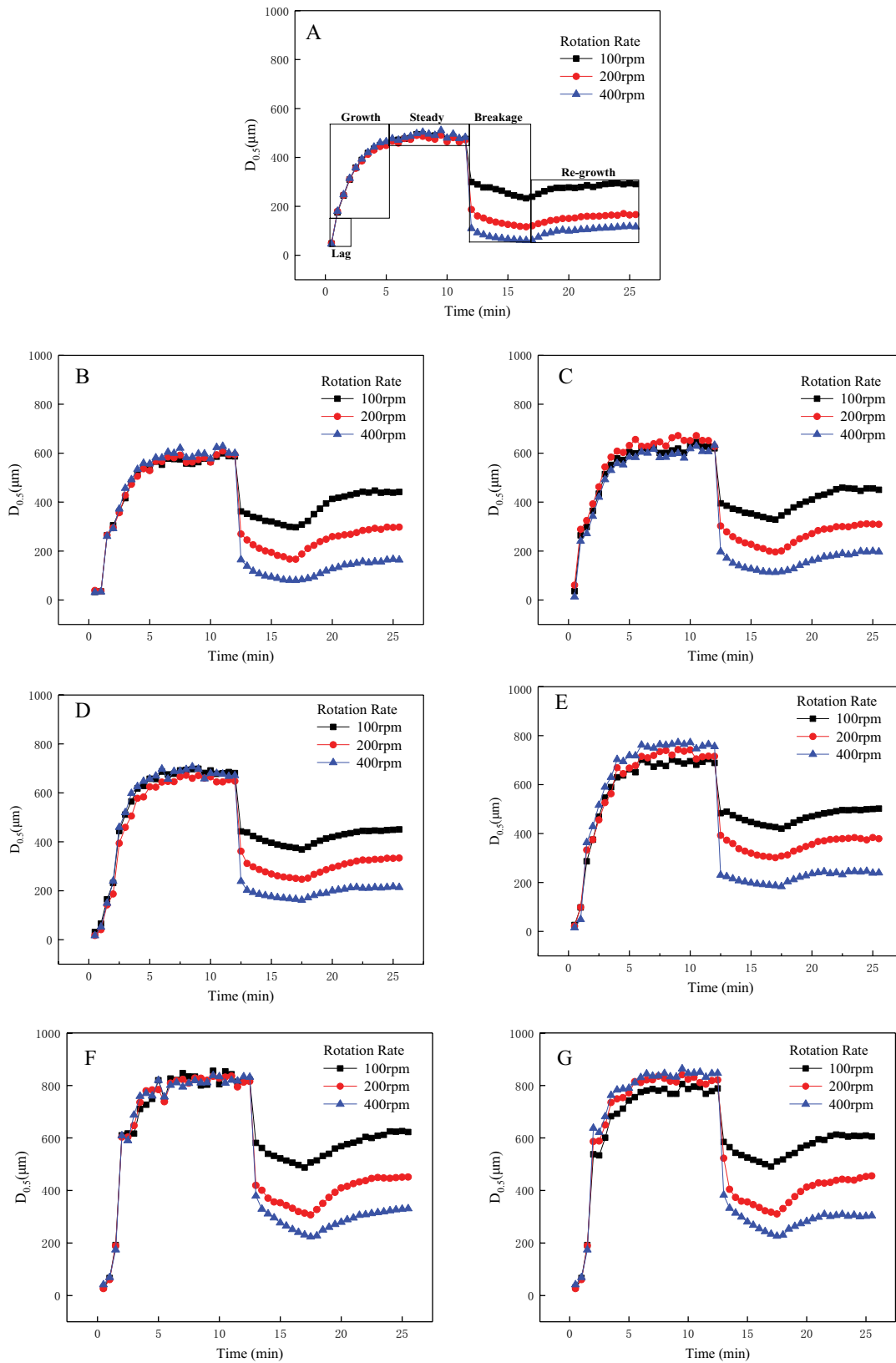


Fig. 6. Floc size variations of PFC&DAM-ECHs during different stages of coagulation: (A) PFC, (B) PFC&DAM-ECH<sub>1</sub>(DAM-ECH<sub>1</sub> dosage 0.5 mg/L), (C) PFC&DAM-ECH<sub>1</sub>(DAM-ECH<sub>1</sub> dosage 1.5 mg/L), (D) PFC&DAM-ECH<sub>2</sub>(DAM-ECH<sub>2</sub> dosage 0.5 mg/L), (E) PFC&DAM-ECH<sub>2</sub>(DAM-ECH<sub>2</sub> dosage 1.5 mg/L), (F) PFC&DAM-ECH<sub>3</sub>(DAM-ECH<sub>3</sub> dosage 0.5 mg/L), and (G) PFC&DAM-ECH<sub>3</sub>(DAM-ECH<sub>3</sub> dosage 1.5 mg/L).



Table 1  
Strength indexes of flocs under varied shearing forces

Rotation (rpm)	Coagulants	PFC	PFC/DAM-ECH <sub>1</sub>		PFC/DAM-ECH <sub>2</sub>		PFC/DAM-ECH <sub>3</sub>	
			0.5 mg/L	1.0 mg/L	0.5 mg/L	1.0 mg/L	0.5 mg/L	1.0 mg/L
100		57.71	53.51	52.57	54.81	54.8	55.13	55.93
200		24.41	20.17	20.21	19.63	20.24	21.51	21.3
400		12.02	11.72	12.37	11.74	11.42	11.82	11.68

Table 2  
Recovery indexes of flocs under varied shearing forces

Rotation (rpm)	Coagulants	PFC	PFC/DAM-ECH <sub>1</sub>		PFC/DAM-ECH <sub>2</sub>		PFC/DAM-ECH <sub>3</sub>	
			0.5 mg/L	1.0 mg/L	0.5 mg/L	1.0 mg/L	0.5 mg/L	1.0 mg/L
100		13.54	25.53	25.88	26.74	27.86	27.27	28.55
200		10.18	20.32	22.67	19.86	21.86	24.06	24.8
400		8.34	12.62	12.98	13.85	14.17	15.60	15.96

that the addition of coagulants (PFC or PFC&DAM-ECHs) reduced the  $R_{fs}$  at the greatest extent, considering the floc parameters, this was because introduction of coagulants destabilized HA-Kaolin colloid in water and formed larger floc with loose structure. When DAM-ECHs dosage was 0.5 mg/L, the total fouling resistances were in the following order: PFC > P/D1 > P/D2 > P/D3, each part of the resistances was in the same order. When DAM-ECHs dosage further increased 1.0 mg/L, the total membrane fouling resistance was still in the same order as DAM-ECHs dosage was 0.5 mg/L. The distribution of resistances also remained the same, the variation of total resistance was slightly reduced. In other words, P/D3 coagulated water achieved lightest external and internal membrane fouling resistance regardless of dosage. On one hand, for external resistance, the result can be explained by combing the results in Figs. 6 and 7, that P/D3 formed largest floc (highest  $D_{50}$ ) with most open structure (lowest  $D_p$ ) that could form the porous cake layer on the membrane surface, which possess supreme permeability and generated the lowest resistance for water infiltration; on the other hand, as for inner fouling resistance, as revealed in Figs. 3 and 4, P/D3 resulted in lowest HA residual, which means there were less micro-particles residual in coagulated water that may enter and block the filter pores to increase  $R_{if}$  [35–40].

When shear was introduced by increasing the stir speed to 400 rpm, the general membrane fouling resistances of all samples rose sharply. Especially the amount and distribution of  $R_{ef}$  was significantly changed, that the increase of  $R_{ef}$  was accompanied by the raise of  $R_{fs}$  and decline of  $R_{fi}$ , which means the external membrane fouling was enlarged because of the breakage of floc. To be specific, the regenerated floc was more compact in structure so that formed denser cake layer with poor osmosis on membrane surface. For PFC water sample, the  $R_{fs}$  increased from 2.1 to 3.47, which was the largest portion of the total membrane fouling resistance. Similar results also occurred for PFC&DAM-ECHs coagulated water samples. However, comparing with

PFC water sample, the total membrane fouling resistances achieved by PFC&DAM-ECHs water samples were apparently lower. Considering the floc characteristics, this phenomena could be owing to the superior recovery ability of PFC&DAM-ECHs flocs, that after breakage, the PFC&DAM-ECHs flocs could regrow to larger size and recover to more open structure (low  $D_p$ ). The total fouling resistances of PFC&DAM-ECHs were in the following order regardless of DAM-ECHs dosage under 400 rpm shearing force: P/D1(S) > P/D2(S) > P/D3(S), which was consist with the floc recovery tendency in Table 2.

Moreover, results indicated that shear force did not apparently effected both parts of internal fouling resistance; take the results in Figs. 2–4 in consideration, it can be concluded that HA-Kaolin removal efficiencies of different coagulants were the decisive parameter for the inner membrane fouling resistance. More specifically, higher HA removal would ensure there were less residual micro particles that can enter the ultra-membrane pore and clog the water passage, which would certainly ensure the reduction of membrane fouling.

#### 4. Conclusions

- DAM-ECHs can enormously increase the HA removal efficiency of PFC especially at low PFC dosage. At same dosage, the higher the viscosity of DAM-ECH, the superior HA elimination it possessed.
- Viscosities of DAM-ECH would remarkably effluence the floc characteristics during coagulation. The higher viscosity the DAM-ECHs possess, larger cationic density it provided, bigger floc size with more open structure and superior recovery ability was generated. Meanwhile, increase of DAM-ECHs dosage would not remarkably change floc strength factor.
- Total membrane fouling resistance was determined by the external and internal fouling resistance. Thereinto, external fouling resistance was depended on the

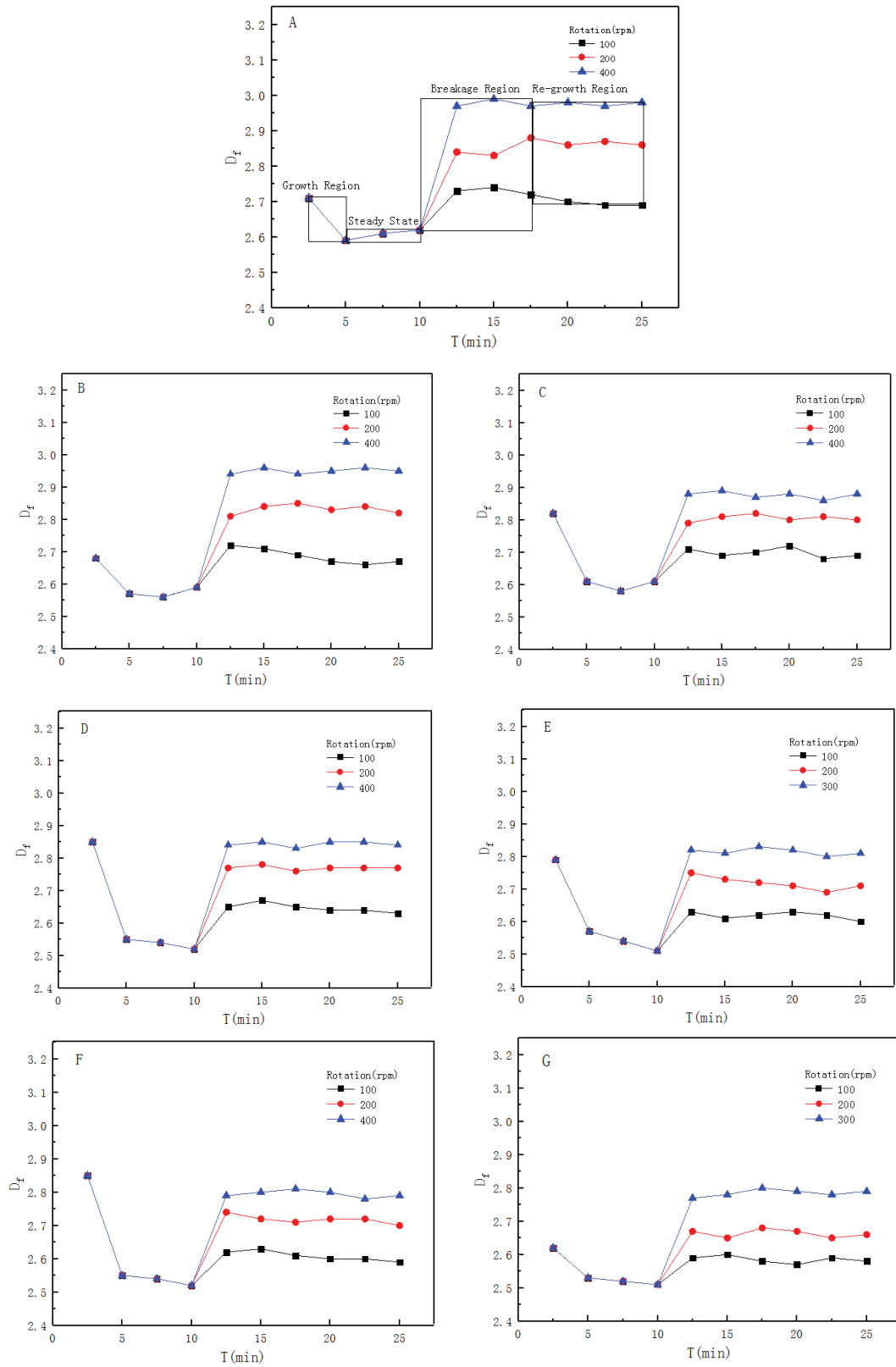


Fig. 7. Fractal dimension of flocs of PFC&DAM-ECHs during different stages of coagulation: (A) PFC, (B) PFC&DAM-ECH<sub>1</sub>(DAM-ECH<sub>1</sub> dosage 0.5 mg/L), (C) PFC&DAM-ECH<sub>1</sub>(DAM-ECH<sub>1</sub> dosage 1.5 mg/L), (D) PFC&DAM-ECH<sub>2</sub>(DAM-ECH<sub>2</sub> dosage 0.5 mg/L), (E) PFC&DAM-ECH<sub>2</sub>(DAM-ECH<sub>2</sub> dosage 1.5 mg/L), (F) PFC&DAM-ECH<sub>3</sub>(DAM-ECH<sub>3</sub> dosage 0.5 mg/L), and (G) PFC&DAM-ECH<sub>3</sub>(DAM-ECH<sub>3</sub> dosage 1.5 mg/L).

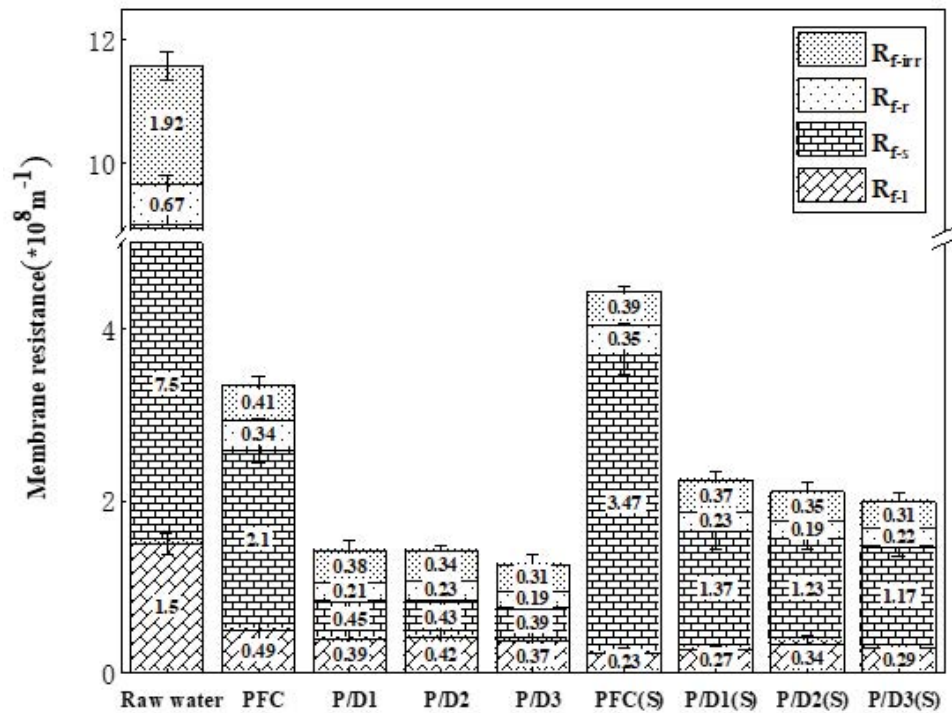


Fig. 8. Variation of membrane resistance distribution under different conditions:  $R_{f-ir}$ , removable external membrane fouling;  $R_{f-r}$ , non-removable external membrane fouling;  $R_{f-s}$ , removable internal membrane fouling;  $R_{f-l}$ , non-removable external membrane fouling. P/D1: coagulated water of PFC&DAM-ECH<sub>1</sub>; P/D2: coagulated water of PFC&DAM-ECH<sub>2</sub>; P/D3: coagulated water of PFC&DAM-ECH<sub>3</sub>; P/D1(s): coagulated water of PFC&DAM-ECH<sub>1</sub>, and the floc was broken under 400 rpm shearing force, P/D2(s): coagulated water of PFC&DAM-ECH<sub>2</sub>, and the floc was broken under 400 rpm shearing force, P/D3(s): coagulated water of PFC&DAM-ECH<sub>3</sub>, and the floc was broken under 400 rpm shearing force

permeability of cake layer formed by floc; meanwhile, the inner fouling resistance relies on the HA elimination efficiencies of coagulants.

- Extreme shear would tremendously increase the membrane fouling resistance by break floc generated through coagulation. Floc recovery ability would be the crucial parameter that determines the membrane performance under such circumstances. Specifically, better recoverability would be beneficial to ensure higher permeability of the cake layer formed by regenerated floc after breakage.

### Acknowledgements

The project obtained financial assistance from China Postdoctoral Science Foundation (2020M673541); Ministry of Education industry-university-research combination project(RC2000003581& RC2000003423); the open fund of Key Laboratory of Eco-geochemistry of the Ministry of Natural Resources (ZSDHJJ201904&ZSDHJJ202103); Geological Survey Project of China (DD20190655); Geological and mineral resources open fund project of Qingdao (2019-QDDZYKF01).

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