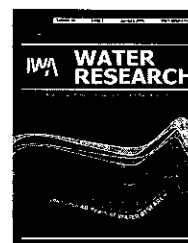




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Removal of humic substances (HS) from water by electro-microfiltration (EMF)

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ARTICLE INFO

Article history:

Received 3 March 2004

Received in revised form

30 October 2005

Accepted 20 February 2006

Available online 17 April 2006

Keywords:

Humic substances (HS)

Microfiltration (MF)

Electro-microfiltration (EMF)

Critical electric field strength

($E_{critical}$)

Trihalomethane formation potential

(THMFP)

¹H nuclear magnetic resonance

(¹H NMR)

ABSTRACT

Humic substances (HS) represent the common agents contributing to flux decline during membrane filtration of natural water. In order to minimize the fouling during microfiltration (MF) of HS, modifying the operation of MF presents a promising alternative. A laboratory-scale electro-microfiltration (EMF) module was used to separate Aldrich HS from water by applying a voltage across the membrane. The presence of an electric field significantly reduced the flux decline. A flux comparable to that of ion-free water was attained when the voltage was near the critical electric field strength ($E_{critical}$), i.e., the electrical field gradient that balances the advective and electrophoretic velocities of solute. At an applied voltage of 100 V (~110 V/cm), it was able to reduce UV absorbance at 254 nm (UV_{254}), total organic carbon (TOC) and trihalomethane formation potential (THMFP) by over 50% in the permeate. Results from ¹H nuclear magnetic resonance (¹H NMR) analysis suggest that the aromatic and functionalized aliphatic fractions decreased significantly in the permeate. The charged HS have large molecule weight compared with those passing through membrane. Results clearly indicate that a combination of electric force with MF can increase HS rejection and decrease flux decline. Electrophoretic attraction was the major mechanism for the improvement of flux and rejection over time.

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1. Introduction

Microfiltration (MF), with a normal pore size exceeding 0.1 μm , is a low-pressure membrane process that commonly has been suggested for the removal of particulates and pathogens such as *Giardia* and *Cryptosporidium* from water (Jacangelo et al., 1995). Due in part to increasingly stringent environmental regulations and the aforementioned low-pressure operation, MF has received considerable attention lately as an emerging technology for solid-liquid separation (Jacangelo and Buckley, 1996). There is also increasing tendency to substitute conventional solid separation practices in water purification with MF. For example, Yoo et al. (1995) have shown that MF has many advantages over

conventional process, e.g., better tolerance to raw water turbidity and lower labor requirements.

It is known that chlorination of natural organic matter (NOM) can lead to the formation of chlorinated disinfection byproducts (DBPs), namely, trihalomethanes (THMs), which is one of the most severe public health issues facing the drinking water industry. Therefore, the removal of NOM before chlorination is necessary as to minimize the formation of DBPs. In principle, any materials, NOM included, whose size is smaller than the average pore size of MF cannot be readily separated from water by MF (Clark et al., 1996; Lee et al., 2000). As mentioned above, there is increasing interest in the removal of NOM by combined MF processes. (Carroll et al., 2000; Clark et al., 1996; Lee et al., 2000; Schafer et al., 2000).

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doi:10.1016/j.watres.2006.02.028

Nomenclature		J'	permeate flux (cm/s)
A	filtration area (m ²)	ΔP	applied pressure (N/m ²)
E	electric field strength (V/cm)	R_f	total filtration resistance (m ⁻¹)
$E_{critical}$	critical electric field strength (V/cm)	u_p	electrophoretic mobility (cm ² /(Vs))
I	current (A)	Greek letters	
k	conductivity (S/cm)	η	viscosity (Ns/m ²)
J	permeate flux (m/s)		

However, all membrane processes suffer from fouling and concentration polarization which causes flux decline, and subsequently increases process costs. Various methods have been proposed to reduce fouling and concentration polarization. These include feed solution pretreatment (Chang and Benjamin, 1996), hydrodynamic manipulations (Seidel and Elimelech, 2002), membrane modification (Bowen et al., 2002; Meier-Haack et al., 2003; Taniguchi et al., 2003), cleaning (Chellam and Jacangelo, 1998) and the application of external electric forces (Wakeman, 1998). Pretreatment of feed solution can either be physical (e.g., sand filtration) or chemical (e.g., pH adjustment, coagulation and adsorption). Hydrodynamic methods create turbulence on the membrane surface, thus facilitate back transport of solute and aid in minimizing fouling. Since charge interactions between the solute and membrane surface significantly influence membrane fouling by humic substances (HS) (Jones and O'Melia, 2001; Jucker and Clark, 1994; Yuan and Zydney, 1999a), it is possible to mitigate fouling and concentration polarization by applying external forces such as electricity or ultrasound to the membrane. The above approaches can inhibit the attachment of HS (presumably negatively charged) to the membrane surface.

The charge characteristics of HS and membrane surface are key factors affecting membrane fouling. Consequently, the application of an electric field provides a potential solution for mitigating membrane fouling by HS. Much has been reported on the theoretical analysis (Chuang et al., 2003; Okada et al., 1997), product separation (Daufin et al., 1995) and applications of electrofiltration to wastewater treatment (Huotari et al., 1999a; Yang et al., 2003). Jagannadh and Muralidhara (1996), Huotari et al. (1999b) and Wakeman and Williams (2002) have reviewed the process of electrofiltration in details. They have reported that electrokinetic phenomena such as electrophoresis and electroosmosis are important processes in electro-microfiltration (EMF). Electrophoresis involves the transport of charged materials in an electric field; that is, charged species transported toward the membrane are counterbalanced by the electric field applied. Thus, no foulants accumulation or deposition occurs on the membrane surface. In contrast, electroosmosis is the movement of liquid dragged by counterions under the influence of the electric field. These two processes occur simultaneously upon applying an electric field across the membrane filtration system. Additionally, other reactions such as electrolysis, oxidation and reduction reactions can occur also near the electrodes if they are not isolated from feed and product streams. Nonetheless, these electrochemical reactions may benefit the MF process as they may mineralize pollutants, which will eventually change the

characteristics of HS. Obviously, these electrochemical reactions should be avoided in the production of useful chemical or food products such as proteins.

There is little available information in the application of electrofiltration to water purification in the presence of HS (Cooper et al., 1965; Weng and Li, 2003; Weng et al., 2005). In addition, it is still not clear about which fractions of HS could be removed during EMF operations. The objective of this research was to examine and assess the performance of EMF in the presence of HS as affected by various conditions such as concentrations of HS and electric voltages. System performance was assessed in terms of total organic carbon (TOC), UV absorbance at 254 nm (UV₂₅₄) and trihalomethane formation potential (THMFP). Scanning electron microscopy (SEM) was used to obtain detailed information on membrane morphology before and after use. Moreover, ¹H nuclear magnetic resonance (¹H NMR) analysis was conducted to provide insight into the chemical features of HS from EMF treatment.

2. Materials and methods

2.1. Filtration module

Polyethersulfone MF membranes with a nominal size of 0.1 μ m (Pall Corp.) were used. Typical characteristics of the membrane are listed in Table 1. Two parallel-plates were assembled to create a cross-flow cell, with a filtration area of 14.5 cm² and channel height of 1 mm. The anodes and cathodes were made of platinum and titanium, respectively. The filtration area was slightly larger than the electrode area. The membrane was located 1 mm from the anode and 3 mm from the cathode. The electrodes were in direct contact with the bulk solution; therefore it is expected that electrochemical reaction may occur during filtration. Fig. 1 shows the schematic diagram of the bench-scale EMF system.

2.2. Feed water

The feed water was prepared by dissolving 1 g of powered HS (sodium salt, Aldrich) in 1 L of Milli-Q water (ion-free). The solution was filtered through a 0.45- μ m filter to remove solid residues. The stock solution was stored at 4 °C until used. A total of 5 L of HS solution was prepared for each experiment. Feed solution was diluted to approximately either 2 or 6 mg/L as TOC before filtration runs. Sodium chloride was used to provide ionic strength and maintain a conductivity of

Table 1 - Characteristics of clean MF membrane^a

Parameter	Characteristics
Manufacturer	Pall corporation
Configuration	Disk
Filter media	Hydrophilic polyethersulfone
Maximum operating temperature	100 °C
Typical thickness	132 μ m
Filtration area	14.5 cm ²
Pore size	0.1 μ m

^a Data were taken from Pall Corporation, Ann Arbor, MI, USA.

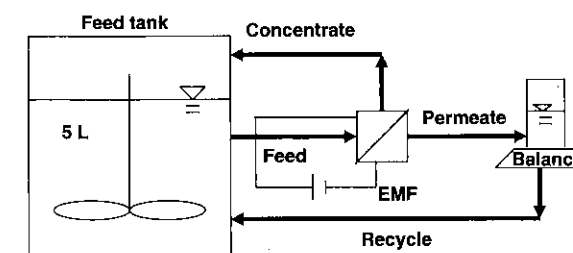


Fig. 1 - Schematic diagram of a laboratory-scale EMF system.

100 μ S/cm (or 0.8 mM) of the feed solution. The original pH of the HS solution in the feed tank was about 6.5. No further pH adjustments were made during the course of filtration.

2.3. Filtration experiments

A 5-L tank was used to hold the feed solution containing the HS at desired concentrations. A peristaltic pump was used to convey the solution to the filtration module, while the applied pressure was controlled at specific levels with a valve. The cross-flow velocity was 0.23 m/s (or 300 mL/min). The retention time of the clean water in the concentrate and permeate chambers was 1 and 25 s, respectively. The recovery efficiency of the module which is defined as the fraction of the feed flow passing through the membrane was low at less than 0.18 (or 18%) owing to its small scale. Before experiments, the membrane was pre-filtered with Milli-Q water as to remove preservatives and then the pure water flux was measured. A new membrane was used for each experiment. Experiments were conducted with and without electric field. The electric field was supplied by a power supply (Chroma 6210K-100/1000W). Permeate collected on a container was recorded by an electrical balance and periodically returned to the feed tank as to maintain a constant concentration of HS in the feed. The concentration difference was less than 15% before and after filtration experiments. The water temperature was kept close to room temperature (24-26 °C) most of the time except several occasions when it increased by 2-3 °C owing to joule heating at high voltage.

For the EMF of electrolyte experiments, membranes were first cleaned with Milli-Q water. Subsequently, the electrolyte

solution was pumped into the module to obtain zero-voltage flux. The electric voltage then was increased stepwise. The time interval between each voltage increment was around 5 min. It is also noted that the pH in the concentrate stream (the anodic) dropped to ca. 4.2 and rose to ca. 10.6 in the permeate (cathodic) due to water electrolysis.

2.4. Filtration resistance and critical electric field strength ($E_{critical}$)

The total filtration resistance can be defined by the following equation:

$$R_f = \frac{\Delta P}{J\eta}, \quad (1)$$

where R_f is the total filtration resistance (m⁻¹), ΔP the applied pressure (N/m²), J the permeate flux (m/s) and η the viscosity (Ns/m²). Based on ΔP and flux J , it is possible to calculate the filtration resistance. The critical electric field strength ($E_{critical}$) required to counterbalance the convective transport of HS toward the membrane can be estimated by (Huotari et al., 1999b)

$$E_{critical} = \frac{J'}{u_p}, \quad (2)$$

where $E_{critical}$ (V/cm) denotes the critical field strength, J' is the permeate flux (cm/s) and u_p (cm²/(Vs)) is electrophoretic mobility of the species of interest. The applied field strength (E , V/cm) during electrofiltration was calculated by the Ohm's law, i.e.,

$$E = \frac{I}{kA}, \quad (3)$$

where I (A) is direct current, k (S/cm) is conductivity and A (cm²) is the filtration area.

2.5. Chemical analyses

TOC was analyzed with an Organic Carbon Analyzer (model OI Analytical 1010). Conductivity and pH were measured with a potentiometer (Consort, model 6230). Additionally, HS were also quantified as UV₂₅₄ measured with a Cintra 20 UV-Visible spectrometer at pH 7.0 \pm 0.1. SEM images of the membrane surface were obtained with a Hitachi-S4700 SEM. Functional groups of HS were analyzed by ¹H chemical shift using a NMR spectrometer (BRUKER DMX-600) with a 5-mm-diameter probe. The detailed procedure for analyzing one-dimensional ¹H NMR was as follows. Water samples (200-300 mL) were collected and freeze-dried after pH adjustment to 7.0. D₂O was used as the solvent and methanol (at 3.3 ppm) was the internal reference standard. The acquisition parameters were 1024 scans, a spectrum width of 8400 Hz, acquisition time of 1 s and pulse delay of 1.5 s.

THMFP analysis was performed by adding 10 mg/L of sodium hypochlorite to the samples, incubated for 48 h, and then determined the total THMs with GC/MS (HP6890/HP5973).

3. Results and discussion

3.1. Effect of voltage on solute rejections

Fig. 2 shows the removal efficiency of HS in terms of TOC and UV_{254} rejection. At 2 mg/L of TOC, the rejection of HS, in terms of TOC and UV_{254} , was less than 10% in the absence of electric field. At 6 mg/L of TOC, the rejection of HS was below 15% without electric field. The result is consistent with that of the previous reports (Lee et al., 2000; Schafer et al., 2000). These authors have demonstrated that it is impossible to remove HS by MF alone (Lee et al., 2000; Schafer et al., 2000). The TOC rejection increased from 10% to 30% then to 55%, when the voltage increased from 0 to 50 then to 100 V in the presence of

2 mg/L TOC, and to 70% then to 85%, when the voltage increased to 50 then 100 V in the presence of 6 mg/L TOC, respectively.

UV_{254} rejection was low (< 5%) during MF filtration of dissolved HS. It is noted that UV_{254} rejection was consistently higher than that of TOC rejection in the presence of the electric field. The UV_{254} rejection increased from < 5% to 55% then to 75%, and from < 5% to 70% then to 90%, when the applied voltage increased from 0 to 50 then to 100 V in the presence of 2 and 6 mg/L of TOC, respectively.

The improvement in solute rejection during EMF is one of the advantages if the size of the pollutants is smaller than pore size of the membrane (Cooper et al., 1965; Huotari et al., 1999b; Wakeman, 1998; Weng and Li, 2003; Weng et al., 2005; Yang et al., 2003). Cooper et al. (1965) reported a complete

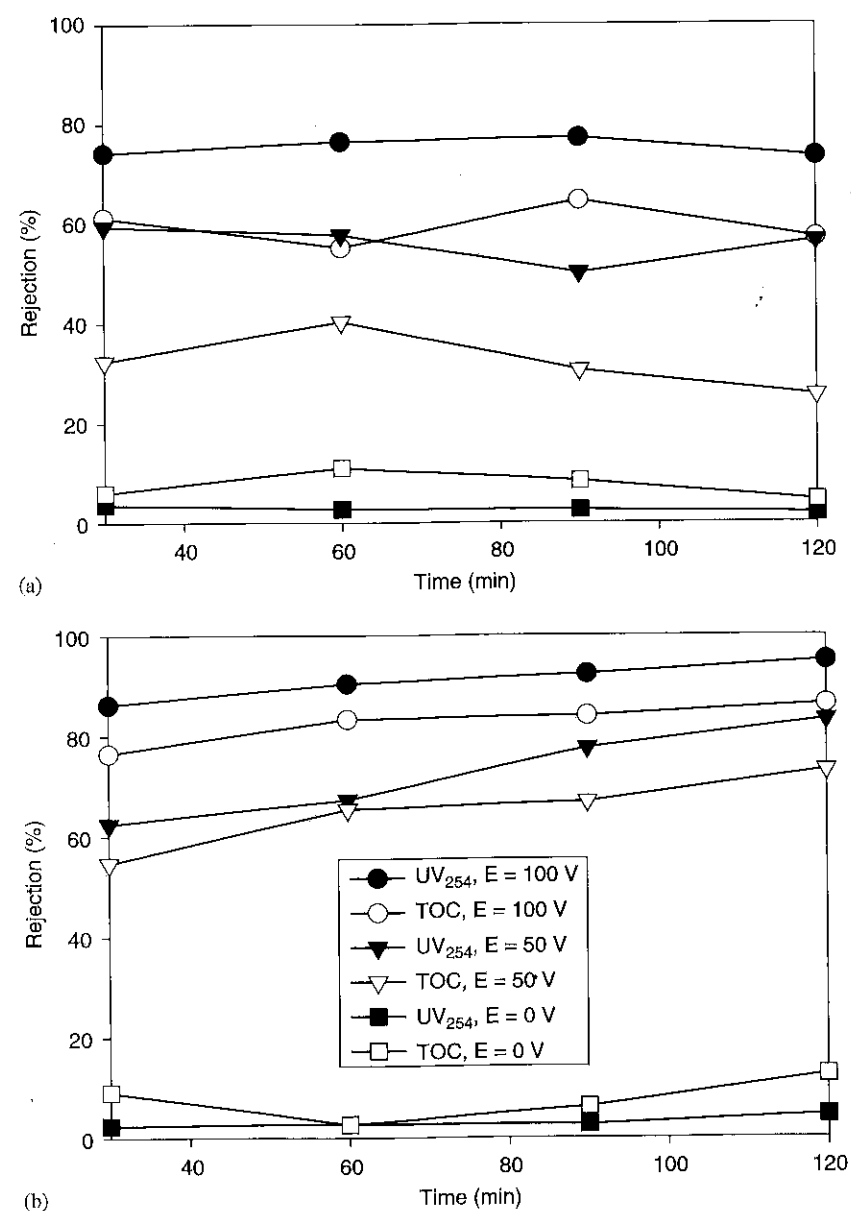


Fig. 2 – Permeate quality over time at various electric voltages. $\Delta P = 49$ kPa and cross-flow velocity = 0.23 m/s (a: TOC = 2 mg/L; b: TOC = 6 mg/L).

removal of pollutants in terms of UV in surface water. Weng and Li (2003) and Weng et al. (2005) also demonstrated that over 90% TOC removal could be achieved using electro-ultrafiltration (EUF). In general, HS are heterogeneous in nature. Although UV_{254} detection is a rapid and reliable method to measure HS which contain aromatic fractions, it is not as representative as TOC measurements which could measure all organics in solution.

Fig. 3 shows the specific ultraviolet absorbance (SUVA) of permeate before and after filtration. SUVA, which is defined as the ratio of the UV_{254} to the TOC concentration, is a simple indicator for sample aromaticity and molecular weight distribution (Letterman et al., 1999; Schafer et al., 2002). A large SUVA is indicative of high aromaticity and molecular weight distribution. As in Fig. 3, SUVA in the feed tank remained constant before and after MF, whereas SUVA in permeate decreased as the EMF time increased. The reduction

of SUVA following EMF suggests that the molecular weight was also decreased (Letterman et al., 1999; Schafer et al., 2002). It is noted that SUVA is closely related to the generation of DBPs, e.g., THMFP. Results shown in Table 2 clearly indicate that by increasing the applied voltage across the MF filter, THMFP can be reduced, e.g., a 87% reduction at 100 V. Clearly, a consistent trend can be delineated among TOC, UV_{254} , SUVA and THMFP. However, no significant relationship between SUVA and THMFP/TOC (or specific THMFP) can be derived.

3.2. Removal mechanism

Several mechanisms are possible for the removal of HS from the water by EMF. These include membrane sieving (i.e., size fractionation), membrane adsorption, electrophoresis and electrochemical mineralization. Membrane sieving is brought about by size-screening due to the sizes of HS relative to the

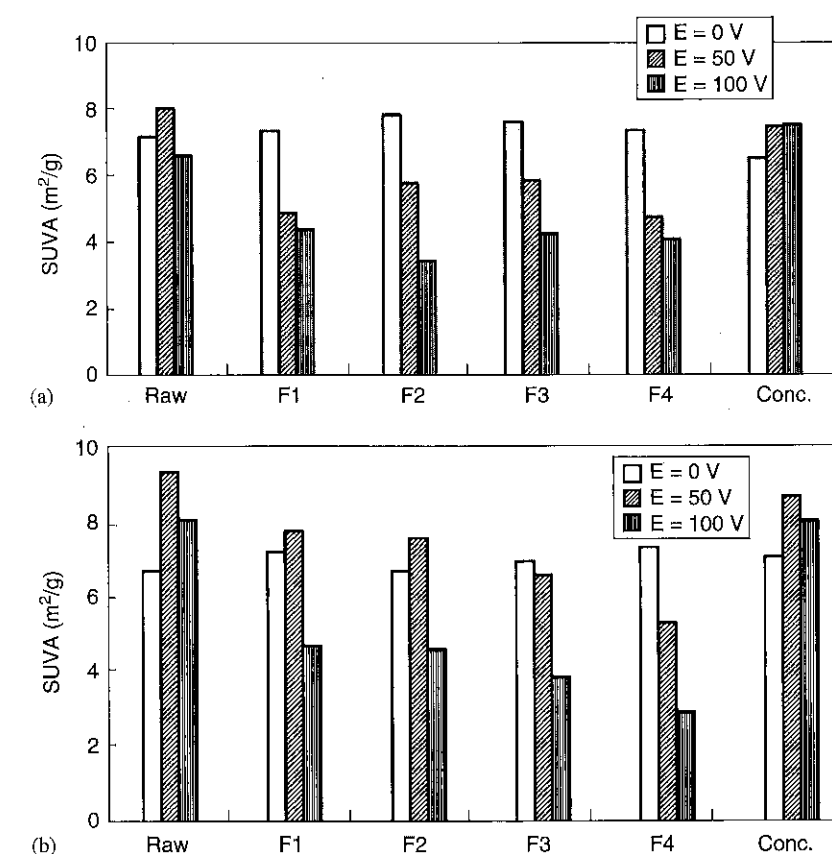


Fig. 3 – Changes of SUVA (UV_{254}/TOC) during MF runs. (a) TOC = 2 mg/L and (b) TOC = 6 mg/L. $\Delta P = 49$ kPa and cross-flow velocity = 0.23 m/s. ("Raw" denotes feed solution, "Conc." represents feed solution after experiment, "F1", "F2", "F3" and "F4" are samples taken at 30, 60, 90 and 120 min of operation, respectively).

Table 2 – Chemical analyses of HS before and after EMF

Sample	TOC (mg/L)	UV_{254} (cm^{-1})	SUVA (m^2/g)	THMFP ($\mu g/L$)	THMFP removal (%)
Feed water	6.2	0.579	9.3	233	—
Filtrate (0 V)	5.4	0.549	10.2	220	5.6
Filtrate (100 V)	0.7	0.025	3.5	31	86.7

membrane pores. Meanwhile, membrane would adsorb HS either on surface or in pores when HS were transported to the membrane surface. Electrophoresis is the transport of charged particles, such as HS, toward the anode by electrostatic attraction. Electrochemical mineralization converts the HS to carbon dioxide and thus reduces the total mass of HS in the feed tank.

Fig. 2 depicts the amounts of HS removed after treatment. Without the assistance of electric field, HS rejections were below 20%. The TOC removal increased to greater than 60–80% in the presence of 100V. Hence, the removal of HS during EMF is not mainly due to either membrane sieving or adsorption alone. Fig. 4 shows the UV absorbance of the HS-containing solutions before and after EMF in the feed and permeate. Results indicate that the UV absorbance in the feed tank before and after filtration remained relatively unchanged whereas it was slightly increased following EMF. It was found that because the total volume of water entering the EMF reactor was about 36L which was about seven times the volume of feed tank, there would be a significant decrease of HS concentration if chemical mineralization occurred significantly. Moreover, the relative inert anode electrode (Pt), short retention time in the filtration cell (1s), moderate pH (pH 6.5) and low conductivity (ca. 100 μ S/cm) may contribute to the low mineralization reaction of organics in water (Brillas et al., 1996; Comninellis and Pulgarin, 1991; Panizza et al., 2000). In this study, the specific electric charge (Ah/dm³), which is a measure of amount of electrons passing through the reactor, was equal to 0.08. This value is quite low compared to the typical value of 5 when electrochemical mineralization occurs actively (Comninellis and Pulgarin, 1991). Therefore, chemical mineralization could be discounted as a significant HS removal mechanism. Instead, it is clear that electrophoretic attraction could be regarded as the major contributor to HS removal during EMF.

Fig. 5 presents the solution ¹H NMR spectra of HS before and after EMF. Table 3 lists chemical shift assignments of the ¹H

NMR of HS. The area of a particular chemical shift range relative to total area of chemical shift was calculated based on the references (Leenheer et al., 1997; Wilson, 1981). As expected, there is no significant difference between pre- and post-treated organic matter in the feed tank. This result supports the conclusion that chemical mineralization is not significant in EMF cell. Although the chemical compositions of HS before and after EMF did not change significantly, it is unclear if there is bond-breaking or conformational change in HS. Further studies are needed to understand the influence of applied voltage on physical and chemical properties of HS during EMF.

Table 3 also presents the aromatic protons and functionalized aliphatic groups (e.g., the aliphatic 3) reduced from 27% to 7% and 24% to 18%, respectively, upon EMF. On the other hand, the composition of the uncharged methyl group (aliphatic 1) and carbohydrate (aliphatic 4) in permeate increased after EMF treatment, e.g., from 18.9% to 33.5% and from 11.4% to 26.0%, respectively. Results appear to indicate that the removal of HS upon EMF was mostly related to the aromatic and functionalized aliphatic (aliphatic 3) groups. That is, some aliphatic and aromatic portions disappeared after EMF. The fact that this fraction possessed unpaired electrons makes it separable electrostatically (i.e., electrophoresis). It has been shown that the alkyl fraction was inversely proportional to the molecular weight of HS as defined by UF (Newcombe et al., 1997). Therefore, it is suggested that EMF can retain more aromatic and charged compounds of larger molecular weight.

Since the electrophoresis dominates the removal mechanisms, Eq. (2) could be used to calculate $E_{critical}$. Here $E_{critical}$ is the electrical field at which hydrodynamic (convective) transport of foulants toward the membrane is balanced by electrostatic transport of foulants away from the membrane (Henry et al., 1977; Huotari et al., 1999b; Wakeman and Williams, 2002). HS are heterogeneous in nature and their averaged feature was used to estimate $E_{critical}$. According to

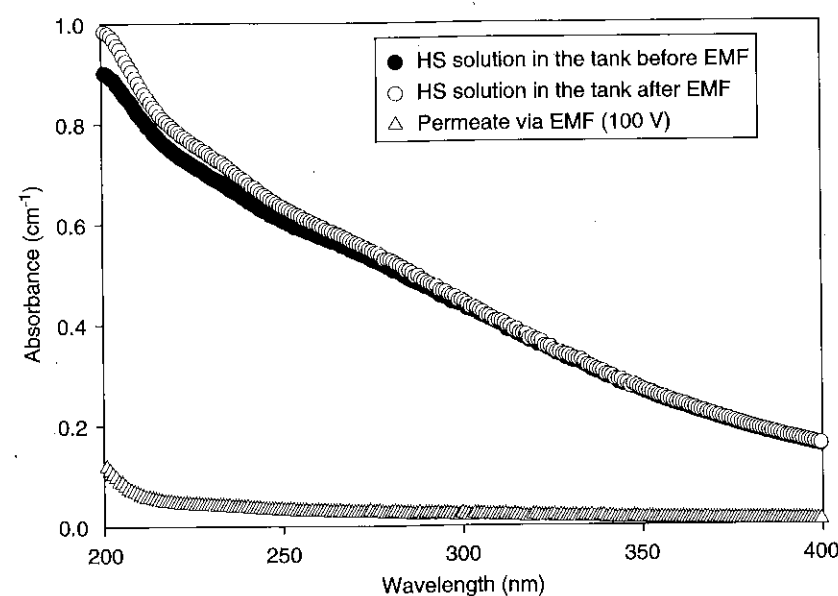


Fig. 4 - UV spectra of water samples.

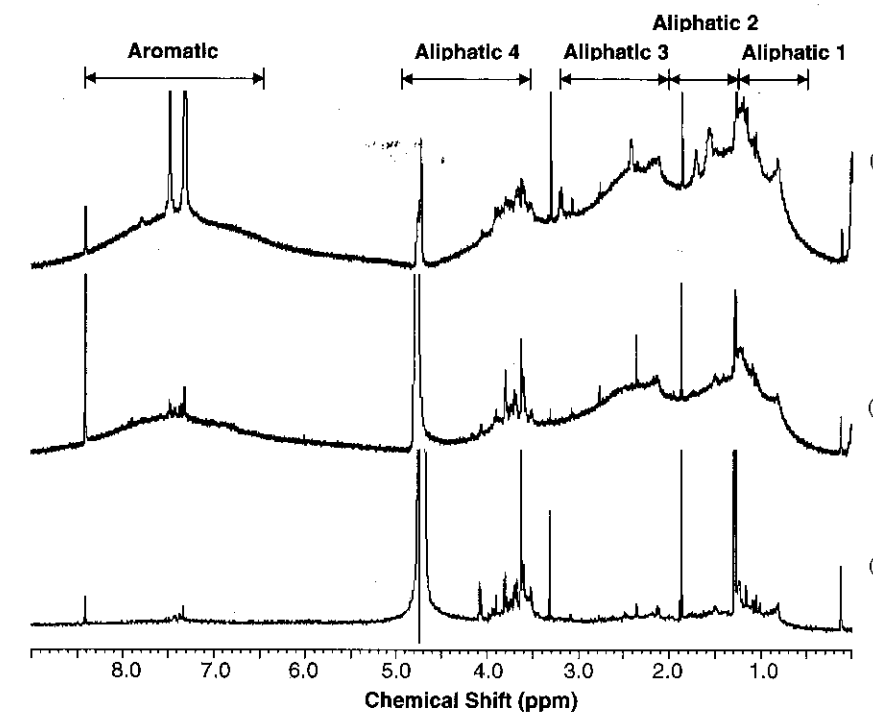


Fig. 5 - Solution ¹H NMR spectra of HS: (a) feed solution before EMF, (b) feed solution after EMF and (c) permeate via 100 V.

Eq. (2), with a u_p value of $3.3 \times 10^{-4} \text{ cm}^2/(\text{Vs})$ (Weng and Li, 2003), the $E_{critical}$ was calculated to be 130V/cm at the operating flux of $4.2 \times 10^{-2} \text{ cm}^3/\text{s}$. This value was comparable to the applied electric field strength of 116 and 107V/cm, respectively, at TOC concentration of 2 and 6mg/L, at a constant 100V. It is noted that it is possible to obtain a high HS removal if the applied electric field is greater than $E_{critical}$ (Weng et al., 2005). The fractions of HS which passed membrane might be those of uncharged functional groups as indicated from ¹H NMR analysis. Hosse and Wilkinson (2001) reported u_p values similar to this study which were in the range of 3.0×10^{-4} – $5.0 \times 10^{-4} \text{ cm}^2/(\text{Vs})$.

The fouled membranes were brown in color. In order to observe the morphological changes of the membrane upon filtration, membrane samples were pasted on carbon gummed tape and coated with platinum for SEM investigation. Fig. 6 shows the morphology after filtration in different modes. The membrane surface was filled with impurities from filtration (Fig. 6b). Fewer impurities were observed after applying electric voltage across the membrane (Fig. 6c). Fig. 6d shows that there is almost no impurity deposited on the membrane surface near $E_{critical}$ (100V). Results also suggest that applying electricity would not damage membrane surface under the experimental conditions of this study. Although it is believed that the sizes of HS could be smaller than the pore sizes of the membrane, the convective transport of the HS toward the membrane did block the pore of membrane during MF. Yuan and Zydney (1999b) reported that certain HS tended to aggregate. Those large molecules might serve as nucleation sites for the HS aggregation. Removing those large molecules could reduce fouling and increase apparent rejection substantially. Alternatively, a boundary layer of high HS concentration may form near the

membrane surface during filtration. Myneni et al. (1999) have shown from X-ray microscope study that HS would aggregate at high concentration in water. Thus, SEM pictures, $E_{critical}$ calculation and ¹H NMR results clearly indicate that the aggregated HS as well as some negatively charged HS were attracted by electric force during EMF. It is clear that the aggregation of HS is dependent on the feed concentration. HS at high feed concentration have higher tendency to be removed than that at low feed concentration (Fig. 2). Yukawa et al. (1983) also showed similar phenomenon during EUF of colloidal solutions.

3.3. Effect of voltage on flux and filtration resistance

Fig. 7 shows the effect of applied voltage on flux during the filtration of water in the presence of dissolved HS. The filtration system was operated at a constant pressure of 49 kPa with a cross-flow velocity of 0.23 m/s. Results indicate that the performance of the MF module, in terms of flux, increased dramatically with the electrostatic field applied. There is an exponential increase of final flux as the applied voltage increased from zero to 100V (Fig. 8a). At the end of a 2-h operation period, the relative flux (Fig. 8b, with respect to zero voltage) increased by 50% and 68%, respectively, in the presence of 2 and 6mg/L of TOC when a 100-V field was applied. Note that the relative flux is calculated with respect to flux of pure water (Milli-Q water), which had a constant value of $4.2 \times 10^{-4} \text{ m}^3/\text{s}$.

The result of control run using Milli-Q water revealed a 10% reduction in flux (Fig. 7). With MF alone, flux reduced to 62% and 42% of its initial values after operating for 2h in the presence of HS at 2 and 6mg/L, respectively. Generally, flux declined with an increase in HS concentration because of

Table 3 - General chemical shift assignments of solution ¹H NMR spectra of HS before and after EMF

Catalog	Chemical shift (ppm)	Assignment ^a	Examples	Relative area (%)		
				Feed solution before treatment	Feed solution after treatment	Permeate (100 V)
Aliphatic 1	0.5-1.3	Methyl groups	$\text{R}-\text{CH}_3$ $\text{O}-\text{C}-\text{CH}_3$ $\text{R}-\text{CH}_2-\text{CH}_2\text{R}'$ $\text{R}-\text{C}-\text{H}$	18.9	17.8	33.5
Aliphatic 2	1.3-2.0	Methylene and methine groups	$\text{O}-\text{C}-\text{CH}_3$ $\text{R}-\text{C}-\text{H}$	18.4	17.9	15.5
Aliphatic 3	2.0-3.2	Protons on carbons with carbonyl groups or aromatic rings	$\text{O}-\text{C}-\text{CH}_3$ $\text{O}-\text{C}-\text{O}-\text{C}-\text{H}$	24.4	27.7	18.0
Aliphatic 4	3.5-4.9	Protons on carbon α to oxygen (carbohydrate)	$\text{O}-\text{C}-\text{H}$ $\text{O}-\text{C}-\text{H}$	11.4	12.6	26.0
Aromatic	6.5-8.4	Aromatic (quinones, phenols, etc.)	$\text{O}-\text{C}-\text{H}$ $\text{O}-\text{C}-\text{H}$ $\text{O}-\text{C}-\text{H}$	27.0	23.9	7.0

^a From Wilson (1981) and Leenheer et al. (1997).

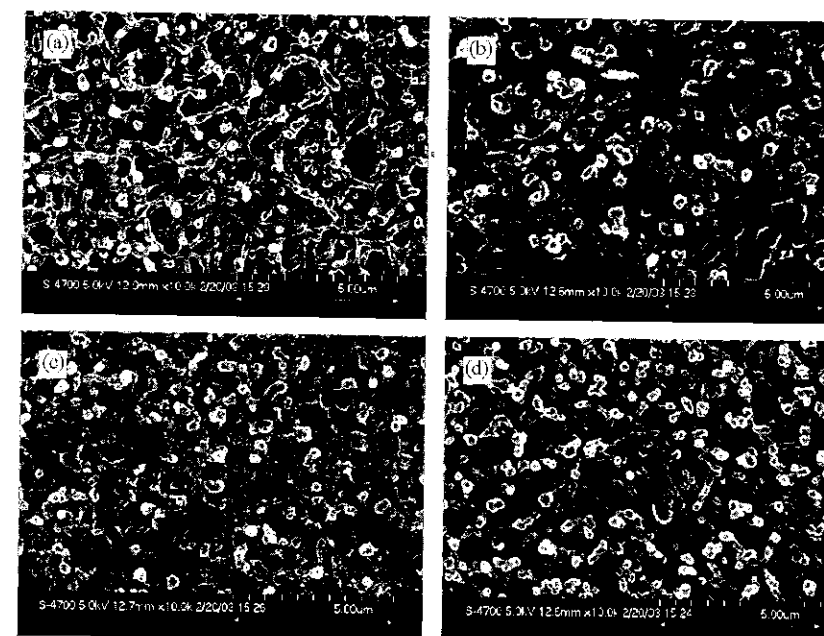


Fig. 6 - SEM photographs of MF membrane after filtration for 2 h under different conditions: (a) filtration of Milli-Q water, i.e., clean membrane, (b) filtration of HS at 6 mg/L, (c) filtration of HS at 6 mg/L and 50 V and (d) filtration of HS at 6 mg/L and 100 V.

increased convective transport of HS toward the membrane surface (Yuan and Zydny, 1999b).

Flux decline continued after operation for 2 h. The extent of fouling in the present study was less than that reported by Yuan and Zydny (1999a). This is due to differences in the mode of filtration, the preparation and the concentration of HS used. Yuan and Zydny (1999a) used dead-end filtration with the humic solution containing solid residues and higher HS concentrations.

Applying electric voltages across the membrane offset the transport of charged HS toward the membrane and slowed flux decline (Fig. 7). The flux decline decreased and reached a quasi-steady state in a matter of 10-30 min for all cases. It must be noted that despite the initial flux decline, flux still exceeded that of pure water situation after operating for 2 h. Final flux in the presence of HS (e.g., TOC = 6 mg/L) and at a voltage of 100 V was comparable with that of Milli-Q water. Flux improved at least by 40% and 60% after 2 h when a voltage of 100 V was applied in the presence of TOC at 2 and 6 mg/L (Fig. 8b), individually. The initial flux decline in HS solution may be due to adsorption or clogging of HS on the surface or in the pore of membrane. Higher initial flux obtained with EMF than pressure filtration provides evidence of electroosmosis. Weng and Li, 2003 reported similar improvement in permeate flux during EUF of HS.

Filtration resistance, R_f (from Eq. (1)), for new membrane was $1.26 \times 10^{11} \text{ m}^{-1}$. After 2 h, filtration resistance increased by 0.7- and 1.9-fold in the presence of HS at 2 and 6 mg/L TOC, respectively (Fig. 8c). It is interesting that the loosely packed impurities on the membrane surface cannot reject HS but cause flux decline (Fig. 6b). Applying electric voltages across the membrane decreased the filtration resistance exponentially. At a voltage of 100 V, the steady-state R_f (neglecting minor temperature changes and with constant viscosity) was

1.2×10^{11} and $1.3 \times 10^{11} \text{ m}^{-1}$ for solution containing 2 and 6 mg/L of HS, respectively (Fig. 8c). This value was identical to that of the Milli-Q water. Results demonstrated that applying an electrostatic field (e.g., 100 V) across the membrane maintained the filtration resistance at the same level as in the absence of HS. This improvement in the performance of the membrane filtration is further demonstrated by Fig. 8b. Results clearly indicate that there is significant flux improvement over that of the Milli-Q water. On the contrary, Yang and co-workers (2003) reported an increase in resistance after electrofiltration of chemical mechanical polishing (CMP) wastewater due to the difference in mode of operation. The feed concentration increased and pH decreased with time in the experiments. Thus, the resistance went up eventually due to continuous increases of feed concentration during batch operation. However, it is possible to achieve a lower filtration resistance in a continuous operation mode, such as in water production.

3.4. EMF of electrolyte

EMF experiments were conducted at various electric voltages in the presence of inert electrolyte, e.g., NaCl, in order to understand the effect of electric field on flux in the absence of the foulant (HS). Sodium chloride solution at $100 \mu\text{S}/\text{cm}$ (0.8 mM) was prepared to determine incremental flux after applying electricity. Moreover, permeate flow rate was normalized with respect to that at zero voltage. Although Chuang et al. (2003) have shown that the electroosmotic flow is dependent on the conductivity of the solution, the solution conductivity contributed from HS was replaced with NaCl due to low HS concentration in this study. Results in Fig. 9 reveal that incremental filtration rate increases with voltage. Flux enhancement contributed by electroosmosis was 4%, 7%, 11%

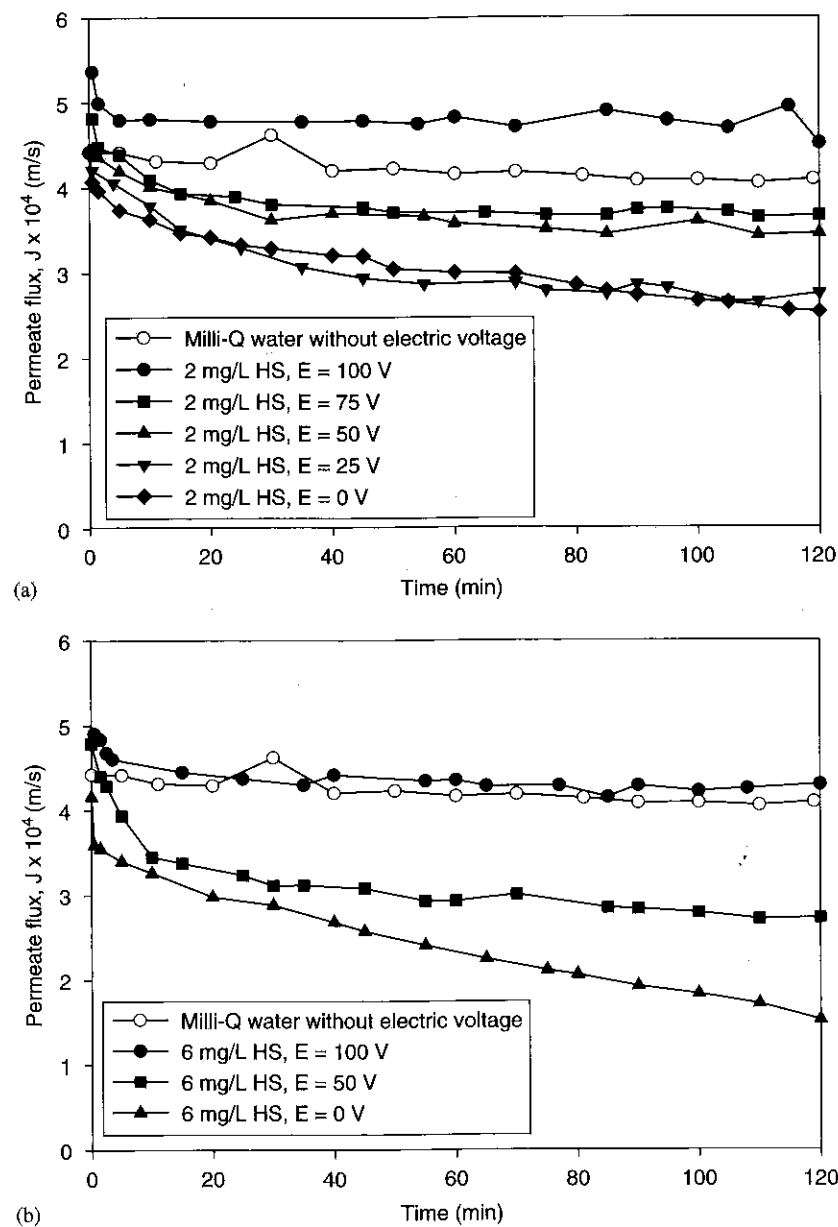


Fig. 7 - Effect of electric voltage on flux during filtration of HS at a concentration of (a) 2 mg/L and (b) 6 mg/L. $\Delta P = 49$ kPa and cross-flow velocity = 0.23 m/s.

and 18% for 25, 50, 75 and 100 V, respectively. It is known that there is no deposition of foulant at $E_{critical}$ during EMF (Henry et al., 1977; Wakeman and Williams, 2002). Therefore, the incremental flux during EMF of electrolyte could be used as an indicator to know whether the applied electric field is greater than $E_{critical}$ or not. Fig. 8(b) shows that there is less than 18% of incremental flux during EMF of HS solution. This result is consistent with previous $E_{critical}$ calculation, which suggests that the applied 100 V (~ 110 V/cm) is still less than $E_{critical}$. At $E < E_{critical}$, the flux increment due to electroosmosis is not as significant as that due to electrophoresis (Chuang et al., 2003). Nevertheless, flux comparable to pure Milli-Q water can be achieved when the applied electric field approaches the $E_{critical}$ in HS-containing solutions. Results in Fig. 9 also demonstrate that unless the filtered solution contains ions,

no current will pass through the membrane (0.002 A). Therefore, no flux enhancement was observed even when 100 V was applied during EMF of Milli-Q water.

4. Conclusions

Applying electric voltages across the membrane could increase flux and rejection ratio during the EMF of water containing foulant such as Aldrich HS. Both UV_{254} and TOC rejections were significantly increased upon applying an electric field across the membrane. In addition, THMFP also reduced substantially after EMF. The fractions of HS which contain aromatic and carbonyl groups were readily removed via EMF based on 1H NMR results. Results of SEM, SUVA and

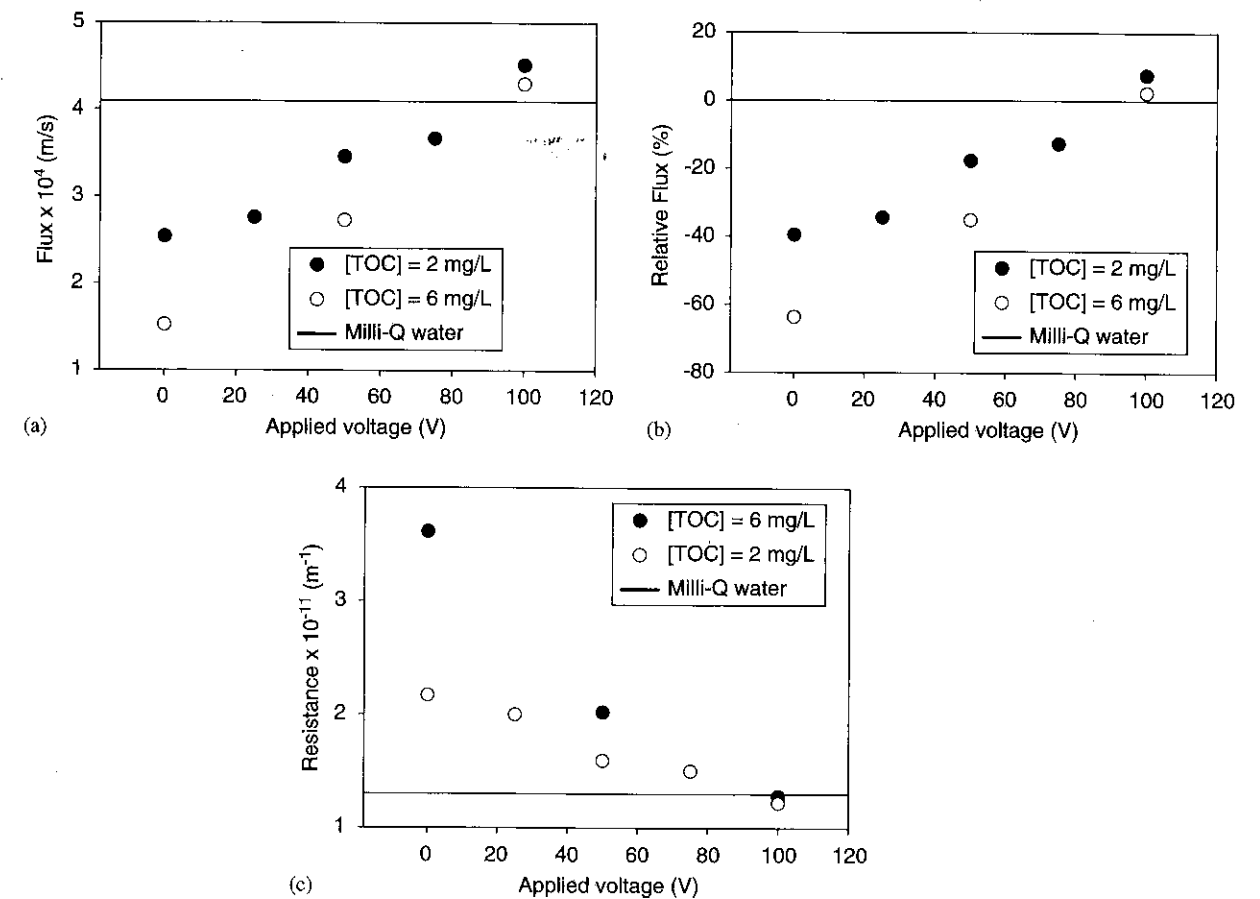


Fig. 8 - (a) Final flux, (b) relative flux and (c) final resistance of the membrane as a function of applied voltage. $\Delta P = 49$ kPa and cross-flow velocity = 0.23 m/s.

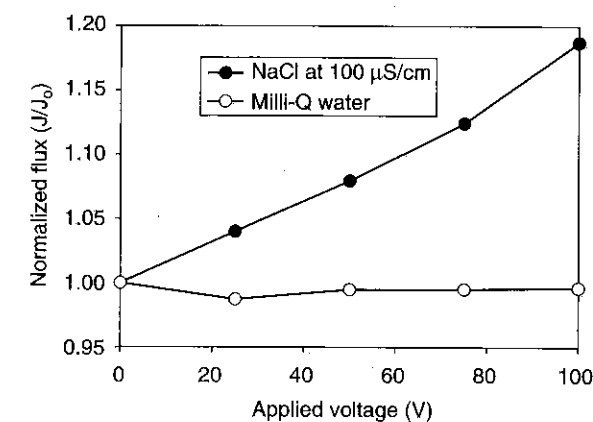


Fig. 9 - Normalized flux during EMF of electrolyte solution and Milli-Q water (ion-free) at various electric voltages. $\Delta P = 49$ kPa and cross-flow velocity = 0.23 m/s.

1H NMR observations clearly indicate that EMF could remove the HS that are charged and have large molecular weight. Electrophoretic attraction of charged HS appears to be the primary mechanism of the removal of the HS. Although the applied electric field is below $E_{critical}$ in this study, there is a dramatic increase of permeate flux. The incremental flux attributed to the electroosmosis effect is relatively insignif-

icant compared to electrostatic attraction of the charged HS by the electrically countercharged collection electrode.

Acknowledgments

This work was partly supported by the National Science Council, Republic of China. The authors would like to thank Mr. Lee for help with SEM analysis, Mrs. Peng for assistance with 1H NMR experiments and Dr. G.S. Wang for help with THMs analysis.

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