Effect of coagulation pretreatment on the fouling of ultrafiltration membrane

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Abstract

The purpose of this study is to understand the effect and mechanism of preventing membrane fouling, by coagulation pretreatment, in terms of fractional component and molecular weight of natural organic matter (NOM). A relatively higher molecular weight (MW) of hydrophobic compounds was responsible for a rapid decline in the ultrafiltration flux. Coagulation could effectively remove the hydrophobic organics, resulting in the increase of flux. It was found that a lower MW of neutral hydrophilic compounds, which could remove inadequately by coagulation, was responsible for the slow declining flux. The fluxes in the filtration of coagulated water and supernatant water were compared and the results showed that a lower MW of neutral hydrophilic compounds remained in the supernatant water after coagulation could be rejected by a membrane, resulting in fouling. It was also found that the coagulated flocs could absorb neutral hydrophilic compounds effectively. Therefore, with the coagulated flocs formed on the membrane surface, the flux decline could be improved.

Key words: drinking water treatment; ultrafiltration; coagulation; fouling

Introduction

Ultrafiltration (UF) membranes have rapidly become an efficient alternative to conventional treatment for drinking water production. The primary problem encountered in the application of membrane technology is membrane fouling (Laine *et al.*, 2003). Fouling can cause flux decline, resulting in an increase in the cost of production of drinking water and even replacement of membrane. A primary factor affecting fouling is natural organic matter (NOM).

As a means of preventing fouling, using pretreatment to lower the feed of NOM has been a useful approach. The pretreatment such as coagulation, adsorption, and ozonation, before the membrane technology, had been used to remove NOM and to mitigate fouling (Park *et al.*, 2002; Maria and Sylwia, 2002). Coagulation is more widely applied and researched because of the low cost and easy use.

It has been shown that coagulation could indeed improve the flux (Guigui *et al.*, 2002; Park *et al.* 2002; Oh and Lee, 2005). However, some research studies have indicated that although coagulation could remove NOM and decrease the resistance of the membrane filtration, the rate and extent of fouling could not be mitigated by coagulation (Veronigue *et al.*, 1990). This phenomenon may be associated with the properties of NOM such as hydrophobicity, hydrophilicity, and molecular weight distribution. Carroll *et al.* (2000),

reported that the neutral hydrophilic fraction of NOM could cause significant fouling. An experiment with three samples of Australian surface water, using polyvinylidene difluoride (PVDF) ultrafiltration, was performed by Fan *et al.* (2001), and their results showed that the primary factor affecting the flux decline was also the neutral hydrophilic fraction. Cho *et al.* (2000) reported that a higher MW of hydrophilic fraction was responsible for the flux decline. However, James *et al.* (1996) investigated the influence of hydrophobic and hydrophilic NOM on nanofiltration and their studies showed that the hydrophobic NOM fraction was responsible for nearly all of the flux decline and the hydrophilic NOM fraction caused little flux decline. Li and Chen (2004) found that NOM with a small MW was responsible for fouling. On the basis of previous studies by several researchers, it can be concluded that the influence of the properties of NOM on fouling is not well elucidated.

The aim of this study was to investigate the effect of coagulation as a pretreatment for UF membrane on NOM removal, and to understand the effect and mechanism of hydrophobicity and hydrophilicity of NOM on membrane fouling.

1 Materials and methods

1.1 Raw water source and NOM fractionation

The source water used in this study was obtained from the river located in the campus of Tongji University. The water qualities are shown in Table 1.

The fractionation procedure is shown in Fig.1. The raw

Table 1 Raw water quality parameters

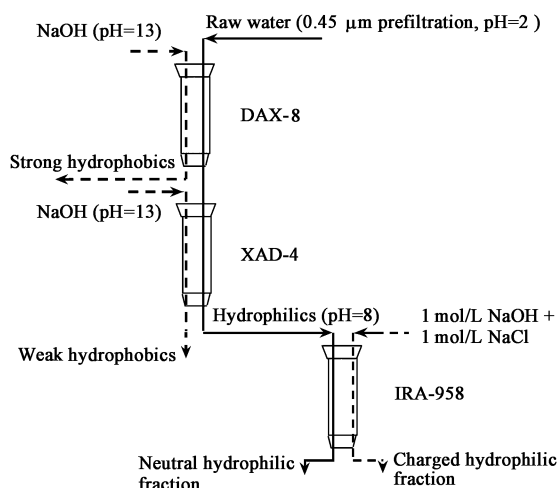| Parameter	Value	Parameter	Value
pH	7.1–7.5	DOC (mg/L)	5.341–6.29
Turbidity (NTU)	5.3–37.6	UV_{254} (cm^{-1})	0.088–0.11
Color	21–65	COD_{Mn} (mg/L)	6.4–7.3

Fig. 1 Outline of raw water fractionation procedure.

water was filtered through a 0.45 μm membrane, adjusted to pH 2, and fed onto a Supelite DAX-8 resin, which retained the strong, hydrophobic organic matter. This fraction was eluted with NaOH. The unabsorbed fraction from the DAX-8 resin was fed onto an Amberlite XAD-4 resin, which retained the weak hydrophobic organic matter. The unabsorbed fraction from the XAD-4 resin was fed onto an Amberlite IRA-958 anion exchange resin, which retained the charged material. This fraction was eluted with a NaOH/NaCl mixture. The remaining neutral material was not retained by any of the resins. The resulting NOM concentrations in each fractionation procedure are shown in Table 2.

Table 2 NOM concentrations in each fractionation procedure

Item	Fraction	NOM conc. (mg/L)
Raw water		5.763
DAX-8	Unabsorbed fraction	3.062
	Adsorbed fraction	2.631
XAD-4	Unabsorbed fraction	2.764
	Adsorbed fraction	0.316
IRA-958	Unabsorbed fraction	2.593
	Adsorbed fraction	0.249
Recovery rate (%)	96.1	

1.2 Ultrafiltration experiments

Prior to the filtration experiment, the coagulation test was conducted. Alum was selected as the coagulant. Alum was added to raw water and then agitated for 30 min (rapidly mixing for 1 min at 100 r/min, slowly mixing for 29 min at 30 r/min). The coagulated water was immediately fed into membrane set-up for coagulated filtration, without any settlement. The remaining fraction was settled for 30 min. The supernatant was then used as a supernatant

filtration. The schematic diagram of the flat-sheet UF setup used in this study is shown as Fig.2. In the filtration phase, feed and filtration valves were opened to allow the feed water be sent to the module for 60 min of filtrate operation. After the filtrate operation, 1 min of backwash was performed by opening the backwash feed and flushing valve. Following this, a flushing operation was conducted for 10 s by opening the feed and flushing valve. Pressure of filtrate and backwash were 0.1 MPa.
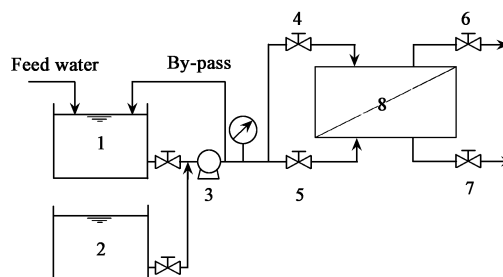

Fig. 2 Schematic experimental setup. (1) raw water tank; (2) backwash tank; (3) pump; (4) feed water valve; (5) backwash water valve; (6) flushing valve; (7) permeate valve; (8) membrane module.

A new membrane was used in each experiment. Prior to each experiment, the clean water of the flux was measured. The ratio of flux measured (J) to ultra-pure water flux (J_0) was designated as J/J_0 for comparing the effects of each experiment.

Polyvinylidene difluoride (PVDF) of flat UF membrane with MW cut-offs of 150 kDa was used for this experiment. The membrane area was 5.841×10^{-3} m^2. Nitto Denko Corporation provided the membrane and the setup.

1.3 Analytical methods

The turbidity was determined using a turbidimeter (Hach 2100N). A UV spectrophotometer (Shimadzu UV-2201) and TOC analyzer (Shimadzu TOC-V$_{CPH}$) were used to measure UV_{254} and DOC respectively.

MW distribution of NOM was fractionated using Amicon membranes: YM30, YM10, YM3, and YM1, corresponding to the MW cut-offs of 30, 10, 3, and 1 kDa respectively. Fractionation was performed in the Amicon 8400 UF cell. A pressure of 0.1 MPa was applied for filtration. The fractional amount of organic matter within each size range was calculated from the difference in TOC concentrations between the adjacent filtration samples.

2 Results

2.1 Raw water fractionation

The fractionation of raw water was performed thrice. The result is shown in Table 3. The components of the raw water studied comprised mainly of hydrophobic acids and hydrophilic neutral fraction. For this reason, the experiment for the effect of NOM fraction on membrane filtration was focused on two fractions: hydrophobic acids (HA) and hydrophilic neutral (Neut).

MW distribution of NOM for different fractions based on DOC and UV_{254} measurements is shown in Fig.3. As

Table 3 Fractional components of the NOM(%)

Fraction	Fraction of NOM	
	Based on DOC measurement (%)	Based on UV_{254} measurement (%)
Hydrophobic acids	44	44.3
Weak hydrophobics	4.1	4.7
Hydrophilic charged compounds	3.3	6.6
Hydrophilic neutral compounds	48.6	44.4

seen in Fig.3a, Neut fraction of DOC in <1 kDa region reached 60%, accounting for the most percent of total NOM. As MW was greater than 1 kDa, the Neut fraction dropped to less than 10%, except for a 3–10 kDa region. HA fraction of DOC in <1 kDa region accounted for 30%, less than that of the Neut fraction. In 1–3 kDa and 10–30 kDa fractions, the HA fraction accounted for 30% and 20% respectively. These results suggest that the majority of Neut fraction of DOC mainly consists of <1 kDa and HA fraction was composed of >1 kDa. It can be seen from Fig.3b that the Neut fraction of UV_{254} accounting for total UV_{254} dropped gradually as the MW increased. Although the HA fraction of UV_{254} was equal approximately to Neut fraction in the <1 kDa region, in the 10–30 kDa region, the HA fraction of UV_{254} accounted for over 30%, far greater than that of Neut fraction. It can be concluded that the more hydrophilic the NOM, the lower its MW and the more hydrophobic the NOM, the higher its MW.

2.2 Effect of coagulation pretreatment on the filtration flux

The variation in J/J_0 for each filtration with and without

coagulation is shown in Fig.4 as a function of time. In the filtration of the raw water, the flux dropped rapidly. At the end of the first filtration cycle, although the flux had somewhat recovered after the backwash, the flux dropped to 20% of pure water flux. As filtration and backwash were repeated, the flux started declining gradually. This suggested that the fouling of the membrane had occurred at the initial filtration.

With coagulation as a pretreatment, the dosage and pH were the primary influencing factors. In the previous studies with the same source, water, and using the same membrane, it was found that when the dosages were over 4 mg/L, the flux had enhanced noticeably, which could be contributed to greater than 1000 MW removed by coagulation (Dong *et al.*, 2005). The experiment was also performed on the effect of pH on membrane fouling in the coagulation pretreatment. The result showed that although lowering the pH could remove and decrease the organics in the feed to membrane effectively, a significant fouling was observed, which could be explained as a fact that the reduction in pH decreased the repulsion force between NOM and the membrane and enhanced the adsorption of NOM onto the membrane (Dong *et al.*, 2006). On the basis of the previous results, the dosage was determined to be 4 and 10 mg/L (Fig. 4) and a neutral pH was selected in this experiment.

With the addition of coagulant 4 mg/L, the flux increased significantly. During the filtration of coagulated water, the flux declined to 50% of J_0. After backwash, the flux recovered completely for each filtration cycle. During the filtration of supernatant water, although the
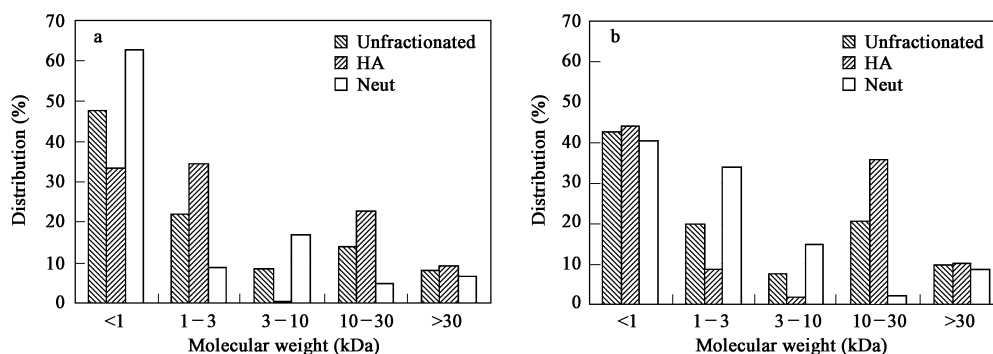

Fig. 3 Molecular weight distribution for different fractions measured as DOC (a) and UV_{254} (b).
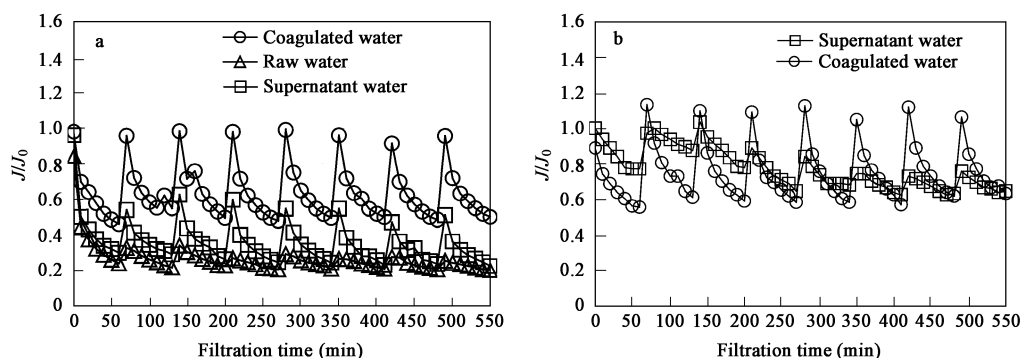

Fig. 4 Effects of filtration of coagulated water and supernatant water on flux and backwash. Coagulant dosage 4 mg/L (a) and 10 mg/L (b).

flux had increased to some extent, the rate of flux decline was considerably greater than the coagulated water. As the addition of coagulant was increased to 10 mg/L, the flux for both coagulated water and supernatant water had enhanced greatly. Similar to adding 4 mg/L, the flux for coagulated water was greater than that for supernatant water.

It is interesting to note that the fluctuation of flux has shown a wider range for filtration of coagulated water than for filtration of supernatant water. These changes in the fluctuation of flux represent the configuration of the cake formed on the surface of the membrane. The cake is more porous, loose, and compressive. According to Carmen-Kozeny equation, this cake represents the lower resistance to filtration.
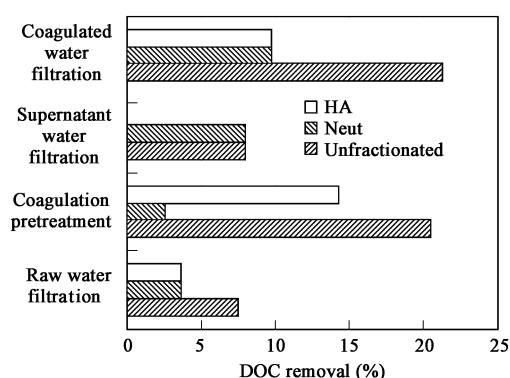

Fig. 5 Unfractionated and fractionated DOC removal by coagulation pretreatment and membrane filtration.

2.3 Effects of coagulation and membrane on removal NOM

The effect of coagulation and membrane on NOM removal is shown in Fig.5. In the filtration of raw water without coagulation, the membrane removed only 7.5% of DOC, with a split in HA and Neut fraction, suggesting that the UF alone was less effective in NOM removal. In the coagulation pretreatment, the NOM removal efficiency had increased to 20.5%, with 14.3% for HA fraction and 2.5% for Neut fraction respectively. This result suggested that the contribution of coagulation to NOM removal was the HA fraction, which was consistent with the result that the coagulation removed the HA fraction more effectively than the Neut fraction (Sinsabaugh III et al., 1986).

Although the membrane filtration only removed 8% of NOM from supernatant water after coagulation, almost all the removed NOM was of Neut fraction. In the filtration of coagulated water, NOM removal by membrane combined with coagulation was increased to 21%, with 9.74% for HA fraction and 9.4% for Neut fraction respectively. In the supernatant filtration model, membrane combined with coagulation removed 28.5% of NOM. This result suggested that a supernatant filtration model might remove more NOM than a coagulated filtration model.

2.4 Effects of coagulation pretreatment and membrane filtration on molecular weight distribution for fractionated NOM

To better understand the influence of MW of NOM on fouling, the amount of NOM deposited on the membrane was investigated by calculating the difference between the feed water and the permeate in every MW fraction.
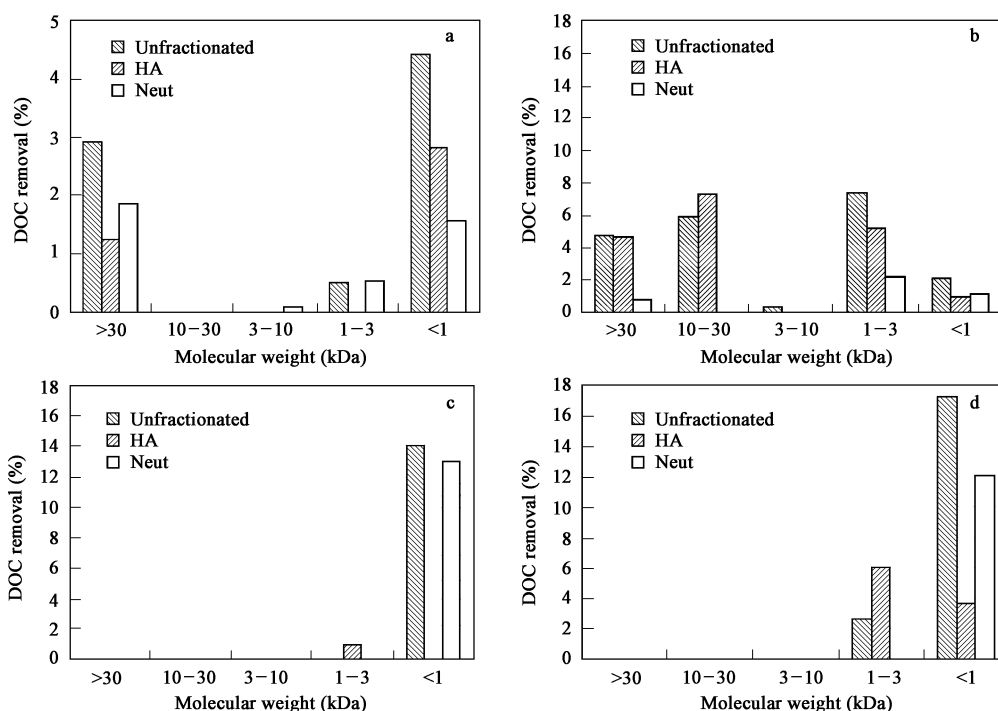

Fig. 6 Effect of direct filtration (a), coagulation pretreatment (b), supernatant water filtration (c), and coagulated water filtration (d) on molecular weight distribution of fractionated compounds.

The effect of membrane filtration, without coagulation pretreatment, on various MW fractions for fractionated compounds is shown in Fig.6a. The membrane primarily rejected DOC greater than 30 kDa and smaller than 1 kDa MW. A similar trend was observed for the HA and Neut fractions. The size of membrane used was greater than 1 kDa, therefore, the removal of <1 kDa fraction might be contributed to the rejection of the cake formed on the surface of membrane during filtration.

The effect of coagulation on various MW fractions for fractionated compounds is shown in Fig.6b. The coagulation was effective in removing greater than 10 kDa and 1–3 kDa MW of NOM and less effective in removing smaller than 1 kDa MW of NOM for unfractionated and HA fraction. As for Neut fraction, the coagulation showed poor removal efficiency in all MW fractions, which was consistent with the result reported by Sinsabaugh III *et al.* (1986).

The effect of removal efficiency in various MW fractions with supernatant water by membrane is shown in Fig.6c, which shows that the membrane primarily rejected <1 kDa of Neut fraction of NOM and had little efficiency for 1–3 kDa of HA fraction. The removal efficiency with coagulated water is shown in Fig.6d, which shows that the membrane rejected <1 kDa and 1–3 kDa fractions of NOM.

3 Discussion

In the ultrafiltration of raw water without coagulation, the flux had declined rapidly and could not be recovered by backwash (Fig.4a). As the coagulation was used as pretreatment, filtration flux of both supernatant water and coagulated water were enhanced to a large extent (Fig.4a and 4b). With coagulation as pretreatment, no HA fraction was found to be removed for ultrafiltration of supernatant water; however, 3.6% of HA fraction was removed without coagulation pretreatment. These results indicate that the HA fraction of NOM in raw water was responsible for the rapid flux decline, which was in agreement with the result achieved by Fan *et al.* (2001) and Nilson and DiGiano (1996), who suggested that hydrophobic acids caused a greater flux decline than transphilic acids.

Coagulation pretreatment selectively removes the hydrophobic fraction of NOM, leaving the hydrophilic fraction in supernatant water. Therefore, the residual NOM plays an important role in determining the rate of fouling in ultrafiltration with coagulation pretreatment. In ultrafiltration of supernatant water, the flux experiences a slow decline. Fig.5 shows that the membrane primarily rejects <1 kDa of the Neut fraction. This finding indicates that a small size of Neut fraction gives rise to a slow decline flux.

It should be noted that although the dosage is the same, the behavior of flux in ultrafiltration of coagulated water and supernatant water is different. The flux with coagulated water is higher than that with the supernatant water. This result implies that the cake consists of flocs formed on the membrane surface during the filtration of coagulated water, which plays a significant role in preventing fouling. With

the existence of a floc cake layers, the Neut fraction gets deposited on the cake layer instead of on the membrane surface. Therefore, the foulant can then be easily removed by removing the floc cake layers by backwashing and flushing.

On the basis of previous results and discussion, the role of coagulation is postulated to interpret the effect of coagulation on fouling, as shown in Fig.7. As the coagulated water is filtrated, the flocs deposit on the surface of the membrane and form the cake that absorbs the Neut fraction of NOM. The cake can be easily removed by backwashing and flushing, because it is not closely adhered to the surface. As the supernatant water is filtrated, the Neut compounds remain in the water after coagulation is rejected by the membrane, according to the results shown in Fig.5. They closely adhere to the surface of the membrane and are not easily removed by backwashing and flushing, resulting in the flux decline.
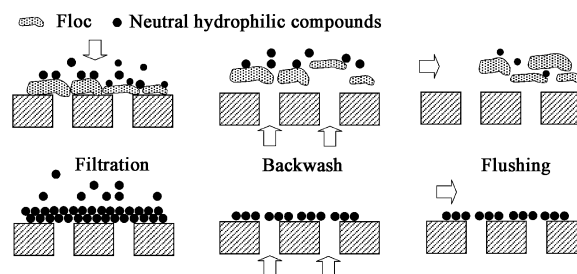

Fig. 7 Mechanism of preventing membrane from fouling by coagulation treatment.

4 Conclusions

Although membrane without coagulation pretreatment rejected less NOM, severe fouling had also occurred. The reason for this may be contributed to the hydrophobic fraction of NOM deposited on the pores or on the surface of the membrane in ultrafiltration of raw water. The contribution of the hydrophobic fraction to fouling presented a rapid decline flux.

When coagulation was used as a pretreatment for ultrafiltration, coagulation could remove the hydrophobic fraction, resulting in the improvement of flux and reduction of fouling.

Although the dosage was the same, no flux reduction with filtration of coagulated water was experienced, suggesting that coagulation could prevent fouling. Flux with filtration of supernatant water experienced a slow decline, suggesting that in spite of a marked improvement in flux, fouling had still occurred. The result indicated that when coagulate water was filtrated, the floc cake layer that formed on the membrane surface could adsorb the hydrophilic neutral fraction of small size, whereas when the supernatant water was filtrated, the membrane rejected much of the hydrophilic neutral fraction with small size. Therefore, the contribution of neutral fraction to fouling presented a slow decline flux.

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