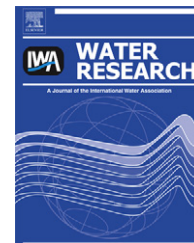


Available at www.sciencedirect.comjournal homepage: www.elsevier.com/locate/watres

Comparison of humic acid rejection and flux decline during filtration with negatively charged and uncharged ultrafiltration membranes

Jiahui Shao*, Juan Hou, Hongchen Song

School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, PR China

ARTICLE INFO

Article history:

Received 17 May 2010

Received in revised form

2 September 2010

Accepted 3 September 2010

Available online 15 September 2010

Keywords:

Charged ultrafiltration membrane

Humic acid

Rejection coefficient

Flux

Membrane fouling

Solution environment

ABSTRACT

Increasingly stringent regulations for drinking water quality have stimulated the ultrafiltration (UF) to become one of the best alternatives replacing conventional drinking water treatment technologies. However, UF is not very effectively to remove humic acid due to the comparatively larger pore size compared to the size of humic acid. Fouling issue is another factor that restricts its widespread application. In this study, rejection of humic acid and flux decline were compared with essentially neutral, negatively charged version of a regenerated cellulose membrane, in which electrostatic interaction was explored for a better humic acid removal and less fouling. Solution environment, including ionic strength, pH and calcium ion concentration, affecting humic acid removal and flux decline on negatively charged and neutral membranes was also compared. Results indicated that the appropriate charge modification on the neutral UF membrane could be an effective way for better removal of NOM and reduction of the membrane fouling due to the electrostatic interactions with the combination effect of membrane pore size. Electrostatic interactions are significant important to achieve high humic acid removal and less fouling, and to improve the water quality and protect people's health.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

Natural organic matter (NOM) is commonly found in surface and ground waters (Kilduff et al., 1996) and considered to react with the major disinfectants to produce a host of disinfection by-products (DBPs) (Krasner et al., 2006; Zularisam et al., 2006). Therefore, the removal of NOM effectively is of significant importance in meeting the stringent DBPs regulations and providing safe drinking water. Ultrafiltration (UF) allows the removal of particles, turbidity, microorganism and certain amount of the dissolved organic matter. It has received considerable attention in recent years and has been increasingly used in drinking water treatment as alternative

technology to convention filtration and clarification (Katsoufidou et al., 2005; Susanto and Ulbricht, 2008).

A major fraction of NOM present in surface or ground waters is composed of humic substances (HS) (Nyström et al., 1996; Zularisam et al., 2006). Humic acid generally makes up the major fraction of humic substance and has thus been studied by many researchers as a model compound for natural organic matter in water (Yuan, 2001; Zularisam et al., 2006; Susanto and Ulbricht, 2008; Campinas and Rosa, 2010). Humic acids are highly polydisperse, with molecular weights ranging from 2 kDa up to over 500 kDa (Stevenson, 1982). Compared to the size of humic acid, UF with comparatively larger pore size is not very effectively to remove humic acid. In

* Corresponding author. Tel.: +86 21 54745634; fax: +86 21 54740825.

E-mail address: jhshao@sjtu.edu.cn (J. Shao).

0043-1354/\$ – see front matter © 2010 Elsevier Ltd. All rights reserved.

doi:10.1016/j.watres.2010.09.006

addition, humic acid has been recognized as one of the key foulants during water treatment using membrane processes (Nyström et al., 1996; Yamamura et al., 2007; Huang et al., 2007; Gray et al., 2007). Not very high removal rate for humic acid and membrane fouling limit the further applications of ultrafiltration to remove NOM from water (Wei et al., 2006; Fan et al., 2001).

Recent studies have shown that charged ultrafiltration membranes can provide much higher solute retention than conventional (relatively uncharged) membranes due to the electrostatic exclusion of the charged solute from the same charged membrane pores (Mehta and Zydny, 2006; Cho et al., 2000; Wei et al., 2006). The thin-film-composite (TFC) UF membrane with a negatively charged surface was found to have greater NOM rejection than the neutral membrane which was made of regenerated cellulose (Cho et al., 2000). Although the TFC membrane used was hydrophobic, the adsorbed NOM was less in quantity and less fouling was found than that on the hydrophilic RC membrane. The study done by Wei et al. (2006) showed that their modified membrane surfaces exhibited more hydrophilic and negatively charged features after the electrophoresis-UV grafting treatment of the original polyethersulfone (PES) membrane, which can improve NOM retention and present lower fouling tendency than the unmodified membrane.

Several studies have shown that UF membrane with negative charge had a greater NOM rejection and less fouling tendency than the neutral membrane with similar nominal MWCO under identical conditions. However, this comparison was normally based on the different membrane materials. Also, there has been no study of comparing the effect of the solution environment including calcium ion concentration on the humic acid removal and fouling on charged and uncharged UF membranes. The objective of this study was to investigate the effect of membrane charge on the removal of humic acid and its fouling during ultrafiltration with charged regenerated cellulose (RC) membrane, and compare with the neutral unmodified version of RC membrane. Solution environment, including ionic strength, pH and calcium ion concentration, affecting humic acid removal and flux decline was also investigated.

2. Materials and methods

2.1. Experimental materials

The diluted humic acid (HA) solution of 2 mg/L was used as the feed water. Humic acid was from Aldrich Chemical Co. and deionized (DI) water was used. Salt solutions were prepared by dissolving pre-weighted quantities of sodium chloride and calcium chloride in DI water. Solution pH was adjusted to the desired value using small amounts of either HCl or NaOH as needed. Solutions were used immediately after initial preparation. All the chemicals used in this study were from Sinopharm Chemical Reagent Corp. (SCRC), China, otherwise being noted.

The apparent molecular weight (MW) distribution of the humic acid sample was determined using the ultrafiltration fractionation method originally developed by Aiken (1984). Humic acid sample was fractionated in a 25 mm diameter

stirred cell (Model 8010, Amicon Corp.) using a series of RC ultrafiltration membranes (Millipore Corp.) with nominal molecular weight cutoffs (MWCOs) of 3, 5, 10, 30 and 100 kDa and microfiltration membranes of 0.22 μm and 0.45 μm . The filtration was performed at a constant pressure of 100 kPa, with the fractional amount of humic acid within each size range calculated from the difference in humic acid concentration between adjacent filtrate samples.

The membranes used for the ultrafiltration were 25 mm diameter regenerated cellulose (RC) and Biomax[®] polyethersulfone (Millipore Corp.) flat membranes, having MWCOs of 30 kDa and 100 kDa. A negatively charged version of the membrane used was made in the laboratory by the covalent attachment of negatively charged sulphonic acid groups to the surface of the membrane using the base-activated chemistry developed by van Reis (2001). Membranes were first flushed with deionized water to remove any residual storage agents. The membranes were then equilibrated with 0.1 M NaOH and immersed in a 2 M solution of 3-Bromopropanesulfonic acid sodium salt (Sigma Chemical) in 0.1 M NaOH for approximately 48 h. The membranes were then flushed with approximately 100 L/m² of 0.1 M NaOH followed by 100 L/m² deionized water.

2.2. Experimental methods

2.2.1. Static adsorption experiment

The hydraulic permeabilities were evaluated for Biomax[®] polyethersulfone, neutral and negatively charged membranes before being soaked in 2 mg/L humic acid solutions of pH 7.5 at 4 °C for 24 h. The hydraulic permeabilities were reevaluated after each membrane was removed from individual humic acid solution. The difference of the hydraulic permeability before and after adsorption shows the humic acid adsorption effect.

2.2.2. Ultrafiltration experiment

UF experiments were performed in a dead-end 25 mm diameter stirred cell (Model 8010, Amicon Corp.) connected to an air-pressurized solution reservoir. The schematic diagram of UF experiment is shown in Fig. 1. The stirred cell and reservoir were initially filled with DI water. The hydraulic permeability (L_p) was evaluated by measuring the flux of water as a function of applied pressure (10–150 kPa), as shown in the following

$$L_p = \frac{J}{\Delta P} \quad (1)$$

where ΔP is the applied pressure and J is the water filtrate flux. The stirred cell was then emptied and refilled with a desired humic acid solution. The system was repressurized, and the stirring speed was set to 600 rpm. The filtrate flow rate was measured by timed collection with the filtrate mass determined using an analytical balance. Filtrate samples were collected periodically for subsequent concentration analysis. At the end of the filtration experiment, the stirred cell was emptied, the membrane was gently rinsed with DI water to remove any labile humic acids, and the stirred cell and reservoir were refilled with fresh DI water. The membrane hydraulic permeability was then evaluated to provide a measure of any membrane fouling.

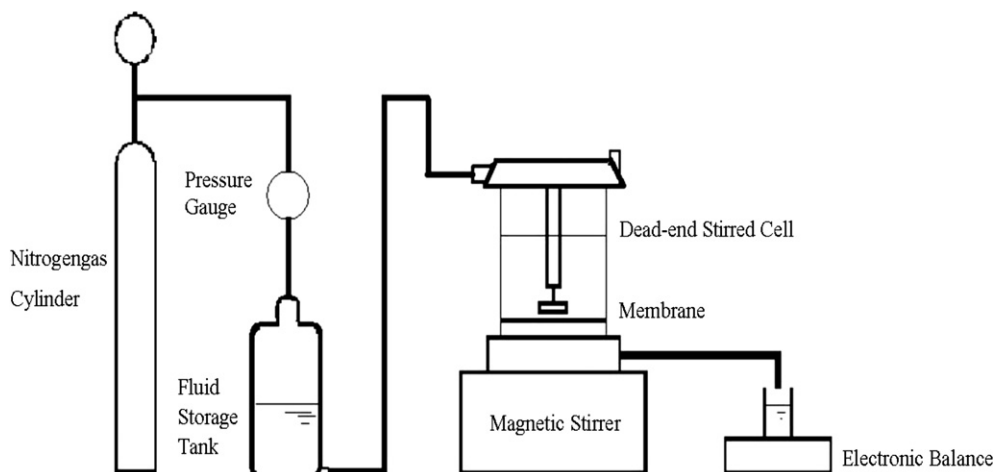


Fig. 1 – Schematic diagram of UF experiment.

2.2.3. Zeta potential measurement

The surface charge property of the ultrafiltration membrane (both before and after charge modification) was examined using streaming potential. The streaming potential was evaluated using a device constructed from two Plexiglas chambers with Ag/AgCl electrodes inserted at each end. Data were obtained using 10 mM KCl at pH 7, with the fluid flow directed through the membrane pores. The schematic of the membrane streaming potential measurement is shown in Fig. 2. The streaming potential (E_z) was measured at a minimum of four applied pressures (ΔP) from 10 to 150 kPa. The apparent zeta potential (ζ) was evaluated from the slope using the Helmholtz–Smoluchowski equation

$$\zeta = \frac{\eta \Lambda_0}{\epsilon_0 \epsilon_r} \left(\frac{dE_z}{d\Delta P} \right) \quad (2)$$

where η is the solution viscosity, Λ_0 is the solution conductivity, ϵ_0 is the permittivity of vacuum, and ϵ_r is the dielectric

constant of the medium. Several studies have shown that Eq. (2) provides useful information on the charge characteristics of ultrafiltration membranes even though the Helmholtz–Smoluchowski equation neglects the effects of surface conductance and overlapping double layers (Nyström et al., 1989, 1994). All results in this study are reported in terms of apparent zeta potential data as calculated from Eq. (2).

2.3. Analytical methods

The total humic acid concentration was evaluated by a spectrophotometer from Shanghai MAPADA Instruments Co., Ltd with the absorbance measured at 254 nm. Fourier transform infrared spectroscopy with attenuated total reflection (FTIR-ATR, EQUINOX 55 from Bruker) was used to identify the organic functional groups on the surface of membranes. Contact angles for three kinds of membrane were measured using OCA 20 video-based contact angle meter (DataPhysics Instruments GmbH, Germany).

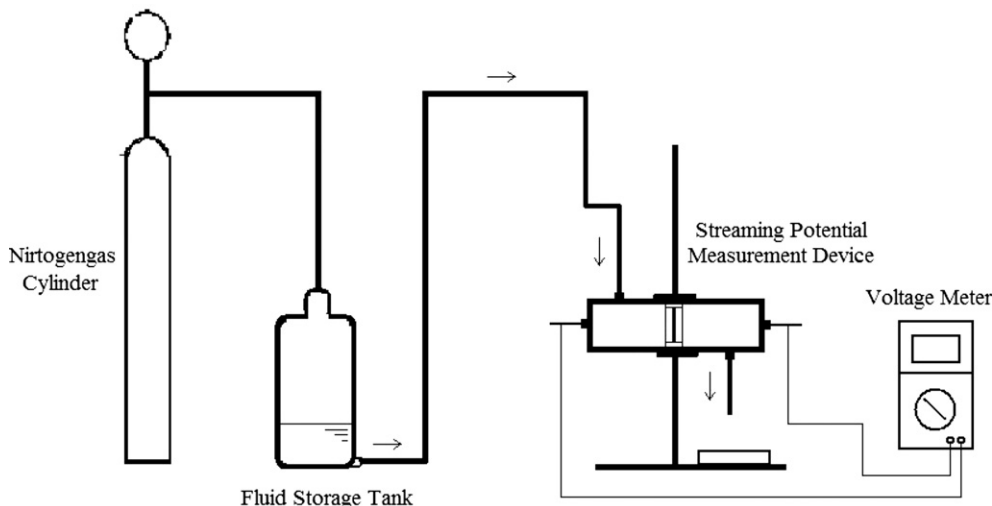


Fig. 2 – Schematic of the membrane streaming potential measurement.

2.4. Resistance analysis

The resistance-in-series model was applied to evaluate the portion of each resistance of the total resistance (R_t) as shown in Eqs. (3)–(7).

$$R_t = \frac{\Delta P}{\mu J} \quad (3)$$

$$R_m = \frac{\Delta P}{\mu J_i} \quad (4)$$

$$R_a = \frac{\Delta P}{\mu J_a} - R_m \quad (5)$$

$$R_{pp} = \frac{\Delta P}{\mu J_f} - R_m - R_a \quad (6)$$

$$R_{cp} = \frac{\Delta P}{\mu J} - R_m - R_a - R_{pp} \quad (7)$$

where R_m is the intrinsic membrane resistance, R_a is the adsorption resistance, R_{pp} is the deposition resistance caused by the humic acid deposited on the membrane surface and within the membrane pores and R_{cp} is the polarization resistance caused by concentration polarization effect; and J is the membrane permeate flux during filtration process, J_i is the water flux on new and clean membrane, J_a is the water flux after the clean membrane soaked in humic acid solution overnight and J_f is the water flux on the membrane after the filtration process.

3. Results and discussion

3.1. Adsorption of humic acid on membranes

The hydraulic permeability of each membrane was evaluated both before (L_p) and after adsorption (L_{p-ads}). The ratio of L_{p-ads} and L_p was used to quantitatively describe the effect of adsorption for each membrane. Zeta potential and contact angle were also measured on each membrane before and after adsorption. The results are summarized in Table 1. The hydraulic permeability had a small decrease after adsorption for both neutral RC and Biomax[®] membrane, with the value of 7% and 5% decrease, respectively. In each case, the adsorption and hydraulic permeability experiments were performed using at least two membranes, with standard deviation of L_{p-ads}/L_p decrease less than 2.5%. Note that the water was spread out completely, that is, the contact angle decreased to

0°, in a few seconds after it was deposited on RC membranes. Since the contact angles at the time of deposition were very small (less than 20°), together with the fast spreading of the water on RC membranes, the values of the contact angles were given as <20°.

In this study, it is interesting to note that the hydraulic permeability for negatively charged RC membrane increased 14% after static adsorption procedure. Control experiment was performed with the negatively charged RC membrane incubated for 24 h in a KCl solution without HA added. The hydraulic permeability of this saline solution incubated membrane was measured with the decrease value of 2%, which concluded that the increase for the negatively charged RC membrane after HA adsorption is not associated with the better wetting of the membrane during the overnight incubation in the HA solution. Zeta potential of negatively charged RC membrane increased from –11.1 mV to –7.4 mV after adsorption of HA. Alternatively, the change in permeability might be due to the effects of counterelectro-osmosis since the permeability was measured using DI water. Fluid flow through the charged pores generates a voltage (streaming potential) across the membrane, which is needed to satisfy the condition of no net current flow due to the unequal convective transport of the co-ions and counter-ions. The solvent flow generated by the streaming potential is always in the opposite direction of the pressure-driven flow. This is known as the counterelectro-osmosis. We obtained permeability values of negatively charged RC membrane before and after HA adsorption using high ionic strength KCl solution (1000 mM), in which the back fluid flow associated with counterelectro-osmosis could be omitted. Our measured permeability value of negatively charged RC membrane using 1000 mM KCl solution increased 11% after HA adsorption compared to that before adsorption. It is concluded that though the adsorption of humic acid shields some of the membrane charge, thereby reducing certain extent of counterelectro-osmosis, the increase of the hydraulic permeability of negatively charged RC membrane after adsorption is not mainly caused by the effect of counterelectro-osmosis.

Aoustin et al. (2001) observed that during humic substance (HS) ultrafiltration period, the flux had a distinct tendency to rise, showing that the HS makes the membrane more hydrophilic. Elimelech et al. (1997) reported a similar effect in nanofiltration. Similarly, we thought that the hydrophilic property of the negatively charged RC membrane might increase after adsorption (though the exact values of contact angle were not able to be obtained), causing the hydraulic permeability increased. The FTIR-ATR spectrum was obtained to determine qualitatively the types of functional groups on

Table 1 – Water flux, zeta potential and contact angle before and after pre-adsorption on neutral, negatively charged RC and Biomax[®] membranes.

Membrane	L_{p-ads}/L_p	Contact angle (°)		Zeta potential (mV)	
		Clean	After adsorption	Clean	After adsorption
Native RC	0.93	<20	<20	–1.1	–2.1
Charged RC	1.14	<20	<20	–11.1	–7.4
Biomax [®]	0.95	56	60	–12.3	–9.1

the membrane surface as shown in Fig. 3. Compared with the FTIR spectrum of clean negatively charged membrane, a much higher band of absorption between 3000 and 3700 cm^{-1} , which is characteristic of hydroxide, was observed on the membrane surface after static adsorption. It was also observed the absorption around 1641 cm^{-1} , typically C=O stretching of amide group. The functional groups of both –OH and C–O are the characteristic property for hydrophilic organic matter. The presence of absorption in these regions further suggests a significant amount of hydrophilic portions of HA on the membrane surface. This confirms our hypothesis that more hydrophilic portions of HA adsorbed on the membrane and caused the hydraulic permeability increase. Further, hydraulic permeability was measured for 30 kDa membrane and 3% increase was observed after adsorption. For the larger pore size 100 kDa membrane, it has the ability to hold more hydrophilic portions of HA and thus the hydraulic permeability increased more than that of 30 kDa membrane.

3.2. Humic acid removal and fouling during filtration

Experimental data for the humic acid rejection coefficient during the constant pressure (69 kPa) filtration through different 100 kDa UF membranes are shown in Fig. 4. Rejection coefficient (removal rate) is defined as $(1 - C_{\text{filtrate}}/C_{\text{feed}})$, in which C_{filtrate} and C_{feed} are the total humic acid concentration in the filtrate and feed solution, respectively. Results showed that the initial removal rate of humic acid increased to 92% on the negatively charged version of RC membrane compared to only 59% removal of HA on the neutral one with the same MWCO. The initial rejection coefficient of HA on the neutral RC membrane was about 59%, which is consistent with certain amount (about 38%) of the low molecular weight components less than 100 kD as shown in Fig. 5. The apparent zeta potential of the clean charged RC membrane was measured at –11.1 mV, compared with almost neutral RC membranes at –1.2 mV. Negatively charged and neutral RC membranes had the similar pore size (the difference of hydraulic permeability within two membranes less than 10%) of the same material but quite different charges. Thus the difference in rejection for humic acid is almost certainly due to the difference in the

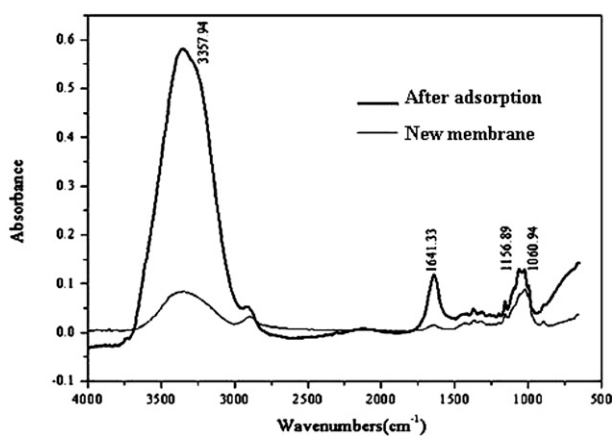


Fig. 3 – FTIR-ATR spectrogram of new negatively charged membrane and the one after static adsorption.

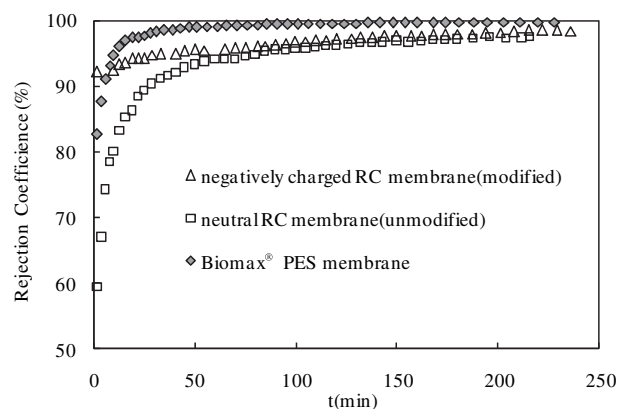


Fig. 4 – Rejection coefficients during filtration of Aldrich HA solution through UF 100 kDa membranes.

membrane charge. Humic acid is strongly negatively charged at a pH greater than 4.7 (Stevenson, 1982), the modified membrane with negative charge would reject the humic acid with the same kind of charge due to electrostatic repulsion and increase the rejection coefficient. Fig. 4 also shows the removal rate of HA through Biomax[®] polyethersulfone membrane. It is observed that the initial removal rate of humic acid on Biomax[®] is 66%, relatively higher than that on the neutral RC membrane. Though initially the removal rates of neutral and negatively charged RC membranes have big differences, they increased rapidly during filtration, approaching almost same values of 97% and 98% at long times. The Biomax[®] membrane had the initial removal rate between neutral and negatively charged RC membranes, but the removal rate at longer times was the greatest one.

Fig. 6 shows the normalized filtrate flux ratio (J_w/J_0) during the constant pressure (69 kPa) filtration of the Aldrich HA through different membranes, J_w/J_0 is the ratio of filtrate flux during the filtration process over the filtrate flux at the

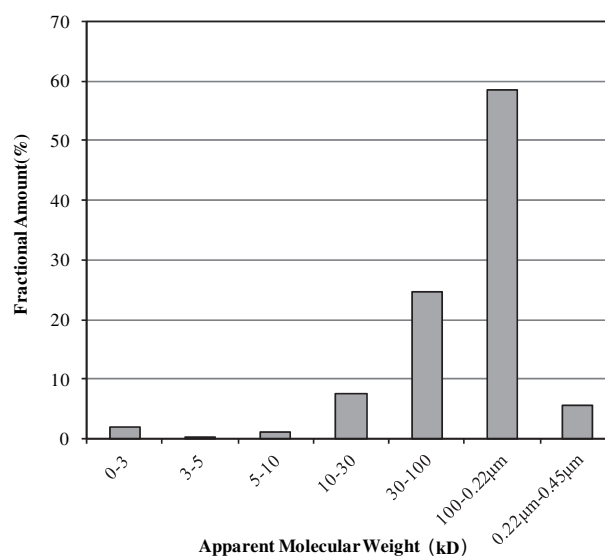


Fig. 5 – Apparent molecular weight distribution for solutions of Aldrich humic acids at pH 7.0.

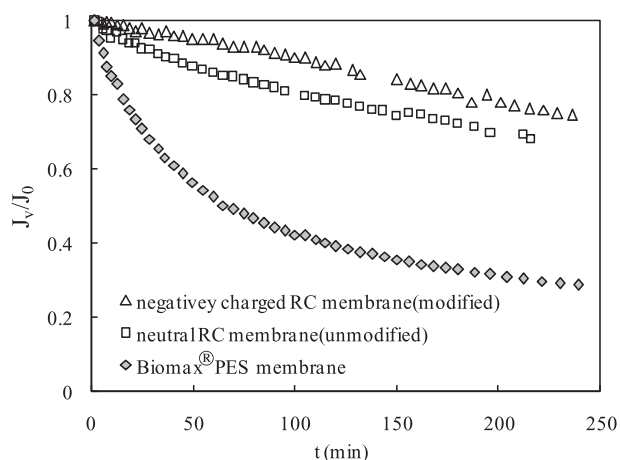


Fig. 6 – Normalized filtration flux during filtration of Aldrich HA solution through UF 100 kDa membranes.

beginning of the filtration for each individual membrane. The flux after 4 h of filtration had declined by 71% for the Biomax[®] membrane but only 32% for neutral RC membrane, even smaller at 25% for negatively charged RC membrane. In general, the main mechanisms responsible for NOM fouling in UF membranes are the interactions between the NOM species and the membrane surfaces. As mentioned before, humic acid is strongly negatively charged at a pH greater than 4.7 (Stevenson, 1982). Negatively charged RC membrane with zeta potential of -11.1 mV would reject the HA more compared to the neutral RC membrane due to the electrostatic repulsion between the negatively charged humic acid and the negatively charged membrane at pH 7. And thus, there is less fouling of HA on the negatively charged RC membrane. However, Biomax[®] membrane is negatively charged with zeta potential measured at -12.3 mV, the fouling during filtration is the worst among these three kinds of membranes. Biomax[®] membrane is more hydrophobic compared to RC membranes seen from the contact angle values. Because of the hydrophobic interactions between Biomax[®] membrane and HA, Biomax[®] membrane experienced the worst flux decline. This indicates that the potential approach used to reduce HA fouling should not only control the electrostatic interactions at the membrane surface but also hydrophobic/hydrophilic interaction.

The flux decline observed during the humic acid filtration is due to the combined effects of humic acid adsorption on or within the membrane pores, humic acid deposition during filtration, and humic acid concentration polarization (Yuan

and Zydney, 2000). To determine the relative importance of these effects, the flux of DI water was evaluated for the clean membrane, for the same membrane after static adsorption in a 2 mg/L humic acid solution for 24 h to achieve equilibrium adsorption and then for the same membrane after a 4 h filtration. Using resistance-in-series model, various resistance results for the uncharged, charged RC and Biomax[®] membranes are calculated and summarized in Table 2.

The humic acid adsorption effects on three membranes were illustrated in Section 3.1. Contact angle data for the pre-adsorbed Biomax[®] polyethersulfone membrane showed slight increase from 56° for the clean membrane to 60° , with a comparatively larger increase for zeta potential from -12.3 mV to -9.1 mV. This indicated that the adsorption for Biomax[®] occurs in thin layer throughout the internal membrane pore structure. Similar experimental results and conclusions were obtained by Yuan and Zydney (2000) on OMEGA series polyethersulfone membranes (Filtron Technology Corp.). Contact angles on both native and negatively charged RC membranes do not show measurable difference. Zeta potential values of the native and charged RC membranes changed from -1.1 mV to -2.1 mV, from -11.1 mV to -7.4 mV, respectively. This also indicated that HA is probably adsorbed on the surface of RC membrane pores (not on the membrane surface). In contrast, contact angle and zeta potential data before and after filtration showed that the humic acid deposition during fouling occurs primarily on the upper surface for both RC and polyethersulfone membranes. The zeta potential of the negatively charged RC was -7.4 mV after HA adsorption and -6.2 mV after HA filtration compared to -11.1 mV for the clean membrane. Similarly, the zeta potential of Biomax[®] changed from -12.3 mV to -9.1 mV after HA adsorption, with only a small additional change to -8.4 mV after HA filtration. Contact angle data for Biomax[®] showed only a slight increase from 56° for the clean membrane to 60° , with a much larger increase to 78° after HA filtration.

The data in Table 2 show that the hydraulic resistance of the HA deposit on the charged RC membrane decreased and accounted for only 1.27% of the total resistance compared to the native uncharged RC membrane with 6.12% resistance attributed from deposit. This is consistent with the fact that the electrostatic interaction between the same charged HA and RC membrane decreases the HA deposit on the membrane surface. It is also noticed that the deposit resistance accounted for 66.9% of the total resistance for Biomax[®] membrane. The contribution from the deposit for Biomax[®] membrane is much higher than that for both neutral and negatively charged RC membranes, which indicated that the hydrophobic property of the membrane has significant effect on the membrane fouling. One has to be very careful to choose

Table 2 – Resistance analysis on 100 kDa unmodified, modified RC membranes and Biomax[®] membranes at pH = 7.5 ($R: \times 10^{10} \text{ m}^{-1}$).

Membrane	R_t /(% of total resistance)	R_m /(% of total resistance)	R_a /(% of total resistance)	R_{pp} /(% of total resistance)	R_{cp} /(% of total resistance)
Native RC	7.68/(100)	5.34/(69.5)	0.37/(4.82)	0.47/(6.12)	1.50/(19.5)
Charged RC	7.36/(100)	6.08/(82.6)	$-0.48/(-6.58)$	0.09/(1.27)	1.68/(22.8)
Biomax [®]	11.73/(100)	2.30/(19.6)	0.22/(1.88)	7.85/(66.9)	1.36/(11.6)

the membrane with the proper hydrophobic property. The relative contribution of concentration polarization to the total flux decline for the negatively charged RC membrane is 22.8%, a small increase compared to that of 19.5% for the native neutral RC membrane. The larger retention of the HA explained the larger contribution from the concentration polarization effect on the charged RC membrane.

3.3. Effect of solution environment on humic acid removal and fouling with charged ultrafiltration membrane

3.3.1. Effect of solution pH

Fig. 7 shows data for the normalized filtrate flux and removal rate of humic acid during filtration 2 mg/L humic acid solution at pH 3.5 and 7.5 through neutral and negatively charged RC 100 kDa membranes at 69 kPa. The filtrate flux decline was more rapid at pH 3.5 for both neutral and negatively charged membranes. For neutral RC membrane, the flux decline at 4 h filtration time is 41% at pH 3.5 compared with filtration flux decline of 33% at pH 7.5 after the same filtration time. For charged RC membrane, the flux decline at 4 h filtration time is 36% at pH 3.5 compared with filtration flux of 26% at pH 7.5 after the same filtration time. These experimental data indicate that the effect of pH on the humic acid

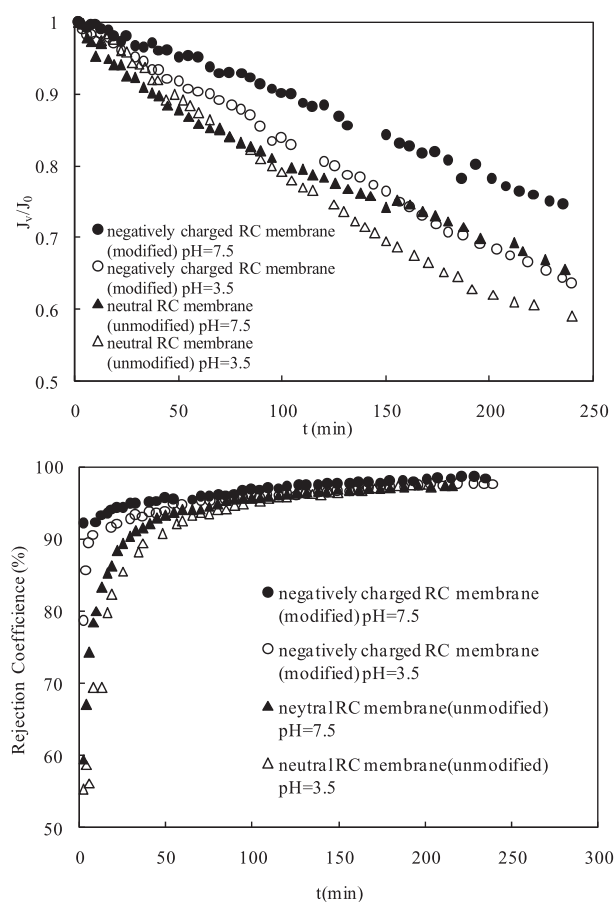


Fig. 7 – Effect of solution pH on the normalized flux and removal rate of humic acid during filtration through neutral and negatively charged 100 kDa RC membranes.

fouling is larger for charged membrane than that for neutral membrane.

It is observed that the removal rate of humic acid was smaller at pH 3.5 for both neutral and negatively charged membranes. For neutral RC membrane, the initial removal rate of humic acid is 55% at pH 3.5 compared with removal rate of 59% at pH 7.5. For charged RC membrane, the initial removal rate of humic acid is 79% at pH 3.5 compared with removal rate of 92% at pH 7.5. These experimental data clearly indicate that the effect of pH on the humic acid removal is much larger for charged membrane than that for neutral membrane.

At low pH, due to the protonation of humic acid functional group $-COOH$, the net charge on humic acid decreases, causing the reduction in intra- or inter-molecular electrostatic repulsion and/or the increase in hydrophobicity of the humic molecules associated the reduced electrical charge. At the same time, the membrane net charge decreases, the electrostatic exclusion of the negatively charged humic acid from the negatively charged membrane pores decreases. All these lead to the increase in humic acid aggregation, more humic acid deposit on the membrane and in turn more humic acid fouling. In contrast, at high pH, the net charges on both humic acid and membrane increase, causing the electrostatic repulsion between humic acids, and the electrostatic repulsion between humic acid and membrane increase, and thus the humic acid fouling decreases, at the same time the removal rate of humic acid increases. Compared with the neutral membrane, the electrostatic interaction has more contribution to the humic acid filtration through modified negatively charged membrane, thus the effect of pH on the humic acid removal and fouling is greater. That is, the filtrate flux declines more during filtration and humic acid removal rate decreases more at low pH.

3.3.2. Effect of ionic strength

Fig. 8 shows the effect of solution ionic strength on the normalized flux and removal rate of humic acid during filtration through neutral and negatively charged 100 kDa RC membranes. It is observed that the rate of flux decline increased with increasing ionic strength for both neutral and negatively charged membranes. For neutral membrane, the flux decline by 73% at 4 h filtration time for the humic acid solution with 100 mM NaCl compared to 67% for the solution with 3 mM NaCl and much smaller value of 32% for the solution without extra NaCl added. For negatively charged membrane, the flux decline by 63% at 4 h filtration time for the humic acid solution with 100 mM NaCl compared to only 35% for the solution with 3 mM NaCl and even smaller value of 26% for the solution without extra NaCl added. In addition, removal rate of humic acid decreased with increasing solution ionic strength for both neutral and negatively charged membranes. For neutral RC membrane, the initial removal rate of humic acid is 59% for the humic acid solution without extra NaCl added compared with removal rate of 32% for the solution with 100 mM NaCl and 43% for the solution with 3 mM NaCl. For charged RC membrane, the initial removal rate of humic acid is 92% for the humic acid solution without extra NaCl added compared with removal rate of 39% for the solution with 100 mM NaCl and 87% for the solution with 3 mM NaCl.

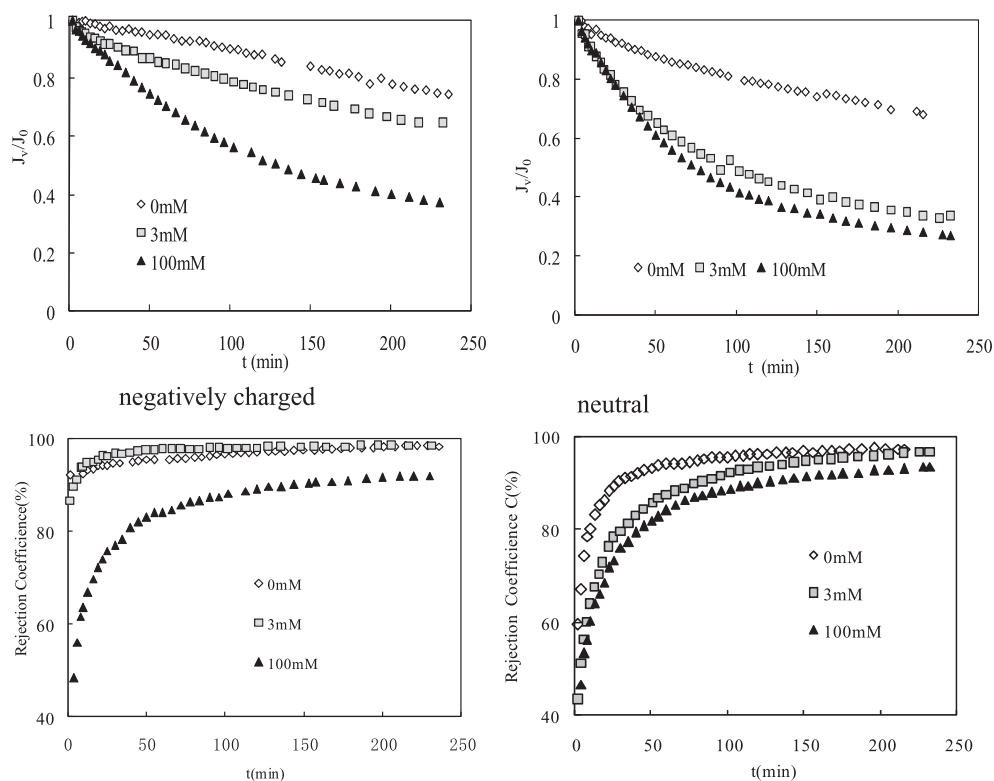


Fig. 8 – Effect of solution ionic strength on the normalized flux and removal rate of humic acid during filtration through neutral and negatively charged 100 kDa RC membranes.

At low ionic strength, intra- and inter-molecular repulsion of the humic acid molecules increases, the humic molecules stretch to more linear chains, the deposition of these linear humic molecules on the membrane surface is loose, and thus the filtration flux is comparatively large. At high ionic strength, intra- and inter-molecular repulsion of the humic acid molecules decreases, the humic molecules transfer to a more coiled state and the net charge of humic acid decrease (Yuan, 2001). At the same time, the increasing electrostatic shielding causes a reduction in electrostatic repulsion between the charged humic acids and the membrane. These then result in the humic molecules densely accumulating on the membrane surface and fouling is more severe at high ionic strength. As to the rejection of humic acid, larger electrostatic shielding of humic acid from the membrane and less charge, more coiled molecules give reduced removal rate.

Compared with negatively charged membrane, Fig. 8 also shows that the small solution ionic strength of 3 mM could have larger effect on the humic acid removal and fouling during filtration for neutral membrane, and this effect does not change much when the ionic strength increases further from 3 mM to 100 mM. This indicates that the effect of ionic strength on the humic acid removal and fouling is smaller for negatively charged membrane than neutral membrane when the ionic strength is comparatively small, which further confirms that electrostatic interactions between the charged humic acid and charged membrane are beneficial to the humic acid removal and anti-fouling.

3.3.3. Effect of adding calcium

Fig. 9 shows the effect of CaCl_2 concentration on the flux decline and removal rate of humic acid through both neutral and negatively charged 100 kDa RC membranes.

For negatively charged membrane, as the Ca^{2+} concentration increases from 0 to only 0.5 mM, the rate of filtrate flux decreased sharply, with the flux decline at 4 h filtration time from 72% to 25%. As the Ca^{2+} concentration increases, the solution ionic strength increases. As explained previously, high ionic strength solution would decrease intra- and inter-molecular repulsion of the humic acid molecules and increase electrostatic shielding, which causes the increase in fouling. In addition, the role of Ca^{2+} is more than just an ionic strength effect (Yuan, 2001; Zularisam et al., 2006). Calcium could bind to the carboxylic acid functional groups, significantly reducing the net humic acid charge. It also could bind with the negatively charge sulfonic group of the membrane. These then cause a large increase in fouling. However, when the calcium concentration is larger than 0.5 mM, as the calcium concentration increased from 0.5 to 10 mM, the observed flux decline is becoming less. One possible explanation is that at this high calcium concentration the complexation/bridging interactions of humic acid with both humic acid and membrane are stronger, the formed humic acid aggregates deposition on the membrane surface becomes larger. The cake formed on the membrane surface however is looser with relatively high permeability, which then results in less flux decline. Katsoufidou et al. (2005) observed the similar phenomenon as ours while

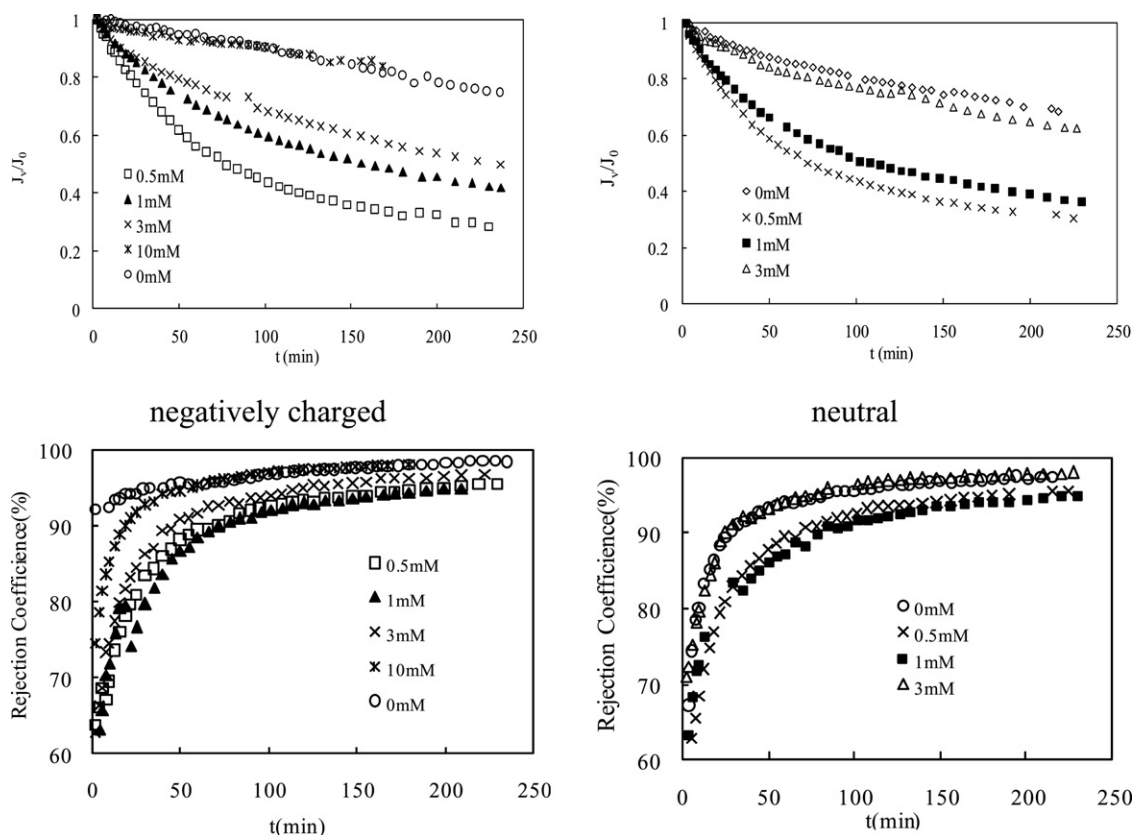


Fig. 9 – Effect of calcium concentration on the normalized flux and removal rate of humic acid during filtration through neutral and negatively charged 100 kDa RC membranes.

studying the effect of calcium concentration on the flux during humic acid filtration through RC membrane.

Fig. 9 shows as the calcium concentration increased from 0 to 0.5 mM, the initial removal rate of humic acid decreased sharply from 92% to 64% and then the trend is reversed at 0.5 mM for negatively charged membrane. As the calcium concentration increased from 0.5 mM to 10 mM, the initial removal rate of humic acid increased from 64% to 74%. One possible explanation can be given as the following. At low calcium concentration of 0.5 mM, the binding effect of calcium reduces the net humic acid charge and electrostatic interactions, leading to the lower humic acid removal. As the calcium concentration increased further from 0.5 mM to 10 mM, on one hand, the size of the formed humic acid aggregates became larger, leading to the larger rejection of humic acid and lower density of the cake formed on the membrane surface; on the other hand, the binding effect of calcium with humic acid and membrane reduced the electrostatic interactions, leading to lower rejection of humic acid. At relatively high calcium concentration, the electrostatic interaction probably is not the dominant effect, and thus it is observed that the removal rate of humic acid increased as the calcium concentration increased.

For neutral membrane, as the calcium concentration increased from 0 to only 0.5 mM, the rate of filtrate flux decreased and removal rate of humic acid decreased. However, as the calcium concentration increased further from 0.5 to 10 mM, the observed flux decline is becoming less and

the removal rate of humic acid increased. The results show that the effect of calcium on the flux decline and removal rate of humic acid through neutral 100 kDa RC membranes is similar to that observed for charged version membrane. The difference is that the filtrate flux as the function of filtration time for solution with Ca^{2+} concentration of 3 mM is close to that without extra Ca^{2+} added for neutral membrane, while only when Ca^{2+} concentration is 10 mM, the filtrate flux as the function of filtration time is close to that without extra Ca^{2+} added for charged version membrane. Compared to the negatively charged membrane, the electrostatic interactions between membrane and humic acid are smaller for neutral membrane and the binding effect is more dominant, thus the increase of Ca^{2+} concentration has more effect on filtrate flux and humic acid removal.

4. Conclusions

This is the first reported attempt to study the rejection of humic acid and flux decline with same material made membranes but only charge difference, that is, essentially neutral and negatively charged version of a regenerated cellulose membrane. The effect of solution environment, including ionic strength, pH and calcium ion concentration, on humic acid removal and flux decline were also investigated and compared. The following conclusions can be drawn from this study.

- (1) The hydraulic permeability had a small decrease after adsorption for neutral RC membranes, while the hydraulic permeability for negatively charged RC membranes increased after static adsorption procedure. It is almost certain that the hydrophilicity of negatively charged RC membrane increased after adsorption, causing the hydraulic permeability increased, which is further confirmed by the FTIR-ATR spectrum.
- (2) The higher removal rate for humic acid and less fouling were observed on the charged RC membrane than that on the neutral unmodified RC membrane, which is confirmed to be due to the increased electrostatic interactions between charged humic acid and charged membrane.
- (3) The extent of humic acid fouling and removal on the charged RC membrane was also found to be strongly governed by solution environment. Though the degrees of the effects are not the same, the trends of the effect of solution environment on the humic acid removal and fouling are same on both neutral and negatively charged membrane. This indicates that the application of the neutral and charged membranes has to consider the solution environment differently in order to have its best membrane performance.
- (4) As the calcium concentration increased from 0 to 0.5 mM, both the rate of filtrate flux and the initial removal rate of humic acid decreased sharply and then the trend is reversed at 0.5 mM. As the calcium concentration increased from 0.5 mM to 10 mM, the removal rate of humic acid and flux increased. The explanation for this phenomenon probably has to be considered from two effects: both the electrostatic interactions and the permeability of the cake layer formed on the membrane.

Results indicated that the appropriate charge modification on the neutral UF membrane could be an effective way for better removal of humic acid and reduction of the membrane fouling at the same time due to the electrostatic interactions with the combination effect of membrane pore size. In the application of ultrafiltration process for humic acid removal, one has to consider not only the properties of membrane itself (including MWCO, hydrophobicity and material), but also the solution environment, to achieve better humic acid removal rate and less membrane fouling.

Acknowledgement

This research was supported by National High Technology Research and Development Program of China (2006AA06Z307).

REFERENCES

- Aiken, G.R., 1984. Evaluation of ultrafiltration for determining molecular weight of fulvic acid. *Environ. Sci. Technol.* 18 (12), 978–981.
- Aoustin, E., Schäfer, A.I., Fane, A.G., Waite, T.D., 2001. Ultrafiltration of natural organic matter. *Sep. Purif. Technol.* 22–23, 63–78.
- Campinas, M., Rosa, M.J., 2010. Assessing PAC contribution to the NOM fouling control in PAC/UF systems. *Water Res.* 44, 1636–1644.
- Cho, J., Amy, G., Pellegrino, J., 2000. Membrane filtration of natural organic matter: factors and mechanisms affecting rejection and flux decline with charged ultrafiltration (UF) membrane. *J. Membr. Sci.* 164 (1–2), 89–110.
- Elimelech, M., Zhu, X., Childress, A.E., 1997. Role of membrane surface morphology in colloidal fouling of cellulose acetate and composite aromatic polyamide reverse osmosis membranes. *J. Membr. Sci.* 127, 101–109.
- Fan, L., Harris, J.L., Roddick, F.A., Booker, N.A., 2001. Influence of the characteristics of natural organic matter on the fouling of microfiltration membranes. *Water Res.* 35 (18), 4455–4463.
- Gray, S.R., Ritchie, C.B., Tran, T., Bolto, B.A., 2007. Effect of NOM characteristics and membrane type on microfiltration performance. *Water Res.* 41 (17), 3833–3841.
- Huang, H., Lee, N., Young, T., Gary, A., Lozier, J.C., Jacangelo, J.G., 2007. Natural organic matter fouling of low-pressure, hollow fiber membranes: effects of NOM source and hydrodynamic conditions. *Water Res.* 41 (17), 3823–3832.
- Katsoufidou, K., Yiantsios, S.G., Karabelas, A.J., 2005. A study of ultrafiltration membrane fouling by humic acids and flux recovery by backwashing: experiments and modeling. *J. Membr. Sci.* 266, 40–50.
- Kilduff, J.E., Karanfil, T., Weber, W.J., 1996. Competitive interactions among components of humic acids in granular activated carbon adsorption systems: effects of solution chemistry. *Environ. Sci. Technol.* 30 (4), 1344–1351.
- Krasner, S.W., Weinberg, H.S., Richardson, S.D., Pastor, S.J., Chinn, R., Scilimenti, M.J., Onstad, G.D., Thruston, A.D., 2006. Occurrence of a new generation of disinfection byproducts. *Environ. Sci. Technol.* 40 (23), 7175–7185.
- Mehta, A., Zydney, A.L., 2006. Effect of membrane charge on flow and protein transport during ultrafiltration. *Biotechnol. Prog.* 22, 484–492.
- Nyström, M., Lindström, M., Matthiasson, E., 1989. Streaming potential as a tool in the characterization of ultrafiltration membranes. *Colloid Surf.* 36, 297–312.
- Nyström, M., Pihlajamäki, A., Ehsani, N., 1994. Characterization of ultrafiltration membranes by simultaneous streaming potential and flux measurements. *J. Membr. Sci.* 87, 245–256.
- Nyström, M., Ruohomäki, K., Kaipia, L., 1996. Humic acid as a fouling agent in filtration. *Desalination* 106 (1–3), 79–87.
- Susanto, H., Ulbricht, M., 2008. High-performance thin-layer hydrogel composite membranes for ultrafiltration of natural organic matter. *Water Res.* 42, 2827–2835.
- Stevenson, F.J., 1982. *Humus Chemistry*. John Wiley & Sons, New York.
- van Reis, R., 2001. Charged Filtration Membranes and Uses Therefor. USA patent WO 01/08792 A2.
- Wei, X., Wang, R., Li, Z., Fane, A.G., 2006. Development of a novel electrophoresis-UV grafting technique to modify PES UF membranes used for NOM removal. *J. Membr. Sci.* 273 (1–2), 47–57.
- Yamamura, H., Chae, S., Kimura, K., Watanabe, Y., 2007. Transition in fouling mechanism in microfiltration of a surface water. *Water Res.* 41 (17), 3812–3822.
- Yuan, W., 2001. Fouling of Humic Acid during Ultrafiltration and Microfiltration for Water Treatment. Ph.D. Dissertation, University of Delaware, Delaware.
- Yuan, W., Zydney, A.L., 2000. Humic acid fouling during ultrafiltration. *Environ. Sci. Technol.* 34 (23), 5043–5050.
- Zularisam, A.W., Ismail, A.F., Salim, R., 2006. Behaviours of natural organic matter in membrane filtration for surface water treatment – A review. *Desalination* 194 (1–3), 211–231.