Flocs' re-growth characteristics in circulation coagulation–membrane filtration process

Jie Wang, Lulu Liu, Hongwei Zhang, Wen Jin Liu and Hui Jia

ABSTRACT

Membrane fouling can be significantly mitigated through circulating coagulation, floc breakage and re-growth under appropriate conditions. In this study, unified membrane filtration index (UMFI) was adopted to analyze the membrane fouling. The effect of circulating coagulation pretreatment on both flocs' average diameter and membrane fouling were investigated under different concentrations of coagulant and reflux flocs. When the concentrations of coagulant and reflux flocs were 6 and 10 mg/L, respectively, the average diameter of flocs and UMFI were 565.416 μm and 0.0004. Floc breakage and re-growth existed in the aeration cleaning; circulating coagulation was conducive to the flocs' re-growth and recombination. The recovery rate of flocs' average diameter could reach 90%. In circulating coagulation–membrane filtration process, flocs underwent re-growth and the characteristic of flocs changed which made size distribution uniform, slowed down the growth of transmembrane pressure and mitigated membrane fouling.

Key words | breakage and re-growth, circulating coagulation, floc morphology, membrane fouling

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INTRODUCTION

As an effective drinking water treatment technology, the coagulation–membrane filtration process has extensive application (Chon *et al.* 2012; Bakker *et al.* 2013). However, the application of membrane technology is limited by membrane fouling. Membrane fouling causes the decrease of membrane flux, rise of transmembrane pressure (TMP), leading to the shortening of lifespan of membrane modules, and increase of operating costs (Zhen *et al.* 2012). In the submerged ultrafiltration membrane, membrane fouling depends largely on the coagulation conditions. The structure characteristics of the flocs, especially their porosity, will affect the efficiency of membrane filtration; thus, the morphology of flocs plays a very important role in the process of membrane fouling, while floc structure is also restricted by coagulation conditions (Jin *et al.* 2004).

Circulating coagulation means that the sedimentary flocs return to the coagulation tank, which enhances the efficiency of coagulation. Lv *et al.* (2010) found that compared with conventional coagulation sedimentation process, sludge recycling could enhance the removal efficiency of pollutants, significantly decrease coagulant dosing, moreover, even improve effluent quality. Circulating coagulation will cause a change in floc morphology, especially the floc size and density degree, which has an important impact on the performance of membrane filtration (Zhou *et al.* 2012). Wang *et al.* (2013) showed that circulating coagulation promoted the formation of large and dense flocs, helpful in mitigating membrane fouling.

Floc breakage occurs frequently in the process of growth (floc growth accompanied floc breakage) and coagulation (change of stirring speed). Floc breakage occurs under the interaction force between vortices and flocs, and the vortices under high shear rate easily cause floc breakage (McCurdy *et al.* 2004). After floc breakage, if stirred slowly with appropriate intensity, broken small flocs gradually become larger. For example, in the agitation zone of the coagulating reaction tank, after experiencing high intensity of shearing force which leads to breakage, re-growth of flocs occurs (Jarvis *et al.* 2005). Zhang *et al.* (2007) thought the

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ability of floc breakage and re-growth was associated with the coagulant dosage, while floc breakage process had significant irreversibility. The mechanism of floc bonding and disconnecting may explain the phenomenon that different mixing conditions generate different coagulation effects and the phenomenon of floc breakage and re-growth. After breaking and re-growing the fractal characteristics and structure of floc will change, and the cake layer formed by changed floc has a certain influence on mitigating the membrane fouling (Qiao *et al.* 2008; Yu *et al.* 2009).

In the submerged membrane filtration process, aeration cleaning is an important method to recover membrane flux. In this experiment, the intermittent aeration was 600 L/h and duration was 2 min. Intermittent aeration can form a high-speed and cross-flow shear area on the membrane surface, thus making contaminants fall off the membrane surface, but at the same time, aeration has a significant impact on floc morphology. The flocs will break and re-grow under membrane aeration cleaning. Therefore, in-depth understanding of the characteristics of floc breakage and re-growth in submerged membrane filtration process is necessary. In this study, we investigate the effect of flocs on membrane fouling when the operating conditions change, mainly from the aspects of floc re-use, floc breakage and re-growth experiments, observe the changes of floc morphology under two operating conditions, and analyze their influences on membrane fouling.

EXPERIMENT AND METHODS

Raw water

Laboratory-scale tests were carried out with natural surface water from the Luan river, Tianjin, China. Characteristics of the water samples are presented in Table 1 of which specific ultraviolet absorption (SUVA) value was calculated from the ratio of UV_{254} to dissolved organic carbon (DOC).

Experimental set-up

In the experiment the flux of the membrane module was maintained at approximately 20 L/h, coagulant was $FeCl_3$, and by changing the dosage of flocs and coagulant ($FeCl_3$), we observed the morphology of flocs and the fouling status of the membrane module. Circulating coagulation refers to collecting the sedimentary flocs in a coagulation basin and membrane tank, after stirring in a reflux floc conditioning tank, and adding the required floc concentration and a certain concentration of coagulant to the reactor at the same time. The operating process was mainly divided into three steps: (1) coagulation–membrane filtration of the raw water; (2) 5 min hydraulic backwashing of the membrane module; and (3) aerating at the bottom of the membrane, 2 min gas washing of the membrane module (Figure 1).

Table 1 | Characteristics of Luan river

Parameter	Unit	Values
UV_{254}	cm^{-1}	0.064 ± 0.016
Chromaticity	PCU	55.0 ± 25.0
Turbidity	NTU	2.34 ± 0.89
pH		7.51 ± 0.38
TOC	mg/L	4.39 ± 1.15
DOC	mg/L	3.71 ± 0.56
SUVA	L/mg m	1.75 ± 0.72
Temperature	°C	18.7 ± 3.0

Analytical method

This experiment was run at fixed flux and increased pressure with time to maintain that fixed flux. In the experiment the growth of the floc was observed by Malvern laser particle size analyzer (Mastersizer2000/2000E, Malvern Instruments Ltd, UK). According to the relationship between the volumes of recycled floc mixed liquor and quality of dry flocs, the standard curve was established to determine the reflux floc concentration. The concentrations of DOC and total organic carbon (TOC) were determined by a total organic carbon analyzer (TOC-VCPH, Shimadzu Corporation, Japan). The ultraviolet (UV) absorbance at 254 nm (UV_{254}) was measured by UV-vis spectrophotometer (UV-2540, Shimadzu Corporation, Japan). Water turbidity and chromaticity were measured by turbidimeter (2100N, Hach Company, USA) and colorimeter (HI93737, Elite and Hanna Ltd, Italy), respectively. The pH of water was measured by pH meter (PHS-25, Shanghai Precision Scientific Instrument Co. Ltd, INESA, China).

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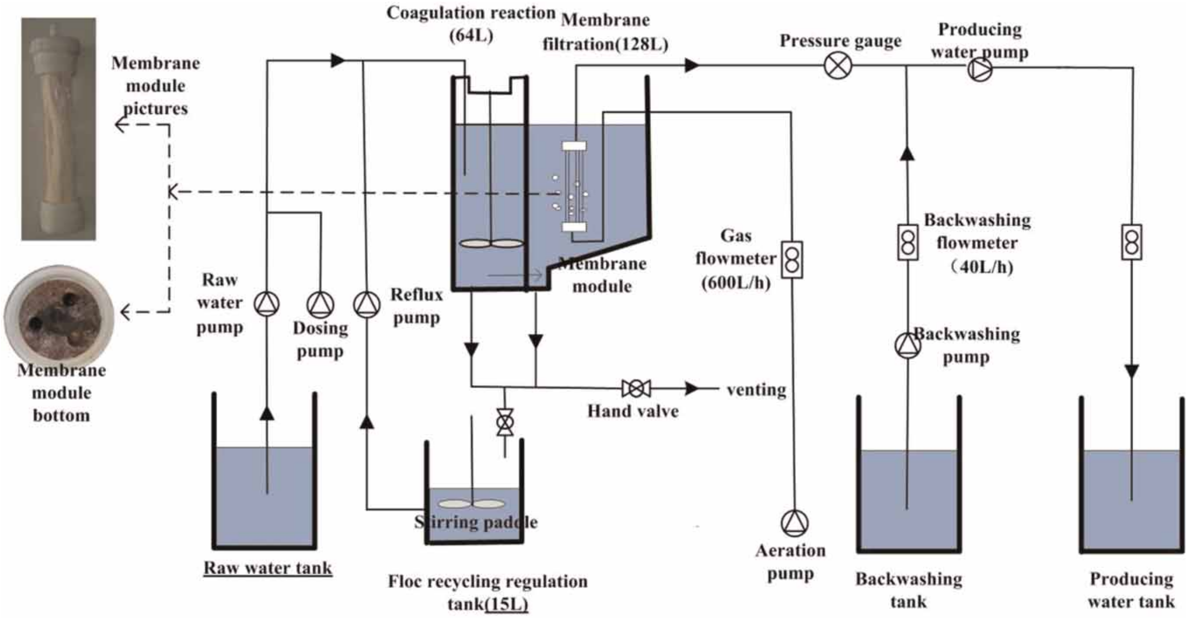

Figure 1 | Schematic diagram of experimental set-up.

Theory

Membrane fouling restricts the application of membrane technology in water treatment and wastewater reuse, thus proper assessment techniques are necessary. Huang *et al.* (2008) presented the unified membrane fouling index (UFMI) to evaluate membrane fouling which is generally defined as Equation (1)

$$\mathrm{UMFI} = \frac{J_{\mathrm{so}}/J_{\mathrm{sp}} - 1}{V_{\mathrm{s}}} \tag{1}$$

where J_{so} is the initial specific flux (L/(m^2 h bar)), J_{sp} is the specific flux (L/(m^2 h bar)) and V_{s} is the unit filtrate throughput (L/m^2). In addition, the specific resistance of cake layer has a certain relationship with the membrane fouling.

According to the Kozeny–Carman equation (Mulder 1996), the specific resistance of cake layer is inversely proportional to floc size

$$\gamma_{\mathrm{c}} = 180\frac{(1-\varepsilon)^2}{[(d_{\mathrm{s}})^2\varepsilon^3]} \tag{2}$$

where γ_{c} is the resistance of the cake layer, d_{s} is the diameter of particle (m) and ε is the porosity of cake layer (%).

RESULTS AND DISCUSSION

The effects of flocs' circulating condition on membrane fouling

The effects of flocs' circulating on floc size

When adding coagulant ($FeCl_3$) only the concentration of coagulant increased from 10 to 30 mg/L, the average floc size increased from 179 to 450.5 μm (Figure 2). When the concentration of coagulant is 20 mg/L, the morphology of the flocs reaches saturated status; the maximum average particle size of floc can reach 450.5 μm and the floc particle size is largely distributed in the range of 300–600 μm. While the concentration of coagulant is 25–30 mg/L, there are no obvious changes to floc size.

As the concentration of coagulant and reflux flocs increases, the floc size also increases under flocs circulating. The results showed that when reflux flocs were 5, 10 and 15 mg/L, respectively, the flocs' diameter ranged from 300 to 500 μm. When the concentration of coagulant and reflux flocs were 6 and 10 mg/L, respectively, most floc particle diameters were in the range of 500–650 μm,

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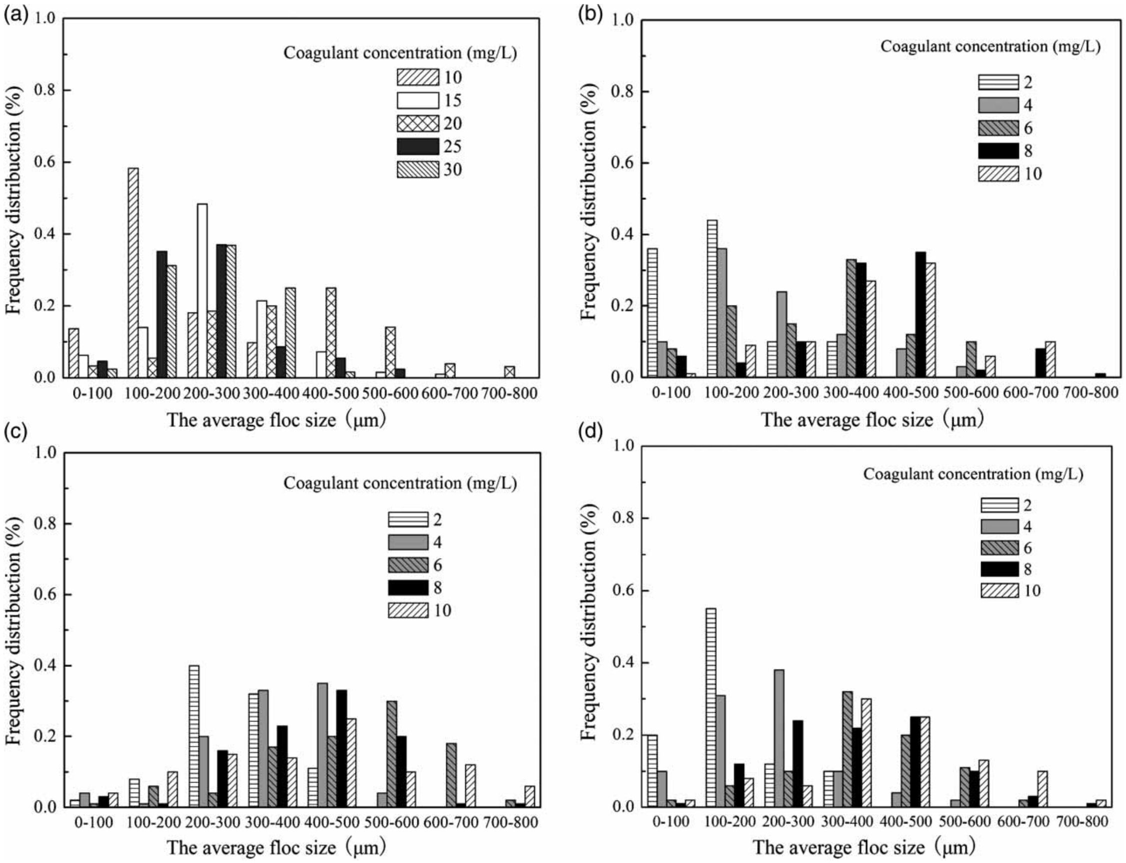

Figure 2 | Effects of reflux flocs dose on the distribution of flocs size: (a) reflux flocs = 0 mg/L; (b) reflux flocs = 5 mg/L; (c) reflux flocs = 10 mg/L; (d) reflux flocs = 15 mg/L.

flocs' average diameter was 588.42 μm, 130 μm larger than that with 20 mg/L $FeCl_3$ only. It demonstrates that circulating coagulation can improve coagulation and increase flocs' average diameter. This is because through the circulating coagulation, tiny or unstable flocs adsorb, deposit, and strengthen particle coagulation effect, so as to form larger flocs than general coagulation flocs formed by adsorption and re-aggregation (Zhao *et al.* 2010). However, if the concentration of coagulant overtakes a certain limit, too many flocs will affect flocs' collisions and therefore flocs of larger diameter cannot effectively be formed (Wang *et al.* 2010).

The effects of circulating coagulation on UMFI

Figure 3(a) indicates that the increase of the coagulant from 10 to 30 mg/L can reduce the UMFI value 0.001–0.000853 m^2/L, while the change of UMFI was not significant when the coagulant dosage was from 25 to 30 mg/L. Figure 3(b) shows that when the concentrations of coagulant and reflux flocs are 6 and 10 mg/L, respectively, the lowest UMFI value is 0.0004 m^2/L. When the concentration of coagulant is above 6 mg/L, the UMFI value increases gradually, which indicates aggravation of the membrane fouling.

It has been suggested that the adsorption capacity of flocs depended largely on the floc morphology. In general, the large particles render a strong adsorption capacity (Huang *et al.* 2008, 2009). According to Equation (2), the specific resistance of cake layer is inversely proportional to floc size. The flocs' reuse could change the floc morphology; the size distribution of flocs was more uniform and the average diameter of flocs was larger. Thus, as the coagulant and reflux flocs were added simultaneously, the specific resistance of the cake layer was smaller and the decline of the membrane flux

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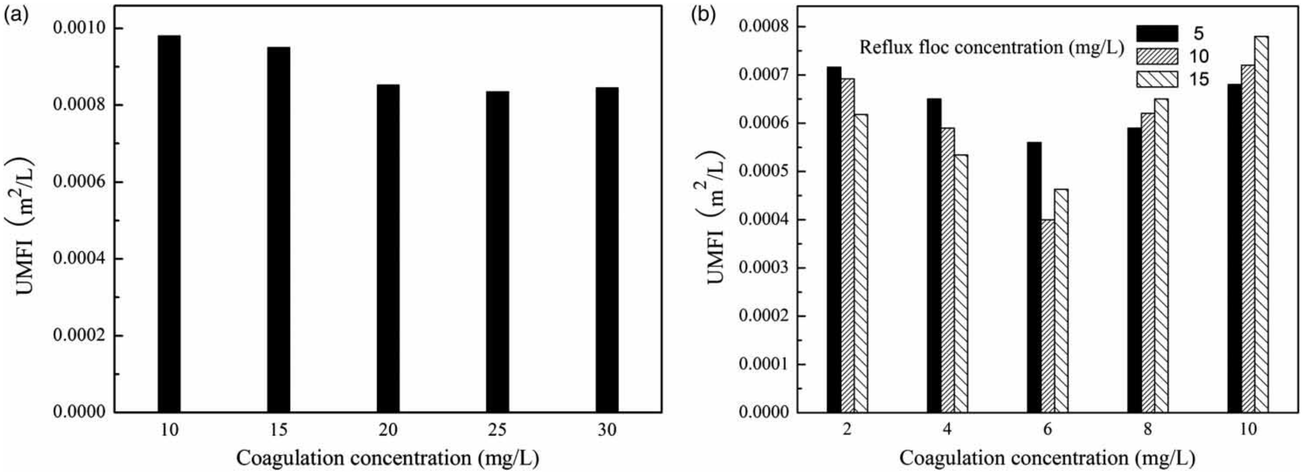

Figure 3 | Effects of reflux flocs dose on the fouling of membrane: (a) reflux flocs = 10 mg/L; (b) reflux flocs = 5, 10, 15 mg/L.

which resulted from the membrane fouling could be controlled.

The effects of flocs' breakage and re-growth on membrane fouling

The effects of flocs' breakage and re-growth on floc diameter

Under the conditions of aeration intensity, 600 L/h, and aeration time, 2 min, the floc size variations were observed and compared (see Figures 4(a)–4(d)). The variations of floc size after breaking and re-growing were similar to those under the condition of only adding coagulant. The average size of the flocs that underwent breakage and re-growth was a little smaller than that before breakage and re-growth, which suggested that the flocs possessed limited restructuring regenerative ability and could not retain their original properties. It can be seen from Figure 4(a), as the concentration of coagulant gradually increases, the particle size of flocs also gradually increases. When it came to aeration, shear force increased, flocs suffered a certain destruction and particle size decreased significantly. However, as time goes on, the broken small flocs bonded with each other and grew, particle size increased gradually, although it cannot recover to the previous floc particle size. The size of the flocs in Figures 4(b)–4(d) shows the state of floc breakage and restructuring after adding reflux flocs under different concentrations of coagulant. When the concentration of reflux floc was 10 mg/L, the growth of floc size was largest. In the range of the coagulant concentration from 6 to 10 mg/L, the largest floc size grows to about 570 μm. Flocs undergo increscent shear stress in aeration and as time increases flocs' restructure gradually, floc size can reach 500 μm and the recovery rate of flocs' diameter could reach 90%.

It can be seen from Figure 4 that flocs via breakage and re-growth could not retain their original properties. Comparing Figure 4(a) to Figures 4(b)–4(d) floc size, we can find, when reflux flocs existed, that the ability of floc breakage and re-growth, namely, floc size recovery ability, was better than that just adding coagulant. Studies have shown (Lin *et al.* 2008; Xiao *et al.* 2011) that under the condition of electric neutralization, floc breakage demonstrated remarkable -reversibility. However, when the coagulant dosing is larger, this may cause the decline of the ability of the breaking point to bind and lead to broken flocs being unable to be restored completely. Circulating coagulation can significantly reduce coagulant dosage, and the floc size can only reach the particle size by adding coagulant. When the concentrations of coagulant and reflux flocs were 6 and 10 mg/L, respectively, the maximum particle size was 540 μm before breaking, the re-growth ability was the strongest and the recovery rate of flocs' diameter could reach 90%.

The effects of flocs' breakage and re-growth on TMP

The slow growth of TMP can extend the membrane lifetime and reduce energy consumption. Figure 5 shows the change

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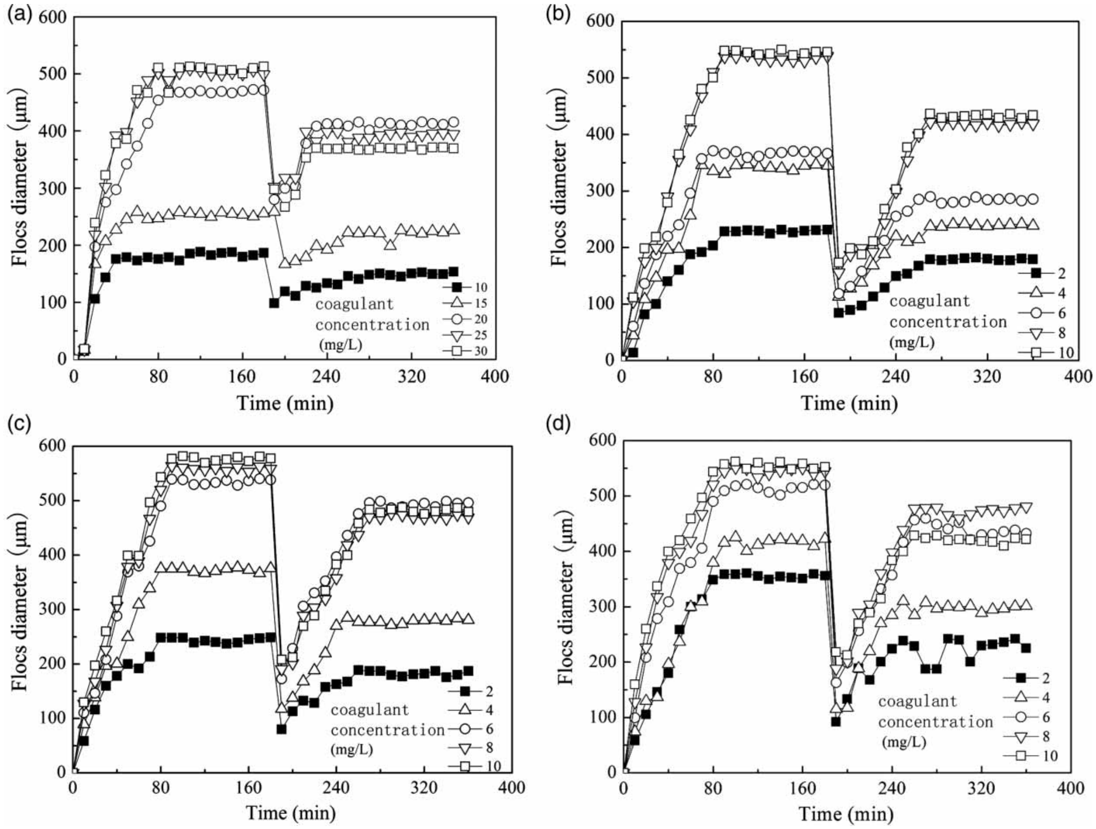
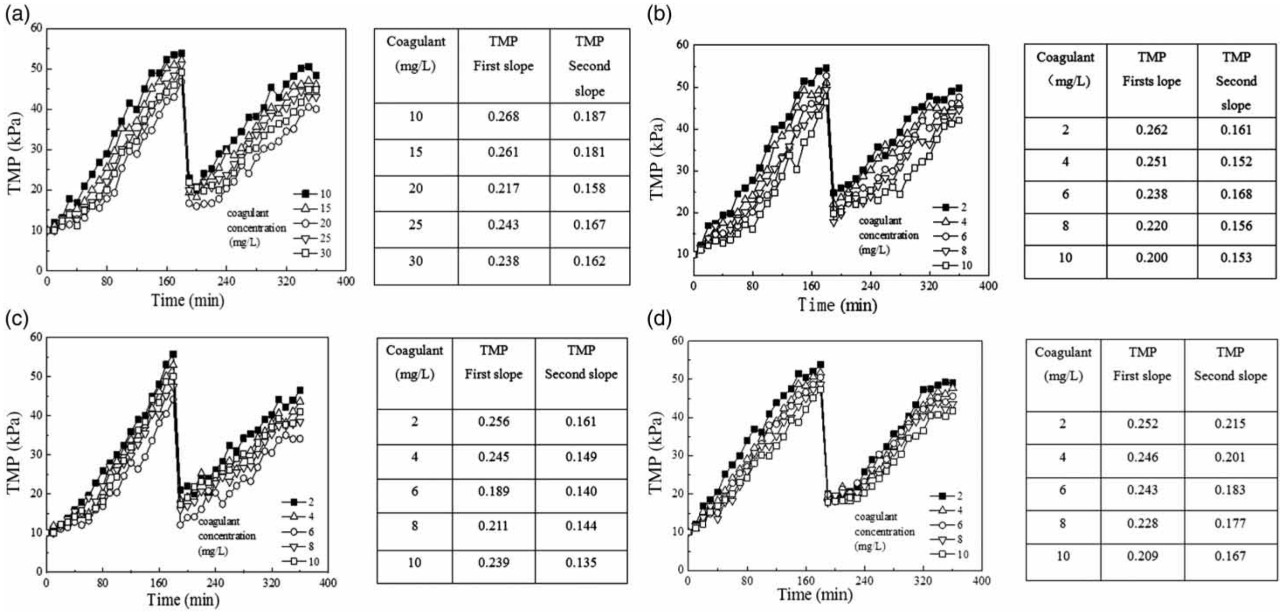


Figure 4 | Effects of reflux flocs dose on the flocs breakage and re-growth: (a) reflux flocs = 0 mg/L; (b) reflux flocs = 5 mg/L; (c) reflux flocs = 10 mg/L; (d) reflux flocs = 15 mg/L.



(a)

Coagulant (mg/L)	TMP First slope	TMP Second slope
10	0.268	0.187
15	0.261	0.181
20	0.217	0.158
25	0.243	0.167
30	0.238	0.162

(b)

Coagulant （mg/L)	TMP Firsts lope	TMP Second slope
2	0.262	0.161
4	0.251	0.152
6	0.238	0.168
8	0.220	0.156
10	0.200	0.153

(c)

Coagulant (mg/L)	TMP First slope	TMP Second slope
2	0.256	0.161
4	0.245	0.149
6	0.189	0.140
8	0.211	0.144
10	0.239	0.135

(d)

Coagulant (mg/L)	TMP First slope	TMP Second slope
2	0.252	0.215
4	0.246	0.201
6	0.243	0.183
8	0.228	0.177
10	0.209	0.167

Figure 5 | Effects of reflux flocs dose on the membrane fouling: (a) reflux flocs = 0 mg/L; (b) reflux flocs = 5 mg/L; (c) reflux flocs = 10 mg/L; (d) reflux flocs = 15 mg/L.

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of membrane fouling after aeration (600 L/h) and mainly inspects the effects of floc breakage and re-growth on TMP. Figures 5(a)–5(d) indicate that with membrane module aeration cleaning, there was a certain reduction of TMP, namely, membrane fouling was mitigated; the TMP reduced to a certain value, then would gradually rise, which showed that the membrane module was fouled. When only adding 20 mg/L coagulation, the growth of TMP was slowest, the maximum value was 41 kPa; as coagulant and reflux were added at the same time, the concentrations of coagulant and reflux flocs were 6 and 10 mg/L, respectively; flocs' diameter reach maximum value, TMP growth was slowest and a maximum value was 32 kPa. Compared with Figure 4 floc size variations, it could be found that the changing trend of membrane fouling was similar to the floc breakage and re-growth, which showed the change of floc characteristics had a certain influence on membrane fouling. When coagulant and reflux flocs were added, the average size of floc breakage and re-growth compared to the original was reduced, but the diameter and distribution of flocs were larger and better than that under only adding coagulant (Figure 2). When the flocs approached the membrane surface, the structure of the floc morphology would have a significant impact on TMP. Floc superposition could form a cake layer on the membrane surface; this process was one of the causes of TMP growth to slow (Lee *et al.* 2011). When adding coagulant and reflux flocs, well-sized and well-distributed flocs could form; this type of floc could form a porous and loose cake layer. In addition, as the specific surface of flocs were relatively large, the probability of small particles adsorbed to the surface would increase and the membrane pores' blockage would decrease. There was no reflux flocs, as the distribution of the floc size was wide, the porosity of the cake layer was easily blocked by different sizes of small flocs, and led to a larger growth of TMP.

CONCLUSION

Following the experiment, we can draw the following conclusions: when the concentrations of coagulant and reflux floc were 6 and 10 mg/L, UMFI value was only 0.0004, TMP growth was the slowest, namely, circulating coagulation can effectively slow down membrane fouling; circulating coagulation can improve the ability of flocs' re-growth and recombination, and the recovery rate of flocs' average diameter could reach 90%; circulating coagulation can effectively promote the small flocs to aggregate to larger flocs, and the floc size distribution is then uniform. In other words, circulating coagulation can enhance the coagulation effect and help lower costs.

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