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Combined Humic Substance and Heavy Metals Agglomeration, and Membrane Filtration under Saline Conditions

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Abstract: Humic substances-heavy metals complexation combined with membrane filtration is reported. The effects of salinity, humic substances (HS) concentration, heavy metals concentration, and trans-membrane pressure (TMP) on HS and heavy metals retention using two membranes are studied. Membrane fouling is also studied at the aforementioned conditions. NF270 experienced higher fouling. Moreover, salinity tests showed increasing fouling rate and reduction in membrane retention with increasing salinity level. While increasing HS concentration reduced HS retention and increased heavy metals retention and membrane fouling. Heavy metals concentration reduced the NF270 HS retention, but did not affect the P005F HS retention. In addition, TMP did not affect HS and heavy metals retention nor NF270 fouling, but increased P005F fouling.

Keywords: Humic substance, heavy metals, nanofiltration, fouling

INTRODUCTION

Humic substances are refractory anionic macromolecules of low to moderate molecular weight. They contain both aromatic and aliphatic components with

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primarily carboxylic and phenolic functional groups. Carboxylic functional groups account for 60–90% of all functional groups (1). As a result, humic substances are negatively charged at the pH range of natural waters (1, 2). Humic substances play an important role as naturally-occurring organic complexants for binding different constituents in water (3). They have an affinity of aggregation with organics (4, 5) and heavy metals like Cu, Co, Ni, Zn, and Cd, owing to the presence of functional groups containing oxygen, and to a lesser extent, nitrogen and sulphur (6–11).

Heavy metals concentration varies significantly with water source (12). The partitioning of trace metals between dissolved and particulate phases is modified by several factors including: specific metal ion, metal concentration, nature of particles, particle concentration, pH, salinity, and dissolved oxygen (13–15). Heavy metals are known to exist as free ions in a strong acidic medium (16). In a study of trace elements, three groups had been distinguished according to their behavior during filtration and association with colloids. Heavy metals like Co, Ni, Zn, Cu, and Cd were grouped as elements of 1–10 kDa molecular weight colloidal fraction that have a tendency to form inorganic or organic complexes (17). The metal binding capacity of several fractionated HS samples revealed that the 20 kDa–100 kDa HS fraction was the most efficient fraction for copper binding (12). In addition, UF experiments showed that metals can be partially transported by low-molecular weight (<1–10 kDa) organic acids (17).

Membrane processes are very successful techniques for the removal of heavy metals. Reverse osmosis (RO) and nanofiltration membranes have moderate to high retention of di-valent metals (18). No retention is expected using UF membranes due to the low molecular weight of metals (16). NF membranes combine size exclusion removal of solutes and ionic

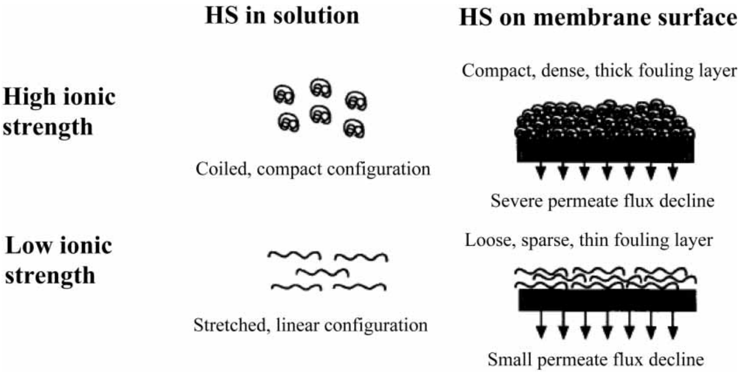

Figure 1. Schematic description of the effect of ionic strength on the conformation of HS in the solution and on the membrane surface and the resulting effect on membrane permeate flux (27).

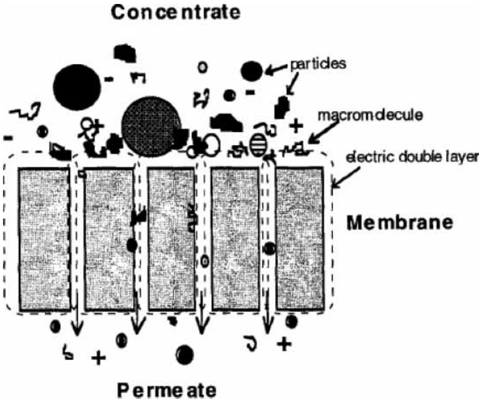

Figure 2. Conceptual sketch of solute and particle retention at charged membrane surface (31).

species removal due to charge effects between the charged solutes and the membrane (3).

Among various contaminants, trace metals are of particular concern in desalination due to their effects on membrane fouling (19–21). The general mechanistic view of HS interactions with membranes which plays a major role on membrane fouling are feed properties and composition, hydrodynamic condition, and membrane geometry and retention characteristics (22–25).

A full understanding of metal chemistry in natural waters and their membrane filtration needs to take into account the competitive reactions of metals with humic matter. The binding ability of HS towards heavy metals is dependent on HS-Metal ratio (16). Heavy metal retention in the presence of HS occurs due to HS-metal complex formation (26).

At low salinity level, HS functional groups are stretched. When the salinity level is increased, these groups curl up and aggregate causing reduction in size of colloids, thus increasing HS permeability, as shown in Fig. 2 (27–29). This phenomenon is double layer compression (30). The effect of salinity level on NF membranes is higher than on UF membrane due to the surface charge of the NF membrane. NaCl cationic species affect the surface of the membrane as well as the HS structure. Braghetta et al. (31) provided a comprehensive explanation of the effects of salinity on NF membrane surface. Negatively charged NF membranes contain electric double layer at their surface which repels anionic HS, thus increasing HS retention. Figures 3 and 4 show the combined effect of steric hindrance, solution chemistry and the chemical properties of the membrane surface on HS retention. An increase in ionic strength will reduce the area of electric double layer (grey area) and increase the area available for the transport of negatively charged species (white area) as shown in Fig. 4.

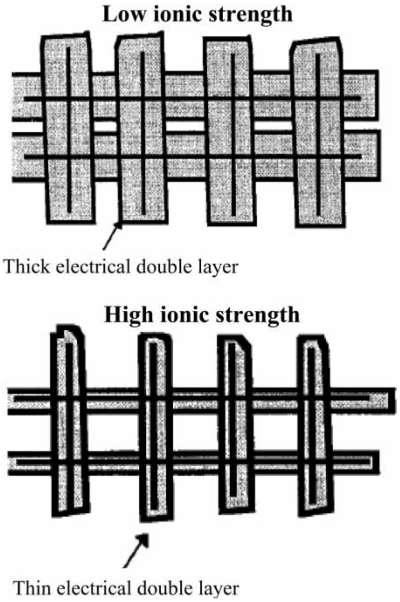

Figure 3. Conceptual sketch of the swollen membrane matrix in different ionic environments (31).

Double layer compression of HS colloids due to increased salinity result in a more densely packed deposition of HS at the surface of the membrane and formation of a compact fouling layer as shown in Fig. 2. Higher fouling using NF membranes that UF membranes is expected. An increase in ionic strength will reduce the area available (bounded by solid lines) for solvent transport of the NF membrane thus increasing fouling as shown in Fig. 4 (31).

The objectives of this study are to investigate and compare the removal of HS and five heavy metals (Cu, Co, Ni, Zn, and Cd) using P005F UF and NF270 NF membrane under synthesized seawater and brackish water environments. The effects of salinity, HS concentration, heavy metals concentration and trans-membrane pressure (TMP) on HS and heavy metals retention are

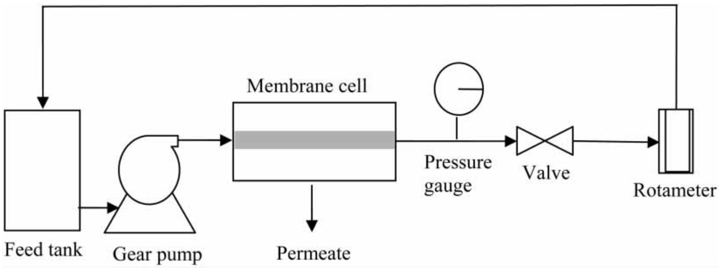

Figure 4. Cross flow filtration model.

investigated. Membrane fouling is also studied under the aforementioned conditions.

MATERIALS AND METHODS

De-ionized water used in this study was obtained through demineralization using ion exchange followed by reverse osmosis. The conductivity of the water was lower than 1 $\mu S/cm$. All the chemicals used in the experiments were reagent grade. All glassware used in the experiments were rinsed with de-ionized water and dried at 70°C overnight. NaCl was purchased from Fisher scientific-UK with purity higher than 99.5%.

Membranes used during the study were 5 kDa UF polyethersulfone (PES) and NF270 polyamide NF membranes. The UF membrane was provided by Nadir filtration GmbH (Germany) and the NF membrane was supplied by FILMTEC and manufactured by DOW chemical company (USA). Molecular weight cut-off (MWCO) of NF270 membrane is 1.1 kDa as measured in a previous paper (32).

Copper (II) chloride $>97\%$ purity, cobalt (II) chloride 97% purity, nickel (II) chloride 98% purity, zinc (II) chloride ACS reagent $>98\%$ purity, and cadmium chloride (II) ACS reagent $>99\%$ purity were purchased from Sigma-Aldrich.

Humic Substance Extraction

Humic acids and fulvic acids (FA) were extracted from soil using a modified procedure originally developed by Thurman and Malcolm 1981 (33, 34). First class soil with low fertilizer contents was purchased from Sainsbury's Homebase. 6.0 M hydrochloric acid (HCl) solution, solid anhydrous sodium hydroxide (NaOH) pellets and non-ionic polymethyl methacrylate (XAD-8) adsorption resin were all purchased from Sigma-Aldrich. 0.5 M NaOH was prepared from NaOH solid pellets and used throughout the experimental work. An oven at 105°C was used to gravimetrically measure the concentration of the solutes i.e., Salt, HS, and other solid contaminants, and a furnace at 600°C was used for salt concentration gravimetric measurements. The purity of the extracted HA and FA are 89.5% and 74.5%, respectively. HA and FA were mixed before performing any experiment in a ratio of 1:1.

Equipment

A Shimadzu total organic carbon analyzer model TOC-5050A was used to measure the concentration of organic carbon of the solution. A user-friendly program was used in conjunction with the analyzer to provide an automated calibration curves and readings. The analyzer took three replicate readings provided that the coefficient of variance was less than 2%. In cases where the precision was greater than 2% the instrument recorded a further 2 readings and the anomalous readings were discarded.

A Perkin Elmer Optima 3300DV inductively coupled plasma—optical emission spectrometer (ICP-OES) instrument with AS-90 plus auto sampler was used to determine the concentration of Cu, Ni, Zn, Co, and Cd in the permeate. Calibration curves of the tested metals were constructed with different salinity levels and HS concentrations. Humic substance did not affect the metals matrices due to its low concentration in the permeate. Salinity level affected all of the metals' matrices. High salinity level ($>$20,000 ppm NaCl) also blocked the nebulizer. Different calibration curves were constructed of the five metals at different salinity levels and solutions having salinity of 20,000 ppm NaCl and higher were diluted to prevent blocking of the nebulizer.

Method

Membrane filtration experiments were carried out in a laboratory scale filtration cell especially designed for this work. Schematic diagram of the experimental set-up is shown in Fig. 4. Five liters of the feed is pumped using a stainless steel gear pump into the filtration cell. A rectangular shaped membrane (3 cm × 10 cm) with an effective membrane area of 30 cm^2 (0.003 m^2) was employed. The operating pressure and volumetric flow rate were adjusted using the concentrate (reject) outlet valve. The pressure was varied between 1–9 bar. The experiments were carried out at ambient temperature in total re-circulation mode, i.e., both the concentrate and the permeate streams are re-circulated into the feed tank, so that the feed concentration is kept approximately constant. 30% of the experiments were repeated three times. Results varied in the range of $\pm 5\%$.

Synthetic stock solutions of 1 g/l concentration were prepared for the tested chemicals by dissolving/diluting using de-ionized water. 0.421 g of $CuCl_2$, 0.414 g of $ZnCl_2$, 0.325 g of $CdCl_2$, 0.439 g of $NiCl_2$, and 0.438 g of $CoCl_2$ were dissolve in 1 liter de-ionized water to make a stock solution of 1 g/l total metals in water. The stock solutions were then diluted with de-ionized water and were used within a week of preparation. Solid NaCl was dissolved in the HS solution and stirred at 400 rpm for 1 hour using a magnetic stirrer to obtain the desired salinity level of the tested HS solution. The desired mixture of HS and heavy metals concentration was obtained by adding the appropriate amount of heavy metals stock solution to the HS solution and stirrer at 400 rpm for an hour. The pH of all solutions was regulated at $\sim$7 before each experiment using NaOH. Prior to any filtration experiment, membrane compaction was undertaken using de-ionized water for 2 hours at 9 bar using NF membranes. No membrane compaction was required for UF membranes. Pure water flux (J_0) was calculated by measuring the time taken to collect 20 ml of permeate and using the following equation:

$$J = \frac{V}{At} \tag{1}$$

Where J represents flux ($L/m^2 \cdot h$); J_0 is pure water flux, and J_v is the solution permeate flux. V is volume of the permeate collected (l), A is the effective membrane area (m^2) and t is the time taken to collect the permeate (hours).

De-ionized water was then replaced by 5 liter of the tested synthetic solution. The system was run until an approximate constant permeate flux was observed. The solution permeate flux (J_v) was measured using Equation (1). The concentration of the permeate collected was analyzed using TOC analyzer. HS and heavy metals retention was measured using (35);

$$R = 1 - \frac{C_p}{C_b} \tag{2}$$

Where R is retention, C_p the permeate concentration (mg/l) and C_b is bulk concentration (mg/l). Membrane fouling is calculated using (36):

$$\text{Fouling} = \left(1 - \frac{J_v}{J_0}\right) \times 100 \tag{3}$$

Where Fouling is total fouling during the period of the filtration (%).

RESULTS AND DISCUSSION

Humic Substance Retention

The influence of salinity, HS concentration, heavy metals concentration, and TMP on HS retention was studied using P005F and NF270 membranes. Studied UF membrane (P005F) experienced lower HS retention compared to NF membrane (NF270) as shown in Fig. 5. HS retention was 0.73 and 0.84 using P005F and NF270, respectively. NF270 membrane higher retention is due to its higher MWCO as investigated previously (32, 37) and its surface charge. NF270 membrane surface is negatively charged, which causes repulsion of the anionic charged HS.

HS retention using NF270 was 0.89 and 0.83 at salinity of 10,000 and 25,000 ppm NaCl, respectively, as shown in Fig. 5. This indicates a reduction in retention as salinity increased. Reduction in retention is due to double layer compression of HS colloids. Higher effect of salinity on NF270 than P005F is because of the negatively charged NF270 membrane surface. Salinity reduces the area of electric double layer of the membrane

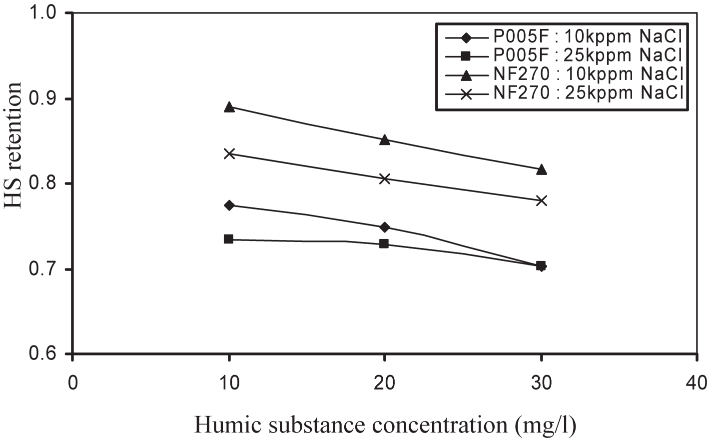

Figure 5. Effect of membrane type, salinity and HS concentration on HS retention; P005F and NF270 membranes operated at 3 and 9 bar, respectively. Initial feed concentration of 5 ppm heavy metals. (1 kppm = 1000 ppm).

surface (grey area) and increases the area available for the transport of negatively charged species (white area) as shown in Fig. 4.

Humic substance retention slightly decreased with increasing HS concentration as shown in Figs. 5–7. HS retention using NF270 was 0.83, 0.80, and 0.78 at HS concentration of 10, 20, and 30 mg/l, respectively. As the HS concentration increases, the number of HS species settling at the surface of membrane will increase. This settling will enhance the concentration polarization at the surface of the membrane and reduce HS retention.

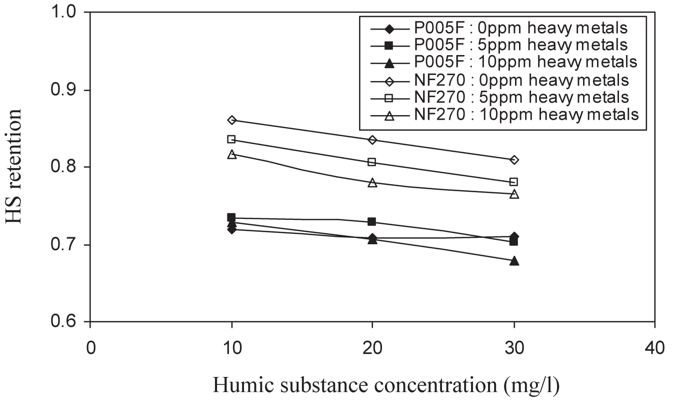

Figure 6. Effects of HS and heavy metals concentration on HS retention; P005F and NF270 membranes operated at 3 and 9 bar, respectively. Initial feed concentration of 25,000 ppm NaCl.

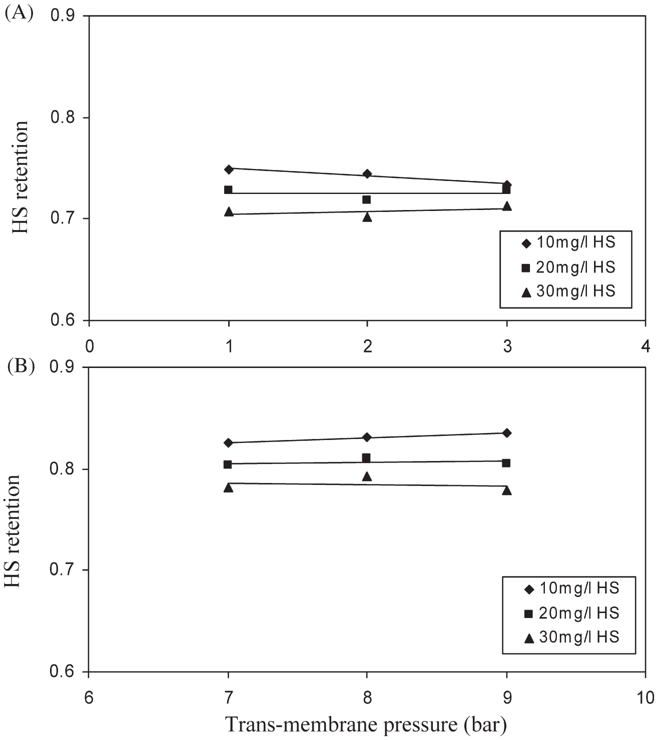

Figure 7. Effects of HS concentration and TMP on HS retention; (A) P005F membrane and (B) NF270 membrane. Initial feed concentration of 25,000 ppm NaCl and 5 ppm heavy metals.

Figure 6 shows the effect of heavy metals concentration on HS retention. Heavy metals concentration did not affect the retention of HS using P005F. Retention of HS using P005F membrane is 0.72, 0.73, and 0.73 at heavy metals concentration of 0, 5, and 10 ppm, respectively. The same trend was experienced by Alpatova et al. (16) and Verbych et al. (38) using UF membranes. It may be hypothesized that the effect of double layer compression (reducing the size of the HS colloids) is opposed by the chemical aggregation of heavy metals with HS (increasing the size of the resultant colloids). Increasing heavy metal concentration reduced HS retention using NF270 membrane. HS retention using NF270 membrane was 0.86, 0.83, and 0.82 at heavy metals concentration of 0, 5, and 10 mg/l, respectively. The slight reduction in heavy metal retention with NF270 membrane could be due to the effect of heavy metals on the electric double layer of the NF membrane surface. Divalent ions (heavy metals) have similar effects on the electric double layer as monovalent ions (NaCl). The cationic metals reduce the electric double layer and increase the area available for the transport of the negatively charged HS as shown in Fig. 4.

No change in HS retention was experienced when TMP was increased as shown in Fig. 7. HS retention using NF270 was 0.83, 0.83, and 0.83 at TMP of 7, 8, and 9 bar, respectively. Two competing phenomena determine the separation behaviour of HS with respect to TMP, concentration polarization and dilution effect. Concentration polarization increases with TMP causing reduction in retention, while the dilution effect counteracts the concentration polarization effect. The dilution effect increases with TMP by increasing the permeate water flux through the membrane, while the ion flux remains virtually unchanged resulting in lower solute concentration at permeate.

Heavy Metals Retention

The influence of salinity, HS concentration, heavy metals concentration and TMP on heavy metals retention is studied using P005F and NF270 membranes. P005F membrane experienced lower heavy metals retention compared to NF270 membranes as shown in Tables 1 and 2. Cu retention is 0.85 and 0.95 using P005F and NF270 membranes, respectively. The same trend is experienced for all studied heavy metals (Co, Ni, Zn, and Cd). In addition to heavy metals aggregation with HS as will be discussed later, NF270 membrane has moderate retention of metal ions due to Donnan exclusion (charge exclusion) (39). This is evident in the results presented in Tables 1 and 2. No heavy metals retention is experienced at 0 mg/l HS feed concentration using P005F, while Cu retention is 0.57 using NF270 membrane with no HS in the feed.

Heavy metals retention decreased with increasing salinity level as shown in Tables 1 and 2. Cu retention using P005F is 0.96, 0.90, and 0.85 at salinity levels of 0, 10,000, and 25,000 ppm NaCl, respectively. The reduction in heavy metal retention with increase in ionic strength using P005F membrane is due to the effect of salinity on the HS structure. As the ionic strength increases, the HS molecules coil up and their surface area is reduced. Heavy metals interact with the surface of the colloidal HS molecules and the reduction in the surface area of the HS molecules will decrease the removal efficiency of the heavy metals. This results in an increase in the quantity of non-associated metal ions, which pass through the membrane pores decreasing their retention (40, 41). In addition to HS-metal interaction, heavy metal retention using NF membranes depends on the interaction between the ionic strength of the solution and the membrane surface. An increase in ionic strength will reduce the area of electric double layer of the NF membrane and increases the area available for the transport of the heavy metals.

Tables 1 and 2 show the effect of HS concentration on heavy metals retention. Heavy metals retention increased when HS concentration increased from 0 to 20 mg/l, but no change in heavy metal retention was experienced when HS concentration is increased further to 30 mg/l at

Table 1. Effects of salinity, HS and heavy metals concentration on Cu, Ni, Co, Zn, and Cd retention using P005F membrane operated at 3 bar

Salinity (ppm)	[HS] (mg/l)	[Heavy metals] (ppm)	[Cu] R (ppm)	[Ni] R (ppm)	[Co] R (ppm)	[Zn] R (ppm)	[Cd] R (ppm)
0	10	5	0.96	0.79	0.77	0.70	0.45
25,000	0	5	0	0	0	0	0
10,000	10	5	0.90	0.73	0.68	0.62	0.37
10,000	20	5	0.94	0.82	0.76	0.66	0.42
10,000	30	5	0.95	0.80	0.75	0.67	0.42
25,000	10	5	0.85	0.65	0.60	0.54	0.29
25,000	20	5	0.88	0.68	0.64	0.57	0.32
25,000	30	5	0.88	0.66	0.65	0.58	0.33
25,000	10	10	0.71	0.60	0.53	0.43	0.22
25,000	20	10	0.81	0.61	0.59	0.53	0.26
25,000	30	10	0.85	0.72	0.64	0.59	0.32

heavy metals concentration of 5 ppm, as shown in Tables 1 and 2. Cu retention using NF270 is 0.57, 0.95, 0.98, and 0.97 at HS concentration of 0, 10, 20, and 30 mg/l, respectively. For heavy metals concentration of 10 ppm, heavy metals retention increased with HS concentration, Tables 1 and 2. Cu retention using NF270 is 0.92, 0.94, and 0.96 at HS concentration of 10, 20, and 30 mg/l. The same trend was experienced for all the heavy metals studied. HS have a great capacity for interaction with heavy metal ions forming soluble complexes, colloidal, and/or insoluble substances because

Table 2. Effects of salinity, HS and heavy metals concentration on Cu, Ni, Co, Zn, and Cd retention using NF270 membrane operated at 9 bar

Salinity (ppm)	[HS] (mg/l)	[Heavy metals] (ppm)	[Cu] R (ppm)	[Ni] R (ppm)	[Co] R (ppm)	[Zn] R (ppm)	[Cd] R (ppm)
0	10	5	1.00	0.93	0.96	0.84	0.68
25,000	0	5	0.57	0.44	0.46	0.39	0.31
10,000	10	5	1.00	0.84	0.83	0.78	0.62
10,000	20	5	1.00	0.87	0.86	0.81	0.78
10,000	30	5	1.00	0.89	0.88	0.80	0.75
25,000	10	5	0.95	0.76	0.79	0.72	0.68
25,000	20	5	0.98	0.82	0.85	0.79	0.75
25,000	30	5	0.97	0.83	0.84	0.78	0.75
25,000	10	10	0.71	0.58	0.53	0.43	0.22
25,000	20	10	0.81	0.60	0.59	0.53	0.26
25,000	30	10	0.85	0.62	0.64	0.59	0.32

of the HS colloidal character and their high number of surface functional groups. This mechanism involves the complexation of metallic ions with soluble HS (42–44). Increase in HS concentration increases HS complexation because more HS molecules are available as binding sites for the heavy metals (11). A limit is reached where an increase in HS concentration does not improve the removal of the heavy metals. Alpatova et al. (16) and Verbych et al. (38) concluded that a HS-metal ratio of 2:1 is optimal for maximum metal removal. Present results show a higher ratio; between 2:1 and 4:1. This may be due to the effect of the ionic strength of the solution on the aggregation of heavy metals with HS molecules. Ionic strength compact the structure of the membrane and reduces their active sites as discussed previously. This will increase the amount of HS molecules required to obtain the same heavy metal removal.

Tables 1 and 2 show the effect of heavy metal concentration on heavy metal retention. Heavy metal retention decreased with increasing heavy metal concentration. Cu retention using NF270 is 0.95 and 0.92 at heavy metals concentration of 5 and 10 ppm, respectively. The same trend is experienced for all heavy metals studied (Co, Ni, Zn, and Cd). Limitation of heavy metals binding with HS leads to higher amount of dissociated heavy metals in solution, which in turn will reduce heavy metals retention.

The retention of different heavy metals with respect to different membranes, HS concentration, heavy metal concentration, salinity level and TMP is studied as shown in Tables 1 and 2. Heavy metals retention is in the range of Cu (II) > Ni (II) > Co (II) > Zn (II) > Cd (II) using P005F. While heavy metals retention using NF270 is in the range of Cu (II) > Co (II) = Ni (II) > Zn (II) > Cd (II). Heavy metals retention is dependent on metal ions size, their stability constants, and the reactivity and selectivity of HS (16, 38). The molecular weights of the studied heavy metals are 63.4, 58.7, 58.9, 65.4, and 112.4 Da for Cu (II), Ni (II), Co (II), Zn (II), and Cd (II), respectively. As metals molecular weight increases, their binding with colloidal HS decreases. Although Cu (II) has higher molecular weight than Ni (II) and Co (II), its retention is higher because it has higher stability constant than the rest of the tested metals. Metals with higher stability constants form more stable complexes with HS. Log K values (stability constant) of the studied heavy metals are in the range of 4.6, 4.4, 4.2, and 3.1 for Cu (II), Ni (II), Co (II), and Zn (II), respectively (45). Cd (II) experienced the lowest retention because of its high molecular weight and low stability constant. The equal retention of Co (II) and Ni (II) using NF270 as opposed to P005F may be due to the sum effects of stability constants and the higher retention of Co (II) using NF270 without HS in feed. Ni (II) has a slightly higher stability constant, which will increase its association with HS colloids, while the results of Co (II) and Ni (II) retention with no HS in feed using NF270 show a slightly higher retention of Co (II) compared to Ni (II). Ni (II) and Co (II) retention is 0.93 and 0.96, respectively using NF270 with no HS in initial feed as presented in Table 2.

Tables 3 and 4 show TMP effect on heavy metals retention. No change in heavy metals retention is experienced with increasing TMP, following the same trend as HS retention discussed in the section on Humic Substance Retention. Cu retention using NF270 is 0.94, 0.95, and 0.95 at TMP of 7, 8, and 9 bar, respectively. A similar trend is observed for all studied heavy metals. As discussed previously in the section on Humic Substance Retention, the concentration polarization and dilution effect determine the separation behavior of heavy metals with respect to TMP. The resultant retention is the sum of these opposing effects.

Membrane Fouling

Many factors affect the membrane fouling such as membrane's properties and surface charge, properties and composition of the bulk solution, and hydrodynamic conditions. Different membranes respond differently to any changes in these factors. The influence of salinity, HS concentration, heavy metals concentration, and TMP on membrane fouling was studied using P005F and NF270 membranes.

P005F membrane experienced lower fouling compared to NF270 membrane as shown in Fig. 8. Total fouling is 32.3 and 66.2% using P005F and NF270, respectively.

Fig. 8 shows the effect of salinity on membrane fouling. Increasing salinity level increased membrane fouling. NF270 fouling is 52.9 and 66.2% at salinity levels of 10,000 and 25,000 ppm NaCl, respectively. As explained previously, increasing the ionic strength compresses the colloidal double layer of HS colloids forming a compact fouling layer as shown in Fig. 2. Salinity affects the NF membrane surface as well as the HS

Table 3. Effects trans-membrane pressure (TMP) on Cu, Ni, Co, Zn, and Cd retention using P005F. Initial feed concentration of 5 ppm heavy metals

Salinity (ppm)	[HS] (mg/l)	TMP (bar)	[Cu] R (ppm)	[Ni] R (ppm)	[Co] R (ppm)	[Zn] R (ppm)	[Cd] R (ppm)
25,000	10	1	0.84	0.63	0.61	0.55	0.31
25,000	10	2	0.83	0.64	0.61	0.54	0.30
25,000	10	3	0.85	0.65	0.60	0.54	0.29
25,000	20	1	0.89	0.66	0.66	0.59	0.34
25,000	20	2	0.86	0.67	0.65	0.57	0.35
25,000	20	3	0.88	0.68	0.64	0.57	0.32
25,000	30	1	0.89	0.69	0.66	0.58	0.34
25,000	30	2	0.86	0.69	0.67	0.57	0.38
25,000	30	3	0.88	0.66	0.65	0.58	0.33

Table 4. Effects trans-membrane pressure (TMP) on Cu, Ni, Co, Zn, and Cd retention using NF270. Initial feed concentration of 5 ppm heavy metals

Salinity (ppm)	[HS] (mg/l)	TMP (bar)	[Cu] (ppm)	[Ni] (ppm)	[Co] (ppm)	[Zn] (ppm)	[Cd] (ppm)
25,000	10	7	0.93	0.77	0.78	0.71	0.67
25,000	10	8	0.95	0.78	0.78	0.72	0.66
25,000	10	9	0.95	0.76	0.79	0.72	0.68
25,000	20	7	0.98	0.84	0.83	0.78	0.73
25,000	20	8	0.96	0.83	0.83	0.77	0.72
25,000	20	9	0.98	0.82	0.85	0.79	0.75
25,000	30	7	0.97	0.82	0.83	0.79	0.73
25,000	30	8	0.98	0.81	0.83	0.78	0.74
25,000	30	9	0.97	0.83	0.84	0.78	0.75

structure. An increase in ionic strength will reduce the area available (bounded by solid lines) for solvent transport of the NF membrane thus increasing fouling as shown in Fig. 4 (31).

Figures 8–10 show the effect of HS concentration on membrane fouling. Increasing HS concentration increased membrane fouling. NF270 fouling is 66.2, 68.2, and 71.2% at HS concentration of 10, 20, and 30 mg/l, respectively. As the HS concentration increases, the number of HS molecules settling at the surface of the membrane increases. This settling enhances concentration polarization at the surface of the membrane and increases membrane fouling.

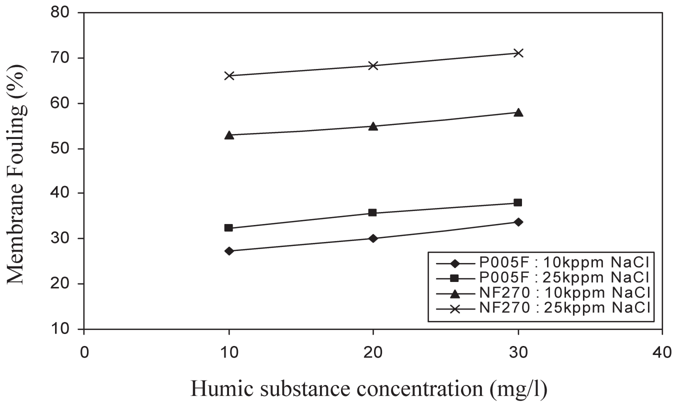

Figure 8. Effect of membrane type, salinity and HS concentration on membrane fouling; P005F and NF270 membranes operated at 3 and 9 bar, respectively. Initial feed concentration of 5 mg/l heavy metals. (1 kppm = 1000 ppm).

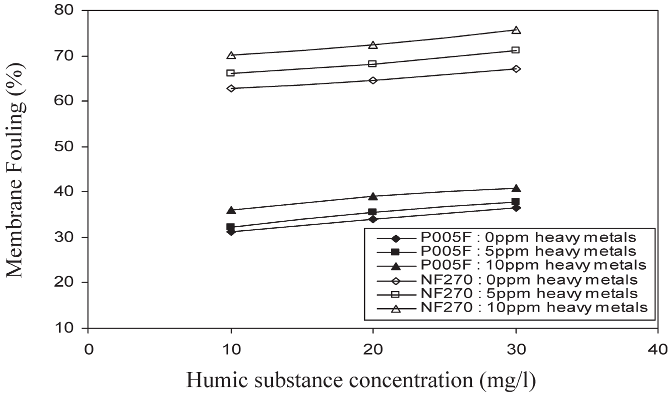

Figure 9. Effect of HS and heavy metals concentrations on membrane fouling; P005F and NF270 membranes operated at 3 and 9 bar, respectively. Initial feed concentration of 25,000 ppm NaCl.

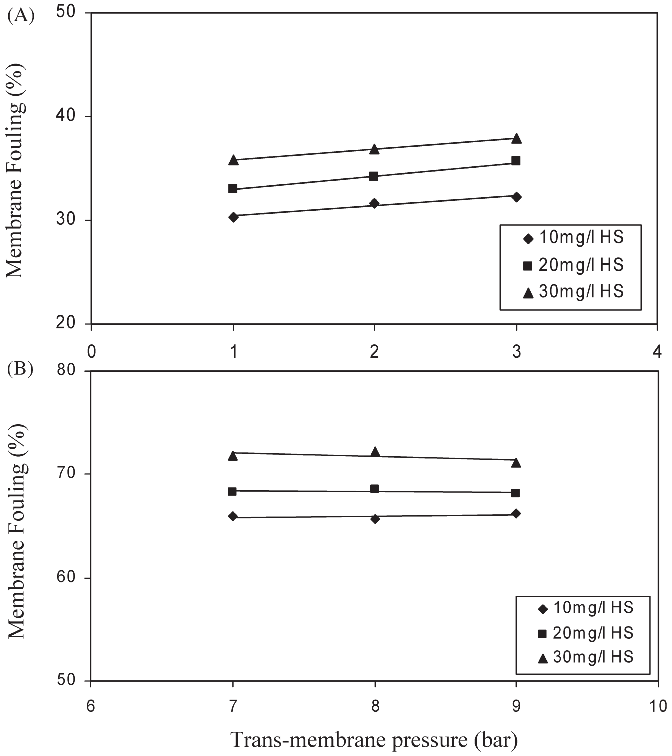

Figure 10. Effect of HS concentration and TMP on membrane fouling; (A) P005F membrane and (B) NF270 membrane; Initial feed concentration of 25,000 ppm NaCl and 5 ppm heavy metals.

Figure 9 shows the effect of heavy metals concentration on membrane fouling. Membrane fouling increased with heavy metals concentration. NF270 fouling is 62.8, 66.2, and 70.3% at heavy metals concentration of 0, 5, and 10 ppm, respectively. Unlike Na^+ cations, divalent cations interact specifically with humic carboxyl functional groups, thus, substantially reducing the HS charge and the electrostatic repulsion between the HS macromolecules. The reduction in HS interchain repulsion results in increased HS deposition at the membrane surface and the formation of a densely packed fouling layer. In addition, using NF270 membrane, heavy metals compress the electric double layer of the membrane, thus increasing the deposition rate of HS on the membrane surface.

Figure 10 shows the effect of TMP on membrane fouling. P005F fouling increased with TMP, while NF270 fouling was independent of TMP. P005F fouling is 30.4, 31.7, and 32.3% at TMP of 1, 2, and 3 bar, respectively, and NF270 fouling was 65.9, 65.7, and 66.2% at TMP of and 7, 8, and 9 bar, respectively. These effects may be due to the compressibility of the fouling layer formed at the surface of the membrane. At P005F studied range of TMP (1–3 bar), the concentration polarization layer was compressed when TMP increases. The compression of the concentration polarization layer reduces the permeate flux, thus increasing membrane fouling. Concentration polarization at the NF270 membrane surface was incompressible at the tested TMP range; 7–9 bar.

CONCLUSIONS

NF270 membrane has higher HS and heavy metals retention due to size exclusion and charge repulsion. The charge repulsion is not experienced by the P005F membrane. The drawback of using NF270 is its vulnerability to fouling under saline conditions. An economical comparison between the two tested membranes is complex. P005F is not highly affected by salinity and provides high HS retention and moderate heavy metals retention. Although it does not remove salinity, which makes it non-ideal as a pre-treatment step to reverse osmosis (RO). On the other hand, NF270 provides high HS, heavy metals retention and moderate salinity removal, which is ideal as a pre-treatment to seawater RO. The drawback is the requirement of higher TMP compared to P005F. NF270 also has a higher fouling rate compared to P005F.

Humic substances are good heavy metals complexants, producing high heavy metals retention using both tested membranes. Although, at high HS concentration, heavy metals retention is not affected indicating a presence of a limiting HS to heavy metals ratio where further increase will not affect heavy metals removal. Results show increase in the said limiting ratio with increasing salinity due to the effect of salinity on HS structure. In addition, heavy metals reduce NF270 HS retention, but do not affect P005F HS retention. Finally, TMP does not affect neither HS and heavy metals retention nor NF270 fouling, but increase P005F fouling.

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REFERENCES

1. Aiken, G.R., McKnight, D.M., Wershaw, R.L., and MacCarthy, E. (1985) *Humic Substances in Soil, Sediment, and Water*; Wiley: New York.
2. Bjelopavlic, M., Newcombe, G., and Hayes, R. (1999) Adsorption of NOM onto activated carbon: effect of surface charge, ionic strength, and pore volume distribution. *Colloid and Interface Science*, 210: 271–280.
3. Guthrie, J.W., Hassan, N.M., Salam, M.S.A., Fasfous, I.I., Murimboh, C.A., Murimboh, J., Chakrabarti, C.L., and Gregoire, D.C. (2005) Complexation of Ni, Cu, Zn, and Cd by DOC in some metal-impacted freshwater lakes: a comparison of approaches using electrochemical determination of free-metal-ion and labile complexes and a computer speciation model, WHAM V and VI. *Analytica Chimica Acta*, 528: 205–218.
4. De Paolis, F. and Kukkonen, J. (1997) Binding of organic pollutants to humic and fulvic acids: Influence of pH and the structure of humic material. *Chemosphere*, 34: 1693–1704.
5. Klavins, M. and Eglite, L. (2002) Immobilisation of humic substances. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 203: 47–54.
6. Dupre, B., Viers, J., Dandurand, J., Polve, M., Benezeth, P., Vervier, P., and Braun, J. (1999) Major and trace elements associated with colloids in organic-rich river waters: ultrafiltration of natural and spiked solutions. *Chemical Geology*, 160: 63–80.
7. Guo, L., Santschi, P.H., and Warnken, K.W. (2000) Trace metal composition of colloidal organic material in marine environments. *Marine Chemistry*, 70: 257–275.
8. Lu, X.Q. and Johnson, W.D. (1997) The reaction of aquatic humic substances with copper(II) ions: an ESR study of complexation. *The Science of the Total Environment*, 203: 199–207.
9. Sanudo-Wilhelmy, S.A., Rivera-Duarte, I., and Flegal, A.R. (1996) Distribution of colloidal trace metals in the San Francisco Bay estuary. *Geochimica et Cosmochimica Acta*, 60 (24): 4933–4944.
10. Town, R.M. and Filella, M. (2002) Crucial role of the detection window in metal ion speciation analysis in aquatic systems: the interplay of thermodynamic and kinetic factors as exemplified by nickel and cobalt. *Analytica Chimica Acta*, 466: 285–293.
11. Zhou, P., Yan, H., and Gu, B. (2005) Competitive complexation of metal ions with humic substances. *Chemosphere*, 58: 1327–1337.

12. Pokrovsky, O.S. and Schott, J. (2002) Iron colloids/organic matter associated transport of major and trace elements in small boreal rivers and their estuaries (NW Russia). *Chemical Geology*, 190: 141–179.
13. Munksgaard, N.C. and Parry, D.L. (2001) Trace metals, arsenic and lead isotopes in dissolved and particulate phases of North Australian coastal and estuarine seawater. *Marine Chemistry*, 75: 165–184.
14. Rengaraj, S., Kim, Y., Joo, C.K., and Yi, J. (2004) Removal of copper from aqueous solution by aminated and protonated mesoporous aluminas: kinetics and equilibrium. *Colloid and Interface Science*, 273: 14–21.
15. Gavriil, A.M. and Angelidis, M.O. (2005) Metal and organic carbon distribution in water column of a shallow enclosed Bay at the Aegean Sea Archipelago: Kalloni Bay, island of Lesvos, Greece. *Estuarine, Coastal and Shelf Science*, 64: 200–210.
16. Alpatova, A., Verbych, S., Bryk, M., Nigmatullin, R., and Hilal, N. (2004) Ultrafiltration of water containing natural organic matter: heavy metal removing in the hybrid complexation–ultrafiltration process. *Separation and Purification Technology*, 40: 155–162.
17. Eyrolle, F. and Benaim, J. (1999) Metal available sites on colloidal organic compounds in surface waters (Brazil). *Water Research*, 33: 995–1004.
18. Abu Qdais, H. and Moussa, H. (2004) Removal of heavy metals from wastewater by membrane processes: a comparative study. *Desalination*, 164: 105–110.
19. Goosen, M.F.A., Sablani, S.S., Al-Hinai, H., Al-Obeidani, S.A., Al-Belushi, R., and Jackson, D. (2005) Fouling of reverse osmosis and ultrafiltration membranes: a critical review. *Separation Science and Technology*, 39: 2261–2297.
20. Goosen, M.F.A., Sablani, S.S., Al-Maskari, S.S., Al-Belushi, R.H., and Wilf, M. (2002) Effect of feed temperature on permeate flux and mass transfer coefficient in spiral-wound reverse osmosis systems. *Desalination*, 144: 367–372.
21. Speth, T.F., Gusses, A.M., and Summers, R.S. (2000) Evaluation of nanofiltration pretreatments for flux loss control. *Desalination*, 130: 31–44.
22. Assemi, S., Newcombe, G., Hepplewhite, C., and Beckett, R. (2004) Characterization of natural organic matter fractions separated by ultrafiltration using flow field-flow fractionation. *Water Research*, 38: 1467–1476.
23. Cho, J., Amy, G., and Pellegrino, J. (1999) Membrane filtration of natural organic matter: Initial comparison of rejection and flux decline characteristics with ultrafiltration and nanofiltration membranes. *Water Research*, 33: 2517–2526.
24. Teng, C.K., Hawlader, M.N.A., and Malek, A. (2003) An experiment with different pretreatment methods. *Desalination*, 156: 5l–58.
25. Lee, H., Amy, G., Cho, J., Yoon, Y., Moon, S., and Kim, I.S. (2001) Cleaning strategies for flux recovery of an ultrafiltration membrane fouled by natural organic matter. *Water Research*, 35: 3301–3308.
26. Martell, A. (1957) The chemistry of metal chelates in plant nutrition. *Soil Science*, 84: 13–26.
27. Hong, S. and Elimelech, M. (1997) Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes. *Membrane Science*, 132: 159–181.
28. Schaefer, A.I., Mauch, R., Waite, T.D., and Fane, A.G. (2002) Charge effects in the fractionation of natural organics using ultrafiltration. *Environmental Science and Technology*, 36: 2572–2580.
29. Schaefer, A.I., Schwicker, U., Fischer, M.M., Fane, A.G., and Waite, T.D. (2000) Microfiltration of colloids and natural organic matter. *Journal of Membrane Science*, 171: 151–172.

30. O'Melia, C.R., Becker, W.C., and Au, K. (1999) Removal of humic substances by coagulation. *Water Science and Technology*, 40: 47–54.
31. Braghetta, A., DiGiano, F.A., and William, P.B. (1997) Nanofiltration of natural organic matter: pH and ionic strength effects. *Environmental Engineering*, 628–641.
32. Hilal, N., Al-Abri, M., and Al-Hinai, H. (2008) Characterization and retention of NF membranes using PEG, HS and polyelectrolytes. *Desalination*, Article in Press.
33. Christensen, J.B., Jensen, D.L., Gron, C., Filip, Z., and Christensen, T.H. (1998) Characterization of the dissolved organic carbon in landfill leachate-polluted groundwater. *Water Research*, 32: 125–135.
34. Pettersson, C. and Rahm, L. (1996) Changes in molecular weight of humic substances in the gulf of Bothnia. *Environment International*, 22 (5): 551–558.
35. Pradanos, P., Arribas, J.I., and Hernandez, A. (1995) Mass transfer coefficient and retention of PEGs in low pressure cross-flow ultrafiltration through asymmetric membranes. *Membrane Science*, 99: 1–20.
36. Kulovaara, M., Metsamuuronen, S., and Nystrom, M. (1999) Effects of aquatic humic substances on a hydrophobic ultrafiltration membrane. *Chemosphere*, 38: 3485–3496.
37. Hilal, N., Al-Abri, M., and Al-Hinai, H. (2007) Characterisation and retention of UF membranes using PEG, HS and polyelectrolytes. *Desalination*, 206: 568–578.
38. Verbych, S., Bryk, M., Alpatova, A., and Chornokur, G. (2005) Ground water treatment by enhanced ultrafiltration. *Desalination*, 179: 237–244.
39. Hilal, N., Al-Khatib, L., Al-Zoubi, H., and Nigmatullin, R. (2005) Nanofiltration of highly concentrated salt solutions up to seawater salinity. *Desalination*, 184 (1–3): 315–326.
40. Spark, K.M., Wells, J.D., and Johnson, B.B. (1997) Sorption of heavy metals by mineral-humic acid substrates. *Australian Journal of Soil Research*, 35: 113–122.
41. Spark, K.M., Wells, J.D., and Johnson, B.B. (1997) The interaction of a humic acid with heavy metals. *Australian Journal of Soil Research*, 35: 89–101.
42. Alvarez-Puebla, R.A., Garrido, J.J., Valenzuela-Calahorro, C., and Goulet, P.J.G. (2005) Retention and induced aggregation of Co(II) on a humic substance: sorption isotherms, infrared absorption, and molecular modeling. *Surface Science*, 575: 136–146.
43. Alvarez-Puebla, R.A., Valenzuela-Calahorro, C., and Garrido, J.J. (2004) Retention of Co(II), Ni(II), and Cu(II) on a purified brown humic acid. modeling and characterization of the sorption process. *Langmuir*, 20: 3657–3664.
44. Alvarez-Puebla, R.A., Valenzuela-Calahorro, C., and Garrido, J.J. (2004) Cu(II) retention on a humic substance. *Colloid and Interface Science*, 270: 47–55.
45. Fukushima, M., Nakayasu, K., Tanaka, S., and Nakamura, H. (1995) Chromium(III) binding abilities of humic acids. *Analytica Chimica Acta*, 317: 195–206.