



ELSEVIER

Desalination 204 (2007) 181–188

---

---

DESALINATION

---

---

www.elsevier.com/locate/desal

## Effect of coagulation pretreatment on fouling of an ultrafiltration membrane

Y. Chen\*, B.Z. Dong, N.Y. Gao, J.C. Fan

*State Key Laboratory of Pollution Control and Resource Reuse, Tongji University,  
1239 Siping Road, Shanghai 200092, China  
Tel. +86 (21) 65982691; Fax +86 (21) 65983616; email: xiaojingmama@hotmail.com*

Received 20 March 2006; accepted 10 April 2006

---

### Abstract

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

*Keywords:* Drinking water treatment; Ultrafiltration; Coagulation; Fouling

---

### 1. Introduction

Ultrafiltration (UF) membranes have rapidly become an efficient alternative to conventional

treatment in drinking water production. The primary problem encountered in application of membrane technology is membrane fouling [1]. Fouling can cause flux decline, resulting in the increase of cost for production of drinking water and even

---

\*Corresponding author.

*Presented at EuroMed 2006 conference on Desalination Strategies in South Mediterranean Countries: Cooperation between Mediterranean Countries of Europe and the Southern Rim of the Mediterranean. Sponsored by the European Desalination Society and the University of Montpellier II, Montpellier, France, 21–25 May 2006.*

replacement of membranes. A primary factor affecting fouling is natural organic matter (NOM).

As a means of preventing fouling, using pretreatment to lower NOM in the feed has been a useful approach. Pretreatment such as coagulation, adsorption and ozonation before membranes has been used to remove NOM and to mitigate fouling [2–4]. Coagulation is more widely applied and researched due to low cost and being easy to use. It was shown that coagulation could improve flux indeed [2,5,6]. However, some research work indicated that although coagulation could remove NOM and decrease the resistance of membrane filtration, the rate and extent of fouling could not be mitigated by coagulation [7]. This phenomenon may be associated with such properties of NOM as hydrophobicity, hydrophilicity and molecular weight distribution. Carroll et al. [8] reported that the neutral hydrophilic fraction of NOM could cause a significant fouling. The experiment with three Australian surface water samples using PVDF ultrafiltration was performed by Linhua Fan et al. [9] and their results showed that the primary factor affecting flux decline was also the neutral hydrophilic fraction. Jaeweon Cho et al. [10] reported that higher MW of the hydrophilic fraction was responsible for flux decline. However, J.A. Nilson and F.A. DiGiano [11] investigated the influence of hydrophobic and hydrophilic NOM on nanofiltration and their work showed that the hydrophobic NOM fraction was responsible for nearly all of the flux decline and the hydrophilic NOM fraction caused little flux decline. Chi-Wang Li et al. [12] found that NOM with small molecular weight was responsible for fouling. On the basis of previous works by several researchers, it can be concluded that the influence of properties of NOM on fouling is not well elucidated.

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

## 2. Materials and methods

### 2.1. Raw water source and NOM fractionation

The source water used in this work was obtained from a river located in a university campus. The water qualities are shown in Table 1.

The fractionation procedure is shown in Fig. 1. The raw water was filtered through a 0.45  $\mu\text{m}$  membrane, adjusted to pH 2, and fed onto a Supelite DAX-8 resin which retains hydrophobic organic matter strongly. This fraction was eluted with NaOH. The unabsorbed fraction from the

Table 1  
Raw water quality parameters

Parameters	Values
pH	7.1–7.5
Turbidity, NTU	5.3–37.6
Color	21–65
DOC, $\text{mg L}^{-1}$	5.341–6.29
UV <sub>254</sub> , $\text{cm}^{-1}$	0.088–0.11
COD <sub>Mn</sub> , $\text{mg L}^{-1}$	6.4–7.3

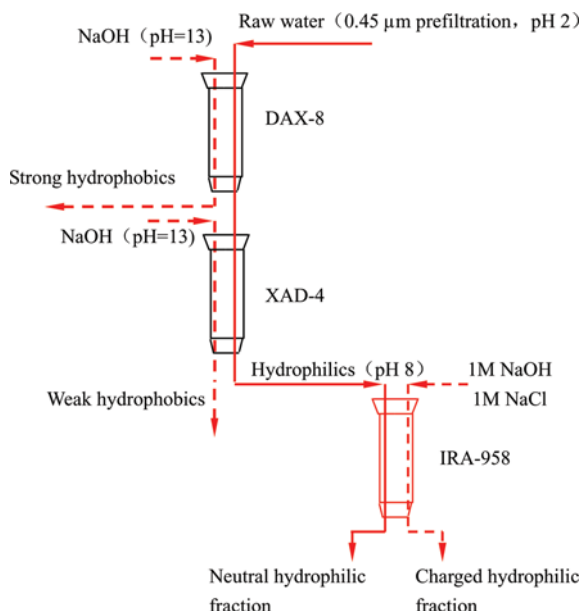


Fig. 1. Outline of raw water fractionation procedure.

DAX-8 resin was fed onto an Amberlite XAD-4 resin, which retains hydrophobic organic matter weakly. The unabsorbed fraction from the XAD-4 resin was fed onto an Amberlite IRA-958 anion exchange resin, which retains charged material. This fraction was eluted with a NaOH/NaCl mixture. The remaining neutral material was not retained by any of the resins.

## 2.2. Ultrafiltration experiments

Prior to the filtration experiment, the coagulation test was conducted. Alum was selected as coagulant. Alum was added in raw water, and then agitated for 30 min (rapid mixing of 1 min at 100 rpm, slow mixing of 29 min at 30 rpm). The coagulated water was then settled for 30 min. The supernatant was then used for the membrane experiment feed water. The schematic diagram of the flat-sheet UF set-up used in this study is shown in Fig. 2. In the filtration phase, the feed and filter valves were opened to allow the feed water to be sent to the module for 60 min of the filtration operation. After the filtration operation, 1-min backwash was performed by opening the backwash feed and flushing valves. Then the flushing operation was conducted for 10 s by opening the feed and flushing valves. The pressure of filtration and backwash was 0.1 MPa.

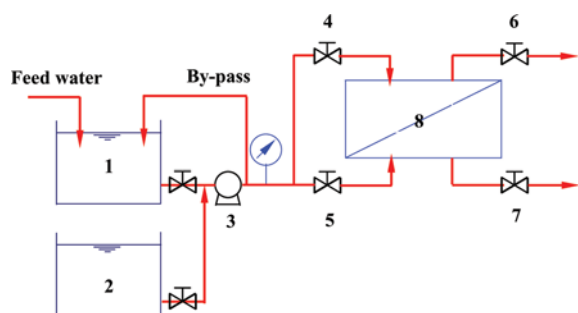


Fig. 2. Schematic of the experimental set-up: 1, raw water tank; 2, backwash tank; 3, pump; 4, feed water valve; 5, backwash water valve; 6, flushing valve; 7, permeate valve; 8, membrane module.

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

A polyvinylidene difluoride (PVDF) flat UF membrane with a molecular weight cut-off of 150 kDa was used for this experiment. The membrane area was  $5.841 \times 10^{-3} \text{ m}^2$ . Nitto Denko Corporation provided the membrane and the set-up.

## 2.3. Analytical methods

The turbidity was determined using a turbidimeter (Hach 2100N). A UV spectrophotometer (Shimadzu UV-2201) and TOC analyzer (Shimadzu TOC-V<sub>CPH</sub>) 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 molecular weight 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 concentration between adjacent filtration samples.

## 3. Results

### 3.1. Raw water fractionation

The fractionation of raw water was performed three times and the results are shown in Table 2. The components of the raw water studied mainly comprised hydrophobic acids and hydrophilic neutral fractions. For this reason, the experiment with the effect of the NOM fraction on membrane filtration was focused on two fractions: hydrophobic acids (HA) and hydrophilic neutral (Neut).

The molecular weight distribution for the fractions of NOM is shown in Figs. 3 and 4. As can be seen in Fig. 3, the amount was Neut compounds in the fraction of less than 1 kDa was greater than that of HA compounds. Although the HA

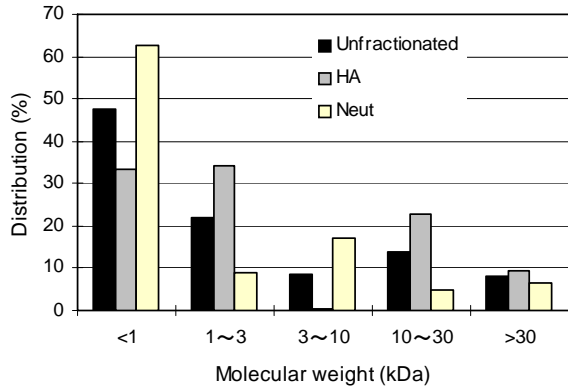


Fig. 3. Molecular weight distribution for the fractions of DOC.

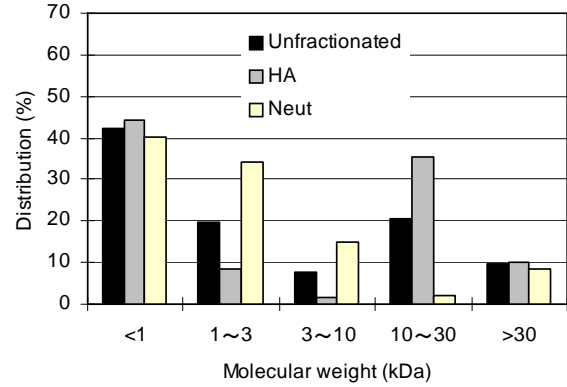


Fig. 4. Molecular weight distribution for the fractions of UV<sub>254</sub>.

Table 2  
Fractional components of the NOM

Fraction	DOC (%)	UV <sub>254</sub> (%)
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

and Neut compounds of UV<sub>254</sub> in the fraction of less than 1 kDa were similar, the amount of HA compounds in the fraction of 10–30 kDa was greater than that of Neut compounds, as shown in Fig. 4. Fig. 4 also shows that the distribution of Neut decreased as the molecular weight increased. This determined result suggests that the smaller the molecular weight, the higher the hydrophilicity of NOM; and the greater the molecular weight, the higher the hydrophobicity of NOM.

### 3.2. Effect of coagulation pretreatment on the filtration flux

The relative flux, the ratio of the permeate flux  $J$  to the pure water flux  $J_0$ ,  $J/J_0$ , is shown in Fig. 5 as a function of time. In the filtration of the raw water, the flux dropped rapidly. In the end of the

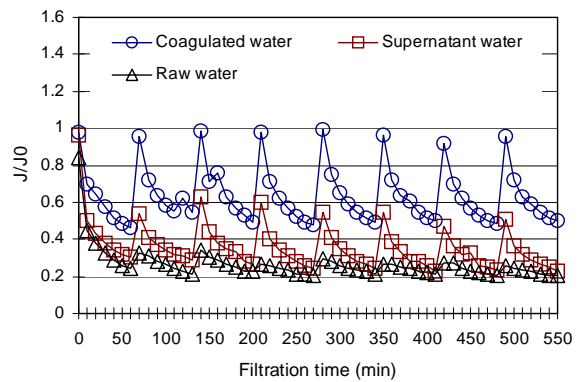


Fig. 5. Effect of filtration of coagulated water and supernatant water on flux and backwash (coagulant dosage 4 mg/L).

first filtration cycle, although the flux somewhat recovered after backwash, it dropped to 20% of the pure water flux. As filtration and backwash were repeated, the flux declined gradually. This suggests that the membrane fouling occurred in the initial filtration.

With the addition of 4 mg/L coagulant, the flux increased significantly. In the filtration of coagulated water, the flux declined to 50% of  $J_0$ . After backwash, the flux recovered completely for each filtration cycle. In the filtration of supernatant water, although the flux was increased to some extent, the rate of the flux decline was consider-

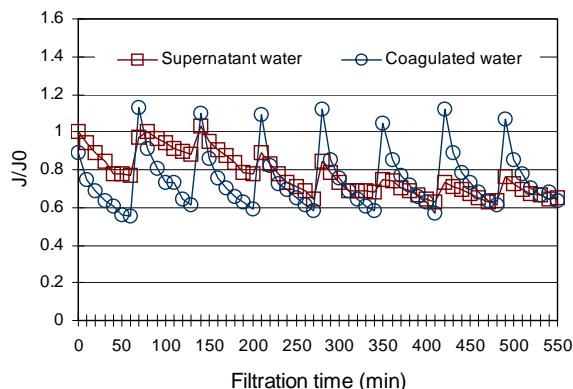


Fig. 6. Effect of filtration of coagulated water and supernatant water on flux and backwash (coagulant dosage 10 mg/L).

ably greater than that of coagulated water. As the added amount of coagulant was increased to 10 mg/L, the flux for both coagulated water and supernatant water was enhanced greatly (Fig. 6). Similarly to 4 mg/L addition, the flux for coagulated water was greater than that for supernatant water.

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

### 3.3. Effects of coagulation and membrane on removal NOM

The effect of coagulation and membrane on NOM removal is shown in Fig. 7. In the filtration of raw water without coagulation, the membrane was less effective in NOM removal, with the HA and Neut fraction accounting for 50% respectively. With the addition of coagulant, the NOM removal efficiency was increased to 20.5%, with 14.3% for the HA fraction and 2.5% for the Neut

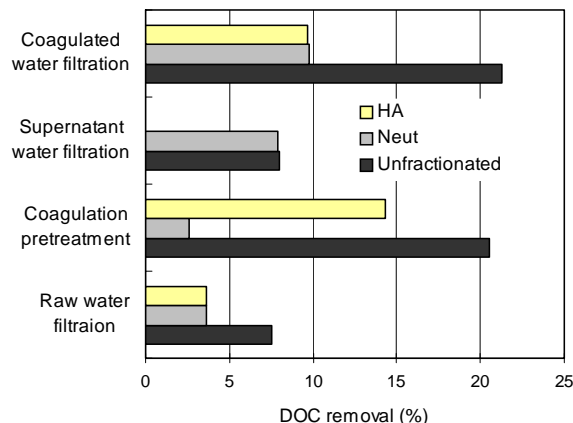


Fig. 7. Unfractionated and fractionated DOC removal by coagulation and membrane filtration.

fraction, respectively. This result suggests that the contribution of coagulation to NOM removal was due to the HA fraction, which is consistent with the result that coagulation removed the HA fraction more effectively than the Neut fraction [13].

Although 8% of NOM was removed by the membrane for supernatant water, almost all removed NOM was the Neut fraction. In the filtration of coagulated water, NOM removal with coagulated water by the membrane was increased to 21%, with 9.74% for the HA fraction and 9.4% for the Neut fraction, respectively.

### 3.4. Effects of coagulation pretreatment and membrane filtration on the molecular weight distribution for fractionated NOM

In order to 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. The effect of membrane filtration without coagulation pretreatment on various MW fractions for fractionated compounds is shown in Fig. 8. The membrane primary rejected greater than 30 kDa and smaller than 1 kDa MW of DOC. A similar trend was observed for the HA fraction and the Neut fraction.

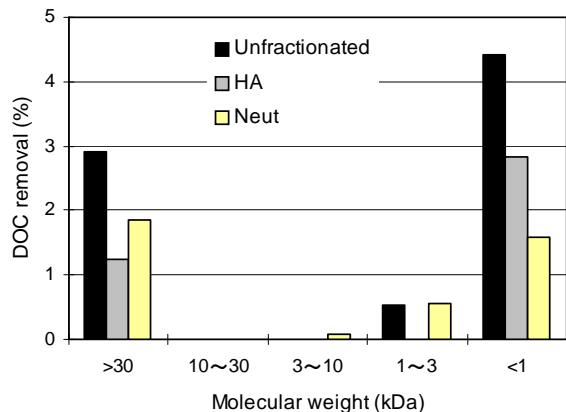


Fig. 8. The effect of direct filtration on the molecular weight distribution of fractionated compounds.

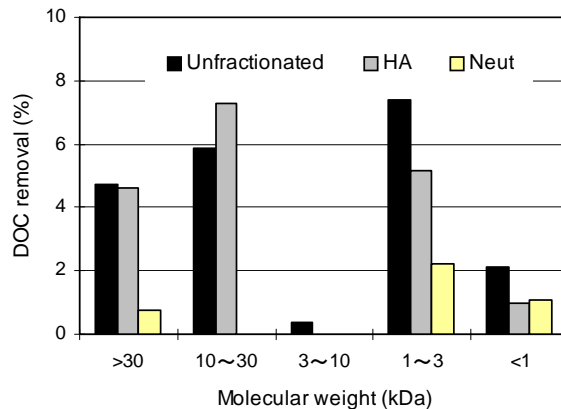


Fig. 9. The effect of coagulation pretreatment on the molecular weight distribution of fractionated compounds.

The size of the membrane used was greater than 1 kDa, therefore, the removal of <1 kDa fraction may be contributed to the rejection of the cake formed on the surface of the membrane during the filtration.

The effect of coagulation on various MW fractions for fractionated compounds is shown in Fig. 9. The coagulation was effective in removing NOM with greater than 10 kDa and 1–3 kDa and less effective in removing NOM with MW smaller than 1 kDa for unfractionated and HA fraction. As for the Neut fraction, the coagulation showed poor removal efficiency in all MW fractions, which was consistent with the results reported by Robert L. Sinsabaugh III [14].

The effect of the removal efficiency in various MW fractions with supernatant water by the membrane is shown in Fig. 10. Fig. 10 shows that membrane rejected primarily <1 kDa of the Neut fraction of NOM and had little efficiency for 1–3 kDa of the HA fraction. The removal efficiency with coagulated water is shown in Fig. 11. Fig. 11 shows that the membrane rejected <1 kDa and 1–3 kDa fractions of NOM.

**4. Discussion**

In ultrafiltration of raw water without coagulation, the flux declined rapidly and could not be

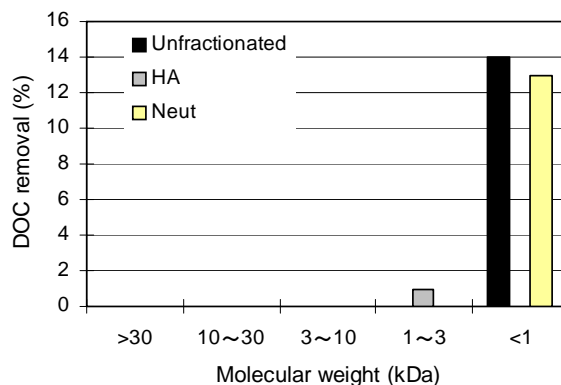


Fig. 10. The effect of supernatant water filtration on the molecular weight distribution of fractionated compounds.

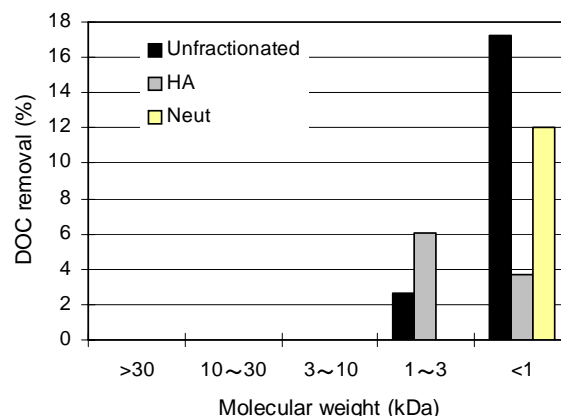


Fig. 11. The effect of coagulated water filtration on molecular weight distribution of fractionated compounds.

recovered by backwash (Fig. 5). As coagulation was used as pretreatment, the filtration flux of both supernatant and coagulated water was enhanced to a large extent (Figs. 5 and 6). No HA fraction was removed in ultrafiltration of supernatant water, in contrast, 3.6% of the 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 is in agreement with the results by Liahua Fan et al. [9] and James A. Nilson [11] who suggested that the hydrophobic acids caused greater flux decline than the transphilic acids.

Coagulation pretreatment selectively removes the hydrophobic fraction of NOM, leaving the hydrophilic fraction in supernatant water. Therefore, residual NOM plays an important role in determining the rate of fouling in ultrafiltration with coagulation pretreatment. In ultrafiltration of supernatant water, the flux experienced slow decline. Fig. 7 shows that the membrane primarily rejected  $<1$  kDa of the Neut fraction. This finding indicates that the small size of the Neut fraction gives rise to the slow decline of flux.

It should be noted that although the addition of dosage was the same, the behavior of flux in ultrafiltration of coagulated water and supernatant

water were different. The flux with coagulated water was higher than that with supernatant water. This result implies that the cake consists of flocs formed on the membrane surface during the filtration of coagulated water play a significant role in preventing fouling. With the existence of a floc cake layer, the Neut fraction deposited on the cake layer instead of on the membrane surface. Therefore, the foulant can then be easily removed by removing the floc cake layer by backwashing and flushing.

On the basis of the previous results and discussions, a role of coagulation is postulated to interpret the effect of coagulation on fouling, as shown in Fig. 12. As the coagulated water was filtered, the flocs deposited on the surface of the membrane and formed the cake that absorbed the Neut fraction of NOM. The cake could be easily removed by backwashing and flushing, because it was not closely adhered to the surface. As the supernatant water was filtered, the Neut compounds that remained in the water after coagulation were rejected by the membrane, according to the results shown in Fig. 7. They closely adhered to the surface of the membrane and could not be easily removed by backwashing and flushing, resulting in flux decline.

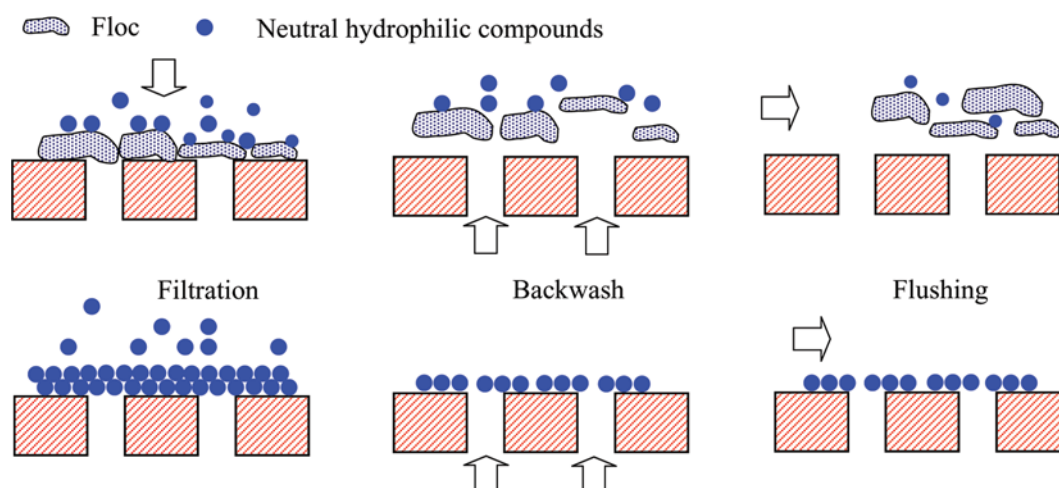


Fig. 12. The mechanism of preventing the membrane from fouling by coagulation treatment.

## 5. Conclusions

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

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

Although the addition of dosage was the same, no flux reduction with filtration of coagulated water was experienced, suggesting that coagulation could prevent fouling; the flux with filtration of supernatant water experienced slow decline, suggesting that in spite of the marked improvement in the flux, the fouling also occurred. The results indicate that when coagulate water was filtrated, the floc cake layer formed on the membrane surface could adsorb the hydrophilic neutral fraction with small size, while when supernatant water was filtered, the membrane rejected large part of the hydrophilic neutral fraction with small size. Therefore, the contribution of the neutral fraction to fouling presented slow flux decline.

## Acknowledgements

This research was funded by National 863 Research Project for High Technology Development (2002AA601130) and the National Science and Technology Research Project (2003BA808A17).

## References

- [1] J.M. Laine, C. Campos, I. Baudin and M.L. Janex, Understanding membrane fouling: a review of over a decade of research. *Water Sci. Technol.: Water Supply*, 3(5–6) (2003) 155–164.
- [2] P.-k. Park, C.-h. Lee, S.-J. Choi, K.-H. Choo, S.-H. Kim and C.-H. Yoon, Effect of the removal of NOMs on the performance of a coagulation–UF membrane system for drinking water production. *Desalination*, 145 (2002) 237–245.
- [3] M. Tomaszewska and S. Mozia, Removal of organic matter from water by PAC/UF system. *Water Res.*, 36 (2002) 4137.
- [4] B. Schlichter, V. Mavrov and H. Chmiel, Study of a hybrid process combining ozonation and microfiltration/ultrafiltration for drinking water production from surface water. *Desalination*, 168 (2004) 307–317.
- [5] C. Guigui, J.C. Rouch, L. Durand-Bourlier, V. Bonnelye and P. Aptel, Impact of coagulation conditions on the in-line coagulation/UF process for drinking water production. *Desalination*, 147 (2002) 95–100.
- [6] J.-I. Oh and S.H. Lee, Influence of streaming potential on flux decline of microfiltration with in-line rapid pre-coagulation process for drinking water production. *J. Membr. Sci.*, 254 (2005) 39–47.
- [7] V. Lahoussine-Turcaud, M.R. Wiesner, J.-Y. Bottero and J. Mallevalle, Coagulation pretreatment for ultrafiltration of a surface water. *J. AWWA*, 82(12) (1990) 76–81.
- [8] T. Carroll, S. King, S.R. Gray, B.A. Bolto and N.A. Booker, Fouling of microfiltration membrane by NOM after coagulation treatment. *Water Res.*, 34(11) (2000) 2861–2868.
- [9] L. Fan, J.L. Harris, F.A. Roddick and N.A. Booker, Influence of the characteristics of natural organic matter on the fouling of microfiltration membranes. *Water Res.*, 35(18) (2001) 4455–4463.
- [10] J. Cho, G. Amy and J. Pellegrino, Membrane filtration of natural organic matter: factors and mechanisms affecting rejection and flux decline with charged ultrafiltration (UF) membrane. *J. Membr. Sci.*, 164 (2000) 89–110.
- [11] J.A. Nilson and F.A. DiGiano, Influence of NOM composition on nanofiltration. *J. AWWA*, 88(5) (1996) 53–66.
- [12] C.-W. Li and Y.-S. Chen, Fouling of UF membrane by humic substance: Effect of molecular weight and powdered-activated carbon (PAC) pre-treatment. *Desalination*, 170 (2004) 59–67.
- [13] R.C. Hoehn, W.R. Knocke, A.E. Linkins and R.L. Sinsabaugh, Removal of dissolved organic carbon by coagulation with iron sulfate. *J. AWWA*, 78(5) (1986) 74–82.