ISSN 1001—0742
Journal of Environmental Sciences Vol. 18, No. 5, pp. 880—884, 2006 CN 11—2629/X

Article ID: 1001-0742(2006)05-0880-05 **CLC number**: X703.1 **Document code**: A

Ultrafiltration with in-line coagulation for the removal of natural humic acid and membrane fouling mechanism

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Abstract: Experimental and theoretical analysis were made on the natural humic acid removal and the membrane fouling of ultrafiltration (UF) with in-line coagulation. The results showed dissolved organic carbon (DOC) and UV_{254} removals by the UF with in-line coagulation at pH 7 were increased from 28% to 53% and 40% to 78% in comparison with direct UF treatment respectively. At the same time, the analysis of high performance liquid chromatography showed that UF with coagulation had significant improvement of removal of humic acid with molecular weights less than 6000 Da in particular. Compared to direct UF, the in-line coagulation UF also kept more constant permeate flux and very slight increase of transmembrane pressure during a filtration circle.

Two typical membrane fouling models were used by inducing two coefficients K_c and K_p corresponding to cake filtration model and pore narrowing model respectively. It was found that membrane fouling by pore-narrowing effect was effectively alleviated and that by cake-filtration was much decreased by in-line coagulation. Under the condition of coagulation prior to ultrafiltration at pH 7, the cake layer formed on the membrane surface became thicker, but the membrane filtration resistance was lower than that at pH 5 with the extension of operation time.

Keywords: natural humic acid; ultrafiltration (UF); in-line coagulation; high performance liquid chromatography (HPLC); membrane fouling

Introduction

The use of low-pressure membrane filtration, microfiltration (MF) and ultrafiltration (UF), has been rapidly increased in the last decade. UF is efficient in reducing turbidity, particles and suspended solids, but it is usually not effective in removal of the humic substances, which have a higher potential for trihalomethane (THM) formation in natural organic matter (NOM). NOM in water may also be responsible for bacterial regrowth in distribution networks. A number of studies (Howe and Clark, 2002; Lin *et al.*, 2000, 2001; Carroll *et al.*, 2000; Yuan and Zydney, 1999, 2000; Cho *et al.*, 1999) have shown NOM contained in the natural water as the foulant causes membrane fouling. Membrane fouling can be described by the progressive saturation of adsorption sites of the membrane material leading to pore constriction, pore blockage, and/or cake/gel layer formation. Many researchers have suggested that the humic substances fraction of NOM is a major foulant which controls the rate and extent of fouling (Combe *et al.*, 1999; Jones and O'Melia, 2000; Yuan and Zydney, 1999) and found that NOM adsorbs both inside pores and on the membrane surface (Combe *et al.*, 1999; Jones and O'Melia, 2000), and forms a gel layer (Yuan and Zydney, 1999).

One of the most effective methods of reducing membrane fouling is to employ coagulation pretreatment (Wiesner and Laine, 1996; Laine *et al.*, 1990), which also improves filtered water quality. However, the characteristic of NOM removal and mechanism of membrane fouling by different precoagulation effects are still not very clear. Guigui *et al.* (2002) reported that good conventional coagulation conditions in terms of coagulant type, dose and pH should also provide good performance and final water quality for in-line coagulation with UF. Bian *et al.* (1997, 1999) suggested that the combination of high flux and good water quality were achieved when they used a lower dose of coagulant prior to membrane filtration than the optimal dose for removal of humic substances during conventional treatment. Lee *et al.*(2000) found that the coagulated suspension under either charge-neutralization or sweep floc condition showed similar steady-state flux under the cross-flow microfiltration mode. Carroll *et al.* (2000) observed that small molecular weight, non-ionic, hydrophilic NOM that were poorly removed by coagulation were responsible for fouling after coagulation processes. Judd and Hillis (2001) investigated that pore blockage can occur when there is poor aggregation of colloidal particles and this can result in pore blocking. Maartens *et al.* (1999) reported treatment of the natural brown water with precoagulation increased NOM adsorption and decreased UF performance. Membrane fouling can be minimized by adjustment of the pH of the feed solution. Kabsch-Korbutowicz (2005) suggested the removal of NOM was highly affected by pH condition of precoagulation.

In-line coagulation used in this paper means coagulant is dosed continuously prior to UF without removal of coagulated solids. The objective of this study is to improve UF performance for the removal of NOM with in-line coagulation under different

Foundation item: The National Natural Science Foundation of China (No. 50138020); *Corresponding author

coagulation conditions with sweep flocculation and charge neutralization. In particular, the removal of different molecular weights (MWs) of NOM are investigated. This study attempts to distinguish different mechanisms between cake formation on the membrane surface and pore blocking and analyze membrane fouling by using cake layer filtration model and pore blocking model with experimental data.

1 Theoretical models of membrane fouling

1.1 Cake filtration model

This model assumes that the macro-solutes rejected by the membrane may form a deposition layer or cake with a resistance to filtration K_c which increases proportionally to the amount of volume filtered V_f (Belfort *et al.*, 1994).

The process of cake filtration can be expressed as:

$$\frac{A P_{tm}}{\mu J} = A R_{m0} + K_c V_f \tag{1}$$

$$K_c = C \cdot \alpha_c$$

Where, K_c is the coefficient of cake filtration, and C is the particle concentration, α_c is the cake specific resistance, A is the membrane area, P_{tm} is the transmembrane pressure, μ is the viscosity, J is the permeate flux, R_{m0} is the membrane intrinsic resistance.

According to the Equation (1), P_{tm}, J and V_f are measurable during experiment, so the slope of the line is K_c, represented resistance of cake layer deposited on the membrane surface.

1.2 Pore narrowing model

This model assumes that a fraction of the micro-solute which penetrates into the membrane pores may adsorb onto the inner surface of the pores in such a way that the pore internal volume decays proportionally to permeate flow rate Q_f (Belfort *et al.*, 1994; Davis and Grant, 1992).

The process of pore blocking can be expressed as:

$$\frac{t}{V_f} = \frac{1}{Q_0} + K_p t \tag{2}$$

Where, V_f is the permeate volume, Q_0 is the initial permeate flow rate, K_p is the coefficient of pore blocking, t is the filtration time.

According to the Equation (2), Q_0, t and V_f are measurable during experiment, so the slope of the line is K_p, represented resistance of pore narrowing.

2 Materials and method

2.1 Experimental set-up

Fig.1 shows the schematic flow of the UF with in-line coagulation. The UF membrane (Mo Tian Membrane, China) module was polyacrylonitrile (PAN) hollow fiber with MWCOs of 10^5 Da. The effective membrane area is 2.8 m^2 and the average membrane flux was 109 $L/(m^2 \cdot h)$.

2.2 Experimental method

Natural humic acids were isolated from lake sediments by NaOH dissolving and HCl precipitation (Peng, 1981). The natural humic acids extracted was firstly filtered by 0.45 μm membrane to remove suspended solids as preparing solution, and then mixed with tap water to dissolved organic carbon (DOC) to 5 mg/L as experimental raw water.

The coagulant adopted was aluminium sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$), and the dosage was 3.5 mg/L calculated as Al^{3+}. The coagulant was added the suption pipe line of feeding pump as the flash mixer as shown in Fig.1. The time of micro-flocculation was about 1 min at an average G (velocity gradient of coagulation) value about 10 s^{-1} in the tube mixer. The pH values of raw water after coagulation adjusted by 0.1 mg/L NaOH and 0.1 mg/L HCl were kept at 5 and 7.

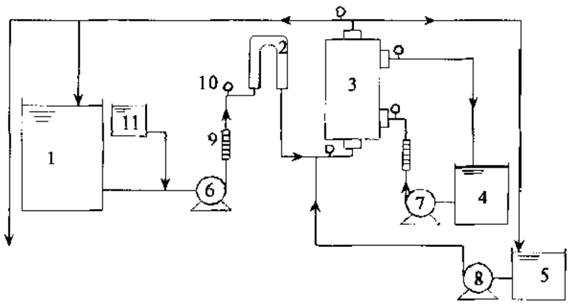

Fig.1 Schematic diagram of the UF with in-line coagulation
1. feed tank; 2. tube mixer; 3. UF module; 4. permeate tank; 5. chemical cleaning tank; 6. feed pump; 7. backwashing pump; 8. chemical cleaning pump; 9. flowmeter; 10. pressure gauge; 11. coagulant tank

2.3 Analytical methods

2.3.1 Chemical analysis

DOC was analyzed using a Shimadzu TOC-5000A analyzer; ultra violet adsorption at 254 nm, UV_{254}, was analyzed using a Shanghai 751G spectrophotometer.

2.3.2 Zeta potential anaysis

The zeta potential of raw water with 5 mg/L DOC concentration was -28.5 mV, and kept 0 mV around after in-line coagulation with 3.5 mg/L coagulant dosage calculated as Al^{3+} on both pH 5 and pH 7. The zeta potential was analyzed using a Macrotech Nichion ZC-2000 analyzer.

2.3.3 HPLC analysis

The raw water and the effluent of UF membrane with and without in-line coagulation was measured with HPLC to analyze the removal of dissolved organic matters of different MWs. HPLC analysis was carried out by a Shimadzu LC-9A HPLC analyzer with Hitachi W520 chromatogram column (mainly used to determine organic matter with MWs less than

6 kDa) and UV detector at 254 nm. Since the membrane fouling mainly results from the NOM with low MWs, it is significant to compare the removal of humic acid with MWs less than 6 kDa by two processes.

2.4 Experimental data processing method

The average transmembrane pressure was caculated through Tutujian equation:

$$P_{tm} = ((P_i + P_o)/2) - P_p \qquad (3)$$

Where, P_{tm} is the transmembrane pressure; P_i is the pressure of inlet of membrane; P_o is the pressure of outlet of membrane; P_p is the pressure of permeate of membrane.

The feed temperature during UF was kept to 20℃ to prevent temperature effect on membrane fouling. Specific permeate flux is permeate flux divided by transmembrane pressure, which would be used to analyze membrane fouling without keeping pressure constant. Normalized permeate flux is permeate flux at any time divided by initial permeate flux. It represents by percentage and shows flux decline more clearly.

3 Results and disscusion

3.1 NOM removal of direct UF and in-line coagulation UF

The removals of natural humic acid represented by DOC and UV_{254} on the conditions of direct UF and hybrid UF with in-line coagulation at pH 5 and pH 7 are shown in Fig.2.

In comparison with direct UF, in-line coagulation UF improved NOM removal greatly in particular on the condition of pH 7, such as the DOC removal increased from 28% to 53% , and UV_{254} removal increased from 40% to 78%.

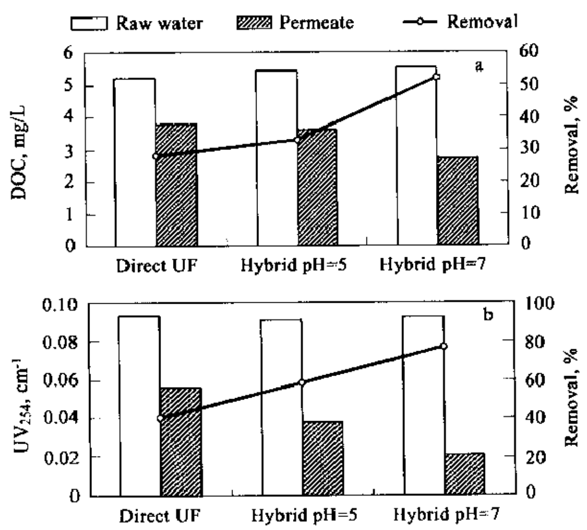

Fig.2 Comparison of DOC (a) and UV_{254} (b) removal

3.2 Molecular weight distribution of direct UF and in-line coagulation UF

HPLC chromatograms of raw water and permeate of direct UF and in-line coagulation UF at pH 7 are shown in Fig.3.

According to the study of Tambo and Kamei (1978), the outflow time of Hitachi W520 chromatogram column is related to different MWs of humic acid, shown as first and second row of Table 1. The humic acid removals were calculated according to the absorption peak areas of raw water and permeate.

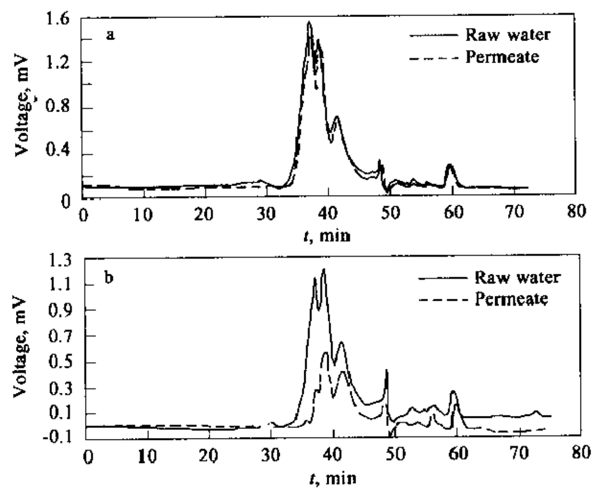

Fig.3 HPLC chromatogram of raw water and permeate
a. direct UF; b. in-line coagulation UF at pH 7

Table 1 shows humic acid with molecular weights (MWs) more than 6 kDa were removed completely by two processes, mainly because the chromatogram column used are not sensitive to that MWs range. In-line coagulation UF at pH 7 increased removal of humic acid with MWs less than 6 kDa evidently compared to direct UF, in which the removal improved from 6.7% to 72% for MWs between 3 kDa and 6 kDa, the removal improved from 6.4% to 48.7% for MWs between 1 kDa and 3 kDa, the removal improved from 1.5% to 33% for MWs less than 1 kDa, and the total removal rate improved from 6.1% to 59.3%.

3.3 Permeate flux and pressure variation of direct UF and in-line coagulation UF

UF membrane fouling could be discussed by normalized specific permeate flux, membrane pressure difference of membrane inlet and outlet, namely headloss, and the variation of transmembrane pressure (Fig.4).

Fig.4a shows that the flux of direct UF declined quickly, in which it decreased 60% after 2.5 h of fouling operation and 75% after 10 h operation. However the UF flux with in-line coagulation at pH 5 decreased a little and that at pH 7 had almost no drop within 10 h operation.

The pressure difference of UF membrane inlet and outlet, namely headloss, reflects the fouling of deposited layer on the membrane surface. Fig.4b shows that the headloss of direct UF increased hardly within 10 h operation, however, that of UF with in-line coagulation at pH 5 increased from 10 kPa to

Table 1 Molecular weight distribution of natural organic matters (NOM) by HPLC

	Retention time, min	<32	32—40	40—45	>45	Σ
	Molecular weight distribution, kDa	>6	6—3	3—1	<1	-
Direct UF	Absorption intensity of raw water	798.9	349216.9	120988.1	68515.8	539519.7
	Absorption intensity of permeate	0	325803.3	113195.3	67481.5	506480.1
	Removal, %	100	6.7	6.4	1.5	6.1
In-line coagulation UF (pH=7)	Absorption intensity of raw water	950.2	270822.3	108662.2	87833.7	468268.4
	Absorption intensity of permeate	0	75807.5	55785.4	58929.2	190522.1
	Removal, %	100	72	48.7	33.	59.3

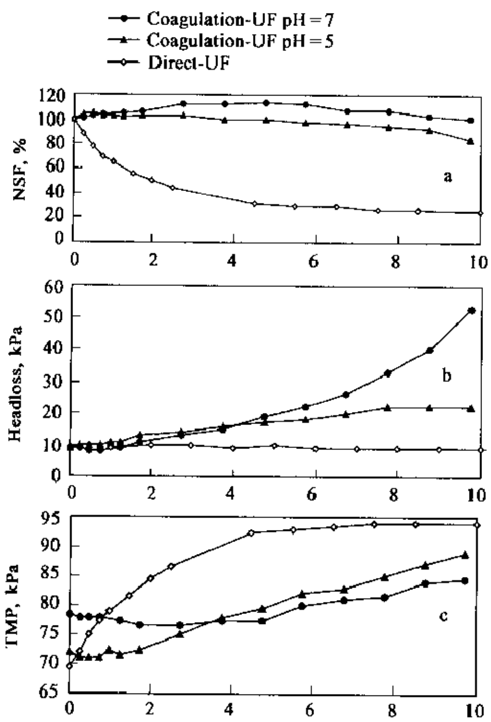

Fig.4 Variation of normalized specific flux (NSF; a), headloss (b) and transmembrane pressure (TMP; c) with time

20 kPa. The headloss of UF with in-line coagulation at pH 7 increased slowly before 4 h, but enhanced quickly after 4 h, and increased to 50 kPa at the end of filtration circle.

The transmembrane pressure (TMP) reflects resistance of the membrane fouling, including pore narrowing and cake layer. Fig.4c shows that the TMP increasing velocity of direct UF was much higher than that of in-line coagulation UF on the initial 4 h operation. After 4 h, the TMP of direct UF became stable on the whole, however the enhancement of TMP with in-line coagulation UF was nearly linear. But at the end of 10 h operation, the TMP of in-line coagulation UF at pH 7 was the lowest, on the contrary TMP of direct UF was the highest.

The experimental results indicated the membrane fouling resistance of direct UF was serious, in-line coagulation UF at both pH values lightened fouling resistance effectively. With the extension of filtration time, the cake layer formed on the membrane surface becomes thicker, but the membrane filtration resistance is lower at pH 7 than at pH 5.

4 Analysis of membrane fouling model simulation results

According to the UF membrane fouling cake filtration model and pore narrowing model, the experimental data was simulated and shown as Fig.5 and Fig.6.

Fig.5 and Fig.6 indicate that the experimental data had a good correlation with the two theoretical models.

Fig.5 shows K_p of direct UF equaled to 0.2708, and the positive slope indicated membrane pore bloacking fouling had happened. However, for in-line coagulated UF at pH 5 and pH 7, the K_p equaled to near zero. It indicated pore narrowing was nearly avoided completely.

Fig.6 shows K_c of direct UF was higher one order of magnitude than that of in-line coagulation UF with both pH values. It indicated the cake layer fouling on the membrane surface of the direct UF was more serious than that of in-line coagulated UF. It noticed in-line coagulated UF at pH 7, the K_c decreased a little before 4 h operation, and then increased slowly. That was just because the loose cake layer formed during the initial filtration became compact gradually under this condition of sweep flocculation.

The model simulation results indicated in-line

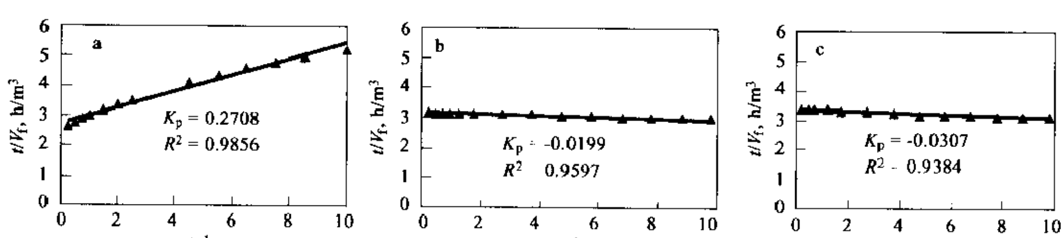

Fig.5 Coefficient K_p in pore narrowing model
a. direct UF; b. in-line coagulation UF pH=5; c. in-line coagulation UF pH=7

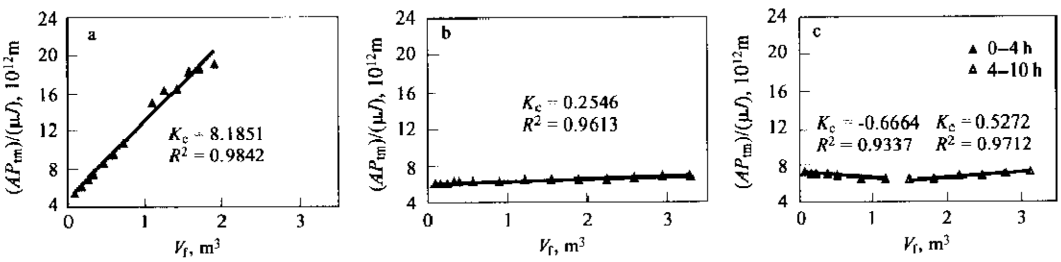

Fig.6 Coefficient K_c in cake filtration model
a. direct UF; b. in-line coagulation UF pH=5; c. in-line coagulation UF pH=7

coagulation not only prevented low MWs NOM from penetrating into UF membrane pore, but also alleviated the deposited layer resistance on the membrane surface. The variations of K_p and K_c in the two models were consistent with the flux change showed as Fig.4a.

5 Conclusions

From the experimental results and theoretical model analysis of direct UF and in-line coagulation UF with charge neutralization and sweep flocculation, the following conclusions were obtained:

(1) A hybrid process of ultrafiltration with in-line coagulation improved the removal of natural humic acids greatly compared to direct UF, such as precoagulation at pH 7, DOC and UV_{254} removals were increased from 28% to 53% and 40% to 78% respectively.

(2) HPLC analysis showed in-line coagulation UF process had significant improvement of removal rate of NOM with MWs less than 6000 Da.

(3) In-line coagulation also reduced the rate of membrane fouling and resulted in more constant permeate flux and very slight increase of transmembrane pressure during a filtration circle.

(4) Two typical membrane fouling models were employed and it became very convenient to analyze membrane fouling mechanism by inducing two fouling coefficient K_c and K_p corresponding to cake filtration model and pore narrowing model respectively. It was found that membrane fouling by pore-narrowing effect was effectively alleviated and that by cake-filtration was much decreased by pre-coagulation.

(5) Under the condition of in-line coagulation prior to UF at pH 7, insoluble aluminum may play important role in the quick formation of microflocs by sweep coagulation. With the extension of filtration time, although the cake layer formed on the membrane surface becomes thicker, the membrane filtration resistance is lower at pH 7 than at pH 5.

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(Received for review October 18, 2005. Accepted January 7, 2006)