Effects of recycling flocculation membrane filtration on drinking water treatment

Jie Wang, Wenjin Liu, Hui Jia and Hongwei Zhang

ABSTRACT

Recycling flocculation membrane filtration (RF-MF) and coagulation membrane filtration (C-MF) were investigated for removal of natural organic matter (NOM) from Luan river in this study. The effectiveness of recycling flocculation pretreatment on both NOM removal and membrane filtration were assessed under different concentrations of coagulant and reflux flocs. Under the conditions of coagulant dosage of 6 mg/L and reflux flocs of 10 mg/L, the removal of dissolved organic carbon (DOC) was 48.4 and 48.2% by coagulation and membrane filtration, respectively. Compared to C-MF, floc recycling benefited the removal of DOC in the coagulation stage. A unified membrane filtration index (UMFI) was used to analyze the membrane fouling, and it was observed that the lowest value was 0.0004 m^2/L at 6 mg/L coagulant and 10 mg/L reflux flocs. According to the results of NOM removal and membrane fouling, it can be concluded that DOC was the main reason for membrane fouling. In addition, the RF-MF contributed to small flocs aggregating into larger flocs with a denser structure. The maximal values of average floc size and the fractal dimension were 588.42 μm and 1.356, under the combination of 6 mg/L coagulant and 10 mg/L reflux flocs.

Key words | floc morphology, hollow fiber membrane, membrane fouling, recycling flocculation

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NOTATION

J_{SO} initial specific flux, L/(m^2 h bar)

J_{SP} specific flux, L/(m^2 h bar)

J_M measured flux, L/(m^2 h)

ΔP_M measured transmembrane pressure, bar

T_M measured temperature, °C

V_s unit permeate throughput, L/m^2

d_s diameter of particles, m

ε porosity of cake layer

r_c resistance of the cake layer

INTRODUCTION

With the rapid growth of the global population and accelerated industrialization, sources of drinking water have been heavily polluted and undoubtedly become scarcer in recent years (Bakker *et al.* 2013). With the intense regulatory activity, scarce high quality source water and the limitation of traditional drinking water treatment systems, membrane technology is considered to be a promising process for drinking water production due to its easy automation and high removal rate of turbidity and organic matter (Gao *et al.* 2011). The application of membrane technology is, however, still hindered by membrane fouling (Gao *et al.* 2011). Membrane fouling, or the loss of membrane permeability, is due to the retention of particles and dissolved contaminants on the membrane surface or in the membrane pores, which consequently reduces the hydraulic permeability of the membrane (Gao *et al.* 2011). It has been found in recent studies that a certain fraction of natural organic matter (NOM) probably contributes to this phenomenon; furthermore, the magnitude of the fouling caused by NOM, especially the irreversible part, is often specific to each membrane and feedwater combination (Huang *et al.* 2007). It has been reported that the mechanisms with regard to fouling are concentration polarization, adsorptive

fouling, cake layer deposition, and so on (Zularisam et al. 2007). Proper pretreatment processes can increase the permeate quality and minimize membrane fouling by reducing the concentration and changing the characteristics of the components in water, besides improving the effluent quality (Gao et al. 2011).

Coagulation combined with a membrane is a promising process with respect to the removal of contaminants and the maintenance of a high membrane performance. Dong et al. (2007) described that in-line coagulation could form an initial floc cake layer on the membrane surface for adsorption of a certain part of NOM, which contributed to the membrane fouling. Cake layer and pore blockage are generally accepted terms for external and internal fouling (Meng et al. 2010). However, when there was coagulation before membrane, the cake layer was perhaps the main contributor to membrane fouling (Yu et al. 2013). Both floc structure and size played significant roles in membrane filtration, which determined the porosity of the cake layer (Wang et al. 2010). Floc density has a major effect on solid–liquid separation processes. The lower fractal dimension means more open or irregular floc structure and lower effective density. Floc size has an important effect on membrane fouling potential in coagulation–membrane processes. Park et al. (2006) and Zhao et al. (2010) found that flocs of smaller size could result in higher specific cake resistance and more severe membrane fouling in coagulation–membrane processes. Barbot et al. (2008) demonstrated that cake layer consisting of flocs which were larger and more resistant to shear stress showed a flux advantage in a hybrid coagulation–membrane system.

In addition, the conventional, although classic, coagulation should be improved, and a new coagulation method be developed to reduce membrane fouling. Based on the existing process in drinking water treatment plants, the reuse of floc sludge is an alternative method to enhance coagulation efficiency and decrease coagulant addition. Specifically, recycled iron-sludge contains a large proportion of insoluble ferric hydroxides, which can be utilized as additional coagulant to enhance the removal of pollutants (Guan et al. 2005). The reflux flocs lead to the formation of larger and denser flocs, which have a significant impact on the cake layer formation and filtration performance. The most recent studies have focused on the dominant

issues of recycled floc sludge, such as appropriate recycling ratio of the sludge and appropriate operating conditions (Guan et al. 2005; Gottfried et al. 2008). However, there are few reports on the combination of recycling flocculation and membrane filtration at present.

In this paper, the recycling flocculation membrane filtration (RF-MF) was used to treat drinking water, and the relationship of RF-MF and organic matter removal, membrane fouling and floc morphology was explored. The objectives of this study were to: (1) investigate the effectiveness of recycling flocculation pretreatment for organic matter removal; (2) evaluate the effects of RF-MF on membrane fouling; and (3) determine the change of floc morphology by recycling flocculation pretreatment.

MATERIALS AND METHODS

Natural surface water

Laboratory-scale tests were carried out with natural surface water from Luan river, Tianjin, China. Characteristics of the water samples are presented in Table 1.

Membrane module

The hollow fiber ultrafiltration membranes were provided by Tianjin Motimo Membrane Technology Co., Ltd (Figure 1). The virgin membrane modules were soaked in deionized

Table 1 | Characteristics of Luan river

Parameter	Unit	Values
pH		7.51 ± 0.38
UV_{254}	cm^{-1}	0.064 ± 0.016
Chroma	PCU	55.0 ± 25.0
Turbidity	NTU	2.34 ± 0.89
TOC	mg/L	4.39 ± 1.15
DOC	mg/L	3.71 ± 0.56
Temperature	°C	18.7 ± 3
SUVA	L/(mg m)	1.75 ± 0.72
NH_3-N	mg/L	1.26 ± 0.25

TOC: total organic carbon; DOC: dissolved organic carbon; SUVA: specific ultraviolet absorption.
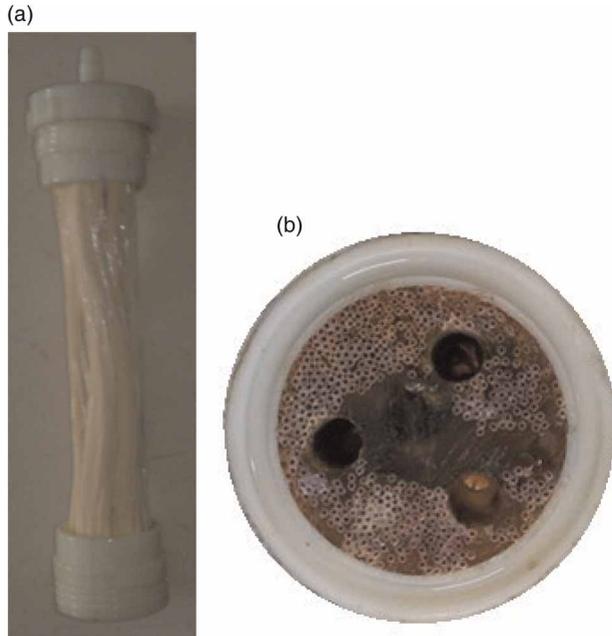
(a)

(b)

Figure 1 | Schematic diagram of hollow fiber membrane module: (a) membrane module and (b) bottom of membrane module.

water for 24 h to remove membrane-coating materials. The membrane was made from polyvinylidene fluoride with an average pore size of 0.1 μm. The inner and outer diameters of single membrane fiber were 0.6 and 1.10 mm, respectively. The effective membrane area of the module

was 0.2 m^2. The membrane module was operated in the constant flux mode in this study. The pure water flux of the new membrane module was 30 L/h·m^2 measured using ultrapure water at $18.7 \pm 3\,°C$. The measured flux was normalized to a standard temperature (20 °C) and pressure using Equation (1) (Howe *et al.* 2006):

$$J_{SP} = J_M \frac{1.03^{(20-T_M)}}{\Delta P_M} \qquad (1)$$

where J_{SP} refers to the specific flux, L/m^2 h·bar; J_M refers to the measured flux, L/(m^2 h); ΔP_M refers to the measured transmembrane pressure, bar; T_M refers to the measured temperature, °C.

Experimental set-up of RF-MF

The schematic diagram of the bench-scale RF-MF is shown in Figure 2. The reactor had a total working volume of 192 L and was divided into a coagulation tank of 64 L and a membrane filtration tank of 128 L. Coagulant (FeCl$_3$) was mixed with the raw water in a 10 mm inner diameter PVC pipe. The mixture was transferred into the coagulation tank, where it was stirred at 120 rpm. The flux of the membrane module was maintained at approximately 20 L/h.
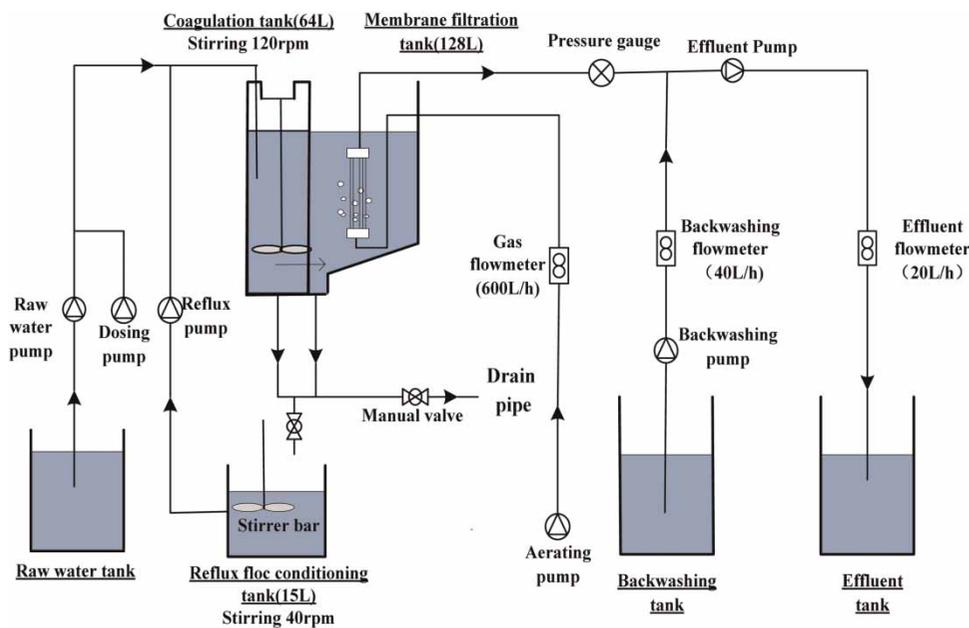

Figure 2 | Schematic diagram of RF-MF experimental set-up.

Intermittent aeration of 600 L/h and backwash of 40 L/h were applied for membrane module cleaning. Reflux floc solution was stored in the reflux flocs conditioning tank (15 L) and stirred at 40 rpm.

The RF-MF experiment was conducted using three sequential steps: (1) 30 min coagulation and membrane filtration of natural water sample; (2) 5 min hydraulic backwash of membrane module; (3) 2 min aeration.

Analytical methods

The concentration of dissolved organic carbon (DOC) and total organic carbon (TOC) was determined by a total organic carbon analyzer (TOC-VCPH, Shimadzu, Japan). The UV absorbance at 254 nm (UV$_{254}$) was measured using a UV-vis spectrophotometer (UV-2540, Shimadzu, Japan). Water turbidity and chroma were measured with a turbidimeter (2100N, Hach, USA) and a colorimeter (HI93737, HANNA, Italy), respectively. Specific ultraviolet absorption (SUVA) value was calculated from the ratio of UV$_{254}$ to DOC. Water pH was measured by a pH meter (PHS-25, INESA, China). Water temperature was measured at the beginning of each test using an ordinary thermometer. Reflux floc concentration was determined by a relationship between the floc volume (mL) and floc mass (mg), meanwhile, making a standard curve according to the relationship.

Image analysis of the flocs

Samples of flocs were acquired below the surface of the solution by a 5 mm inner diameter hollow plastic tube. After transferring the sample to petri dishes with deionized water, the images of the flocs in the sample were captured by a charge coupled device (CCD) camera (MLM3XMP, OPT, China). The camera had a sensor matrix consisting of 1,392 (horizontal) × 1,040 (vertical) pixels. Each pixel was recorded using 8-bit resolution, i.e., there were 256 gray levels for each pixel image. The floc fractal dimensions were obtained by processing the floc images using Image software to obtain the average size.

Assessment of membrane fouling

Proper techniques for the assessment of membrane fouling are necessary. At present, many methods have been developed for membrane fouling evaluation, such as the change of membrane flux and transmembrane pressure. Since the membrane flux and transmembrane pressure are both vulnerable to external influences, the assessment of the whole process is inaccurate. Huang *et al.* (2008) presented a new parameter, the unified membrane fouling index (UMFI), to evaluate membrane fouling which is generally defined as:

$$\text{UMFI} = \frac{J_{so}/J_{sp} - 1}{V_s} \tag{2}$$

where J_{so}/J_{sp} and V_s are the inverse of the normalized specific flux (dimensionless) and the unit permeate throughput (L/m^2), respectively.

RESULTS AND DISCUSSION

Effects of floc recycling on DOC and UV$_{254}$ removal

Figure 3 shows the DOC and UV$_{254}$ removal efficiency at different concentrations of coagulant and reflux flocs. The optimal coagulation dosage of 20 mg/L was found in the coagulation membrane filtration (C-MF) system. In comparison, the RF-MF system had an optimal combination of coagulant dosage of 6 mg/L and reflux flocs 10 mg/L. In the C-MF system, the organic matter removal rate was increased in the range of the coagulant dose from 5 to 20 mg/L, and gradually declined when the coagulant dose was higher than 20 mg/L. For the RF-MF system, the findings demonstrated that the removal rate of organic matter was not always enhanced by increasing reflux flocs. In the RF-MF system, an increase of the coagulant dose from 2 to 8 mg/L can result in improving the removal efficiency of the organic matter with a constant concentration of reflux flocs; however, a coagulant dose from 8 to 10 mg/L can lead to reduction of the removal rate. The enhancement of removal efficiency in the RF-MF was mainly attributed to physical adsorption and/or sweep flocculation by hydroxide precipitates and improved collision frequencies and efficiencies among particles. At the same time, the reused flocs and the new additional coagulant can increase the concentration of the particles and collision efficiency, and also increase the number of active flocs which cohere other small flocs, which
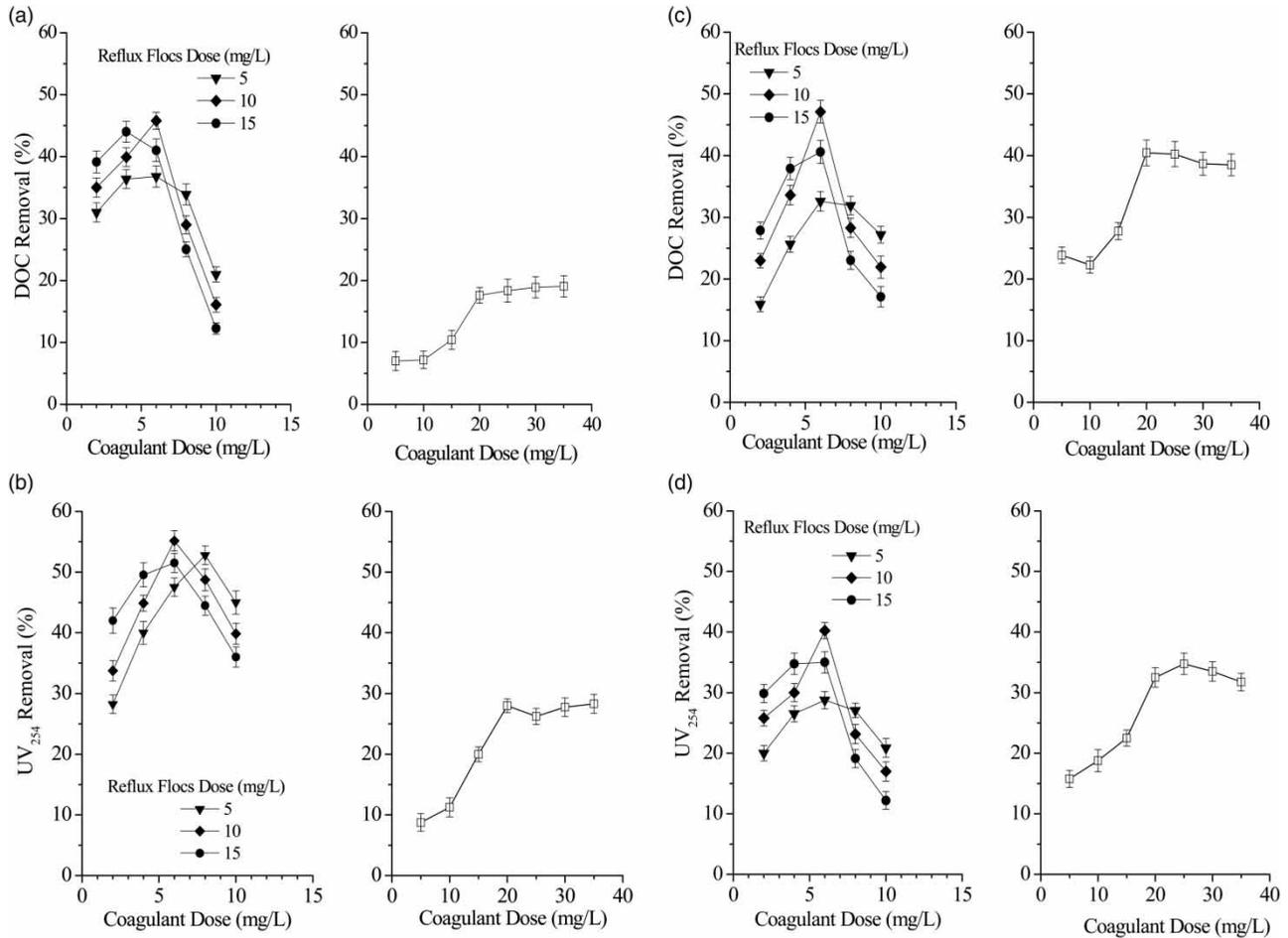
Figure 3 │ NOM removal efficiency as a function of different concentrations of reflux flocs for coagulation ((a) and (b)) and membrane filtration ((c) and (d)).

is very important in the reuse process for enhancing organic matter removal. The higher particle concentrations and diameters would result in higher collision probability, which favored the flocculation process. But the amount of organic matter released from the flocs was related to the coagulant concentration (Zhou *et al.* 2012). The trapped organic matter released at higher coagulant concentrations could increase the concentration of organics, which further leads to a decline in removal efficiency. When the coagulant concentration was high enough, the excessive flocs reached saturation. At this point, it was difficult to realize effective collision between the flocs (Yang *et al.* 2009; Yu *et al.* 2010) because of a decrease in the contact activity of flocs.

It can be seen from Figures 3(a) and 3(b) that the removal efficiency of UV_{254} was generally higher than that of DOC in the supernatant under different

concentrations of coagulant and reflux flocs. A maximum of 48.4% of DOC and 55% of UV_{254} were removed by the RF-MF system at the coagulant dosage of 6 mg/L and the reflux flocs of 10 mg/L. Interestingly, the best removal rates of DOC and UV_{254} were 20.8 and 30.8% by the C-MF system at the coagulant dosage of 20 mg/L. Compared to the supernatant, the removal efficiency of DOC was higher than that of UV_{254} in the membrane effluent (Figures 3(c) and 3(d)). The maximum removal efficiencies of DOC and UV_{254} were 48.2 and 41% at the coagulant dosage of 6 mg/L and the reflux flocs of 10 mg/L. In the C-MF system, the best removal efficiencies of DOC and UV_{254} were 41.5 and 36.8% at the coagulant dosage of 20 mg/L. In comparison with C-MF, the removal of DOC by coagulation was improved greatly in the RF-MF system. Moreover, substantial removal of DOC was observed
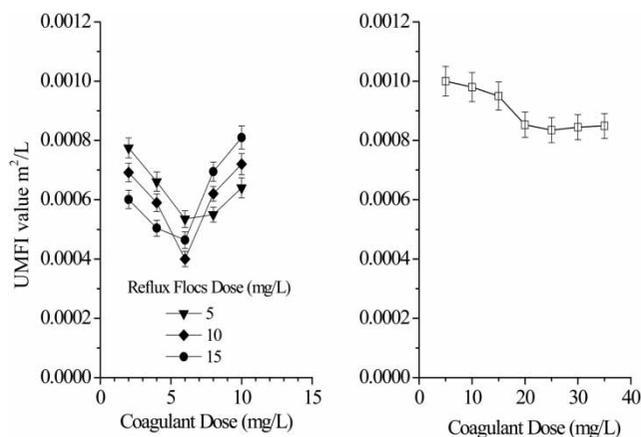
Figure 4 │ Effects of coagulant and reflux flocs dose on the membrane fouling.

through the membrane filtration in the C-MF system. Because UV_{254} represented a kind of macromolecular hydrophobic organic compound containing benzene ring and conjugated double bonds, it could be removed easily in the coagulation through the mechanisms of sweep and adsorption (Nuray *et al.* 2007). DOC is the hydrophilic organic matter, and it could be removed mostly in the membrane filtration. Furthermore, most studies of organic fouling are concentrated on the fractionation method to investigate the specific fraction of NOM responsible for fouling (Gao *et al.* 2011). In this study, the effective removal of DOC was supposed to mitigate effectively the membrane fouling during the subsequent membrane filtration.

Effect of floc recycling on membrane fouling

Coagulation could remove the compounds that preferentially contribute to membrane fouling, and it could thus improve the membrane performance (Howe *et al.* 2006). The change in organic matter after the coagulation pretreatment affected the membrane fouling. The UMFI value was used to assess the membrane fouling during the filtration (Figure 4). For the C-MF system, the increase in the coagulant dosage from 5 to 25 mg/L can reduce the UMFI value from 0.001 to 0.000853 m^2/L, and the change of UMFI value is not at significant the coagulant dosage from 25 to 35 mg/L. For the RF-MF system, at a coagulant dosage of 6 mg/L and reflux flocs of 10 mg/L, the best membrane permeation with the lowest UMFI value of 0.0004 m^2/L was obtained. When the coagulant concentration was above

6 mg/L, the UMFI value increased gradually, which indicates aggravation of the membrane fouling.

The initial floc cake layer formed on the membrane surface could absorb the organic matters. Park *et al.* (2006) exploited a precoating method in both standard coagulation and in-line coagulation, demonstrating that removal of DOC could make the membrane more filterable, and also found that 13.0 mg/L $FeCl_3$ presented a more enhanced filterability than 4.1 mg/L poly-aluminum chloride due to the cake layer having better permeability (Cao *et al.* 2011). It was reported by Huang *et al.* (2007) that the DOC was strongly related to the total and irreversible fouling of low pressure membrane filtration in the treatment of drinking water. Meanwhile, Carroll *et al.* (2000) and Fan *et al.* (2001) reported that the effect of hydrophilic organic matter (such as DOC) contributed markedly to membrane fouling. It was described that a possible adverse interaction existed, and the DOC gave rise to more severe fouling. The recycling flocculation could greatly improve the DOC removal rate by the adsorption of flocs and reduce the UMFI value.

Effect of floc recycling on floc morphology

Figure 5 shows the images of flocs captured in different cases. In this study, a large number of flocs were involved in the calculation of fractal dimension and average size, therefore it is impossible to determine solely from Figure 5 that the floc structures formed at 6 mg/L coagulant and 10 mg/L reflux flocs were irregular. Clearly, Figure 5 shows that the floc sizes at 6 mg/L coagulant and 10 mg/L reflux flocs were larger and more compact than those of the control trials.

For the C-MF system, an increase of the coagulant dose from 5 to 35 mg/L would enlarge the average particle size from approximately 179 to 450.5 μm, and enhance the fractal dimension from 1.16 to 1.234. A maximum value was obtained at 20 mg/L for C-MF. When the coagulant concentration was from 25 to 35 mg/L, the distribution of the average floc size was stable as well as that of the fractal dimensions. For the RF-MF system, when the 6 mg/L coagulant and 10 mg/L reflux flocs were added into the coagulation reactor, both the average floc size and the fractal dimension reached their maximal values, which were 588.42 μm and 1.356, respectively. Both of them were
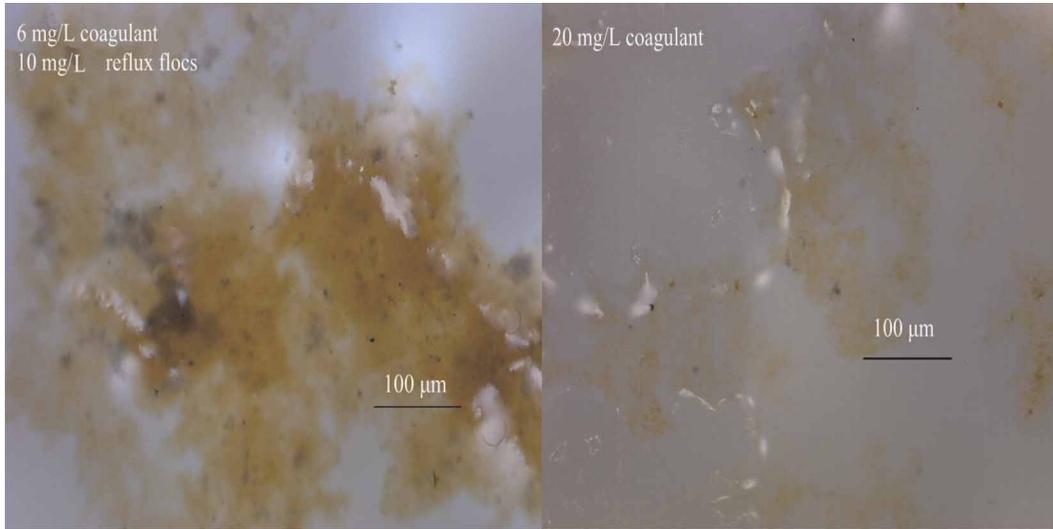
Figure 5 │ Images of the flocs formed at RF-MF and C-MF.

higher than the best values in the C-MF system, which indicated that the flocs formed were large and irregular in comparison with those of the C-MF system (Figure 6).

In addition to particle size, surface morphology of the flocs also affects the behavior of aggregated particles, particularly with regard to collision efficiency and settling rates. In the coagulation process for water treatment, the flocs with high density are preferable because of their better settability in the subsequent settling unit. Compared to the C-MF system, the RF-MF system promoted the formation of flocs with large and dense structures, which also demonstrated a more regular morphology via the effective collision between the flocs (Zhao *et al.* 2010). The decrease in perimeter-based fractal dimension was associated with an increase in floc size. However, both of them were better in the RF-MF than in the C-MF at the optimal combination of 6 mg/L coagulant and 10 mg/L reflux flocs. Reusing flocs was an important step for active floc reunion in forming large and dense structures in the coagulation process (Lin *et al.* 2008; Xiao *et al.* 2011). Meanwhile, it was suggested that the adsorption capacity of flocs depended largely on the floc morphology. In general, the large particles render a strong adsorption capacity (Yu *et al.* 2010). It has thus been proposed that the majority of absorbable DOC is enmeshed in flocs through coagulation in the main treatment train (Guan *et al.* 2005). On the other hand, the high floc size and fractal dimension would
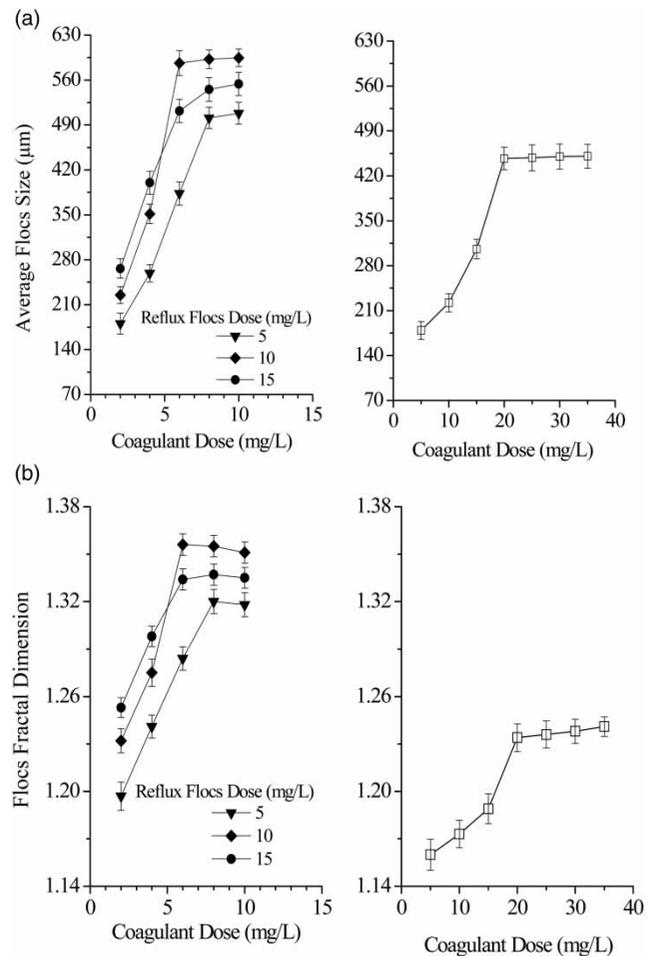

Figure 6 │ Effects of coagulant and reflux floc dose on (a) average floc size and (b) flocs' fractal dimension.

slow down the membrane fouling based on the Kozeny–Carman equation (Equation (3)):

$$r_c = 180 \frac{(1-\varepsilon)^2}{[(d_s)^2 \varepsilon^3]} \qquad (3)$$

where r_c is the resistance of the cake layer; d_s and ε are the diameter of particles, (m) and the porosity of cake layer, respectively. As indicated by Equation (3), the resistance of the cake layer was positively relative to d_s and ε. In the RF-MF system, the reflux flocs significantly increased the flocs average size. Additionally, d_s was also improved since the diameters of recycled floc particles were larger than those in raw water. Therefore, the resistance of the formed cake layer was smaller than that in C-MF, and the decline of the membrane flux resulting from the membrane fouling could be controlled.

In this study, it was reported that at 6 mg/L coagulant and 10 mg/L reflux flocs that the RF-MF could change the floc morphology to form a large size and dense flocs; further remove effectively the hydrophilic organic matter lowering the amount of organic matter attached to the membrane surface; reduce the resistance of the formed cake layer. Thus, the membrane fouling was alleviated. In a word, the RF-MF can improve effectively organic matter removal efficiency and weaken membrane fouling.

CONCLUSIONS

The combination of 6 mg/L coagulant and 10 mg/L reflux flocs achieve the highest removal efficiency of organic matter. Moreover, the recycling flocculation had a substantial impact on the removal of organic matter, especially the DOC in the supernatant, lowering the amount of DOC attached to the membrane surface. DOC in solution was supposed to play an important role in membrane fouling, and the removal of DOC could slow down membrane fouling. In comparison with C-MF, the RF-MF system was able to mitigate effectively the membrane fouling. The RF-MF promoted the formation of large and dense flocs, which is also helpful in mitigating membrane fouling. Consequently, the RF-MF system was superior to the C-MF system in the removal of DOC and membrane fouling control.

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