DESALINATION

ELSEVIER

Desalination 221 (2008) 244–252

www.elsevier.com/locate/desal

Characterization of marine organic matters and heavy metals with respect to desalination with RO and NF membranes

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Received 7 February 2007; accepted 13 February 2007

Abstract

The transmission and toxicity of metals and metalloids were initially investigated with various nanofiltration (NF) and seawater reverse osmosis (SWRO) membranes, under oxic condition, using wastewater effluent and seawater samples. Various metals and metalloids were categorized into three groups according to their properties, such as specific gravity and concentration level, as well as others. The levels of various transition metals and metalloids included in the wastewater effluent and seawater samples were within ng/L–μg/L range; the concentrations of almost all compounds were substantially reduced to ng/L or a few μg/L levels after membrane filtrations, as measured by ICP-MS. Toxicity measurements were performed using bioassays, including both the Microtox and daphnia methods, for raw and membrane treated samples of wastewater effluent and seawater. The results indicated that (1) the SWRO membrane exhibited very good removal efficiencies for all metals and metalloids tested, (2) most metals and metalloids tested were efficiently removed by the tight NF membranes employed; however, some metals and metalloids included in seawater were not efficiently removed by the relatively loose NF membrane, (3) based on the Microtox measurements, only the seawater sample treated using the relatively loose NF membrane provided a relatively high toxic unit close to 1.0; otherwise, all other samples (both raw and membrane treated samples) exhibited relatively low toxicities.

Keywords: Metals and metalloids; Toxicity; NF/RO membranes; Wastewater reclamation; Desalination

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Presented at the conference on Desalination and the Environment. Sponsored by the European Desalination Society and Center for Research and Technology Hellas (CERTH), Sani Resort, Halkidiki, Greece, April 22–25, 2007.

doi:10.1016/j.desal.0000.00.000

1. Introduction

Over recent decades, many studies on nanofiltration (NF) and reverse osmosis (RO) membranes have been performed, in the areas of water treatment, wastewater reclamation, and desalination. Thus, further research on membranes needs to focus on new topics, especially on water qualities in relation to human health. Processes involving NF or RO membranes are believed to provide safe water, even from wastewater effluent waters, including various micropollutants which may be refractory to other treatment processes, to satisfy drinking water regulations and guidelines [1]. The next steps in the research involving NF and RO membranes will require more robust investigations on the quality of waters treated by both NF and RO membranes possessing different properties, such as pore size and other chemical/physical characteristics. Therefore, new targets for investigation may encompass (i) metals and metalloids, and (ii) micropollutants (endocrine disruptor chemicals and pharmaceuticals); micropollutants concentrations in drinking water sources and membrane treated samples from wastewater effluent and seawater are very low, within ng/L–μg/L range; thus, rigorous measurement techniques with either gas chromatography–mass spectroscopy (GC–MS) or liquid chromatography–mass spectroscopy–mass spectroscopy (LC–MS–MS), have to be used [2,3]. Evaluating methods for membrane treated waters may include aquatic toxicity measurements [4–6], human-health related bio techniques using human whole cells [7,8], and many others. With respect to these new targets, our new research attempts were directed toward NF and RO membranes in relation to wastewater effluent and seawater, focusing on selected metals and metalloids.

Research papers on the use of membranes for the treatment of metals and metalloids (except arsenics), for both wastewater reclamation and desalination, are very rare. Meanwhile, there have been many studies on aquatic toxicity influenced by individual heavy metals and/or their combination in solution with dissolved organic matters in wastewater effluents [4,6,9]. Research on toxicity analyses using membrane treated samples has also rarely been conducted, mainly as a result of the relatively low concentrations of potential contaminations, such as organics, metals, and other ions. Therefore, there is a need to investigate (1) the removal efficiencies of metals and metalloids with relatively low concentrations using NF and RO membranes (incorporation with inductively coupled plasma mass spectrometry (ICP-MS) analysis), and (2) aquatic and human-health related toxicity measurements for membrane treated waters, including metals/metalloids, ions, and dissolved organic matters.

2. Materials and methods

2.1. Tested water samples

Effluent from a wastewater treatment plant, located in Damyang City, Korea, and seawater obtained from near Masan City, Korea, were tested in this work; the two water samples were pre-filtered, using 0.45 μm glass fiber, to remove particulates prior to the filtration tests. The fundamental water characteristics, as well as the concentrations of the metals and metalloids included in the two tested samples are listed in Table 1. Pre-filtered solutions (5 L) were used for each filtration, which lasted for approximate 100 min, until 600 mL of permeate had been collected. 500 mL of the collected samples were used for toxicity measurements, with the remaining filtrate used for various other analyses. All membrane filtration experiments were performed under oxic condition. Twelve metals and metalloids were selected, which were categorized into three groups (see Table 1, groups I–III). The concentrations of metals and metalloids were measured by ICP-MS (Agilent, 7500ce, US), using an octoploe reaction system, with

Table 1
Characteristics of used water samples for membrane filtrations

Samples	pH	Conductivity (μS/cm)	DOC (mg/L)	UV absorbance at 254 nm (1/cm)	Concentrations of metals and metalloids (μg/L)
Wastewater effluent from Damyang plant	7.1	906	5.54	0.165	I: Cu (76.2), Ni (4.2), Zn (89.1), Cd (B.D.[a]), Ag (0.02), Pb (3.6), Hg (B.D.) II: Al (5.3), Fe (8.6), Mn (22.4) III: As (2.5), Sb (0.2)
Seawater from Masan City	8.0	46,100	2.01	0.030	I: Cu (224.0), Ni (7.7), Zn (194.7), Cd (B.D.[a]), Ag (0.3), Pb (14.2), Hg (B.D.) II: Al (11.6), Fe (15.8), Mn (36.0) III: As (2.6), Sb (0.3)

[a]B.D.: below detection limit.

ultra pure hydrogen and helium gases. All the samples were acidified to a final nitric acid concentration of 2% using 70% nitric acid solution. To construct standard calibration curves, a 10 μL/mL multi-element standard solution (Agilent, std-2A and std-4) was used, with exception of antimony, where a 100 μg/mL standard solution (SCP Science, PlasmaCal, Sb) was used. The average concentrations of the tested metals and metalloids in the two membrane feed water samples are listed in Table 1. For measurement verification, two different methods were used; internal and standard samples with known concentrations were measured along with actual samples, using standard reference materials (SRM 1640, NIST) and those used for the calibrations, respectively. Every sample was measured in triplicate and then averaged. The relative standard deviation values were found to be adversely proportional to the metals and metalloids concentrations, as shown in Fig. 1. When the concentrations were too low or close to the limits of detection, the results were unreliable; three metals (Cd, Ag, and Hg) were identified as being in this category; thus, were investigated no further.

The levels of organic matters in the wastewater effluent and seawater were measured using the non-purgeable organic carbon method employing a total organic carbon (TOC) analyzer (TOC-V_{CPH}, Shimadzu), equipped with a combustion chamber filled with highly sensitive catalyst. This method has been identified (through this works) to successfully measure dissolved organic carbon (DOC) levels of water samples with an ultra high salt content, such as seawater; but from our experiences, the DOC of seawater sample cannot be effectively measured using TOC analyzers when the oxidation method employing both UV oxidation and oxidizing chemicals is

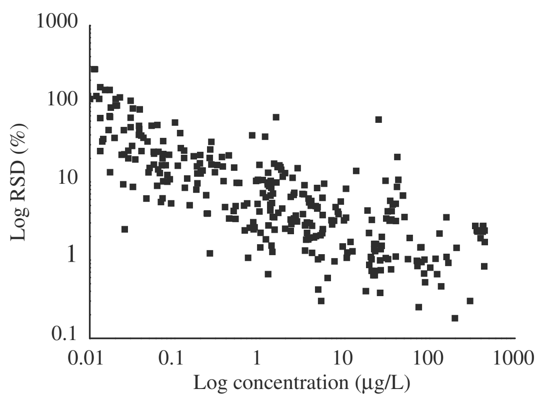

Fig. 1. Measurement uncertainty: plot of log value of relative standard deviation (RSD) versus log concentration measured by ICP-MS.

adopted. All the measurements were conducted in triplicate and then averaged. The UV absorbance at 254 nm of all the samples was measured using a UV-visible spectrophotometer (UV-1601, Shimadzu).

2.2. Membrane filtrations

A flat-sheet type of membrane, with a bench-scale cross-flow membrane unit, was used. A SEPA CF II membrane element cell (Osmonics Inc.), which was able to accommodate a very high trans-membrane pressure, up to 1000 psi (=6.90 MPa), with a stainless steel cell, was used for the membrane filtration tests, with a constant cross-flow and permeability of 0.5 L/min and 654 L/day m^2, respectively, during experiments. The Reynolds number and active area of the membrane were 195.3 and 138.7 cm^2, respectively. Prior to all filtration experiments, the membranes were stabilized for at least 4 h by filtrating deionized water to obtain a stable water flux. Permeate and retentate were recycled into the feed tank during the experiments, with the temperature of the feed solutions maintained at 25°C using a re-circulating chiller. The pH of the solutions during experiments was not adjusted. Commercially available RO and NF membranes, with different properties in terms of hydrophobicity and the surface charge, were used to evaluate the metals and metalloids removal performances (see Table 2). The molecular weight cutoff (MWCO) of the membranes was measured using the fractional rejection method with polyethylene glycols [10]. The membrane surface charge was measured using an electrophoresis method (ELS-8000, Otsuka, Japan) employing polystyrene latex particles, with a nominal size of 520 nm (Otsuka Electronics, Japan), coated with hydroxyl propyl cellulose having a molecular weight of 300,000 [11]. The contact angel of the membranes was measured using the sessile drop method with a contact angle meter (ráme-hart, standard goniometer with drop image, 200-00, NJ, US).

2.3. Toxicity measurements

According to the sample conditions, one of two different bioassay methods was adopted. Seawater samples, and their membrane filtrates, were analyzed using the Microtox® method; while, the wastewater effluent samples, and their membrane filtrates, were analyzed using both the whole effluent toxicity with *Daphnia magna* and the Microtox® methods [6,12]. *D. magna* were cultured and handled according to the procedures outlined in the U.S. EPA manual [13]. Organisms were fed with a suspension of yeast, CEROPHYLL® and trout chow (YCT), as well as *Selenastrum capricornutum*. All toxicity measurements were performed in a clean bioassay room maintained at 25±1°C. Illumination was maintained as a 16 h-light 8 h-dark cycle,

Table 2
Properties of tested membranes

Membrane	Classification	MWCO[a] (Da)	Contact angle (°)	Zeta potential at pH 7 (mV)	Roughness (nm)
SR	Seawater RO (SWRO)	100–500[a]	34.9	−20.8	47.3
FL	Relatively tight NF	100–400[a]	33.6	23.6	53.3
NF90		200[b]	43.8	−21.6	84.9
NE70	Relatively loose NF	500[a]	22.6	−46.2	8.7

[a]MWCO measured by fractional rejection method [10].
[b]MWCO provided by corresponding manufacturer.

with a light intensity of 10–20 μE/m^2/s. The bioassay tests using *D. magna* were performed according to the guidelines of the 48-h acute toxicity test provided by the U.S. EPA [13], with a static-non-renewal acute toxicity test conducted. Food was sufficiently supplied for 2 h prior to each test, with no food supplied during the test. When the conductivity of membrane filtrates became significantly low, which is not favorable for the growth of *D. magna*, two tests were performed, either with or without the addition of pure minerals for hardness control.

The Microtox® tests were performed according to the whole effluent toxicity test protocol [12], where *V. fishery* colonies were seeded to the samples, under adjusted osmotic pressure using sodium chloride. The seawater samples were directly applied to the whole effluent toxicity test, without adjustment of the osmotic pressure. The luminescence inhibition after 15 min exposure was taken as the endpoint, which was measured using a Microtox® Model 500 Analyzer (AZUR Environment).

3. Results and discussion

Overall, the tested RO and NF membranes were found to exhibit relatively high removal efficiencies for all metals and metalloids, with the exception of three metals (Cd, Ag, and Hg), as their concentrations in the membrane feed solutions were very low (subsequent RSD is high) or below the limits of detection, as measured using ICP-MS (see Table 3, as well as Figs. 2 and 3). With regard to the removal of organic matters, the overall trends were similar to those for metals and metalloids, but the SWRO membrane provided poor efficiencies in terms of DOC removal compared to those expected based on the lowest MWCO and metals and metalloids removal capabilities (see Table 4).

3.1. Metals and metalloids aspects

Firstly, for the SWRO (i.e., the SR membrane), with exception of the three metals already mentioned, the membrane exhibited fairly high removal efficiencies (higher than at least 50%), as expected based on the lowest MWCO value. *Secondly*, with the tight NF membranes (i.e., FL and NF90); (1) the two membranes exhibited high removal efficiencies (≥50%) for all the metals and metalloids in the wastewater effluent (see Fig. 2). However, (2) less than 50% removal efficiencies were achieved for Ni, Al, and Sb in the seawater, as shown in Fig. 3. The reasons and

Table 3
Removal tendencies of element groups in wastewater and seawater by different types of membranes

Removal tendency (%)	Loose NF (NE70)		Tight NF (NF90, FL)		RO (SR)	
	Wastewater	Seawater	Wastewater	Seawater	Wastewater	Seawater
≥50	I: Cu, Ni, Pb II: Al, Fe III: As, Sb	I: Ni II: Fe, Mn III: As	I: Cu, Ni, Zn, Pb II: Al, Fe, Mn III: As, Sb	I: Cu, Zn, Pb II: Fe, Mn III: As	I: Cu, Ni, Zn, Pb II: Al, Fe, Mn III: As	I: Cu, Ni, Zn, Pb II: Al, Fe, Mn III: As, Sb
<50	I: Zn (~30%) II: Mn (~40%)	I: Cu (~40%), Zn (~20%), Pb (~40%) II: Al (~5%) III: Sb (~5%)		I: Ni (40–50%) II: Al (0–10%) III: Sb (~0%)	III: Sb (~40%)	

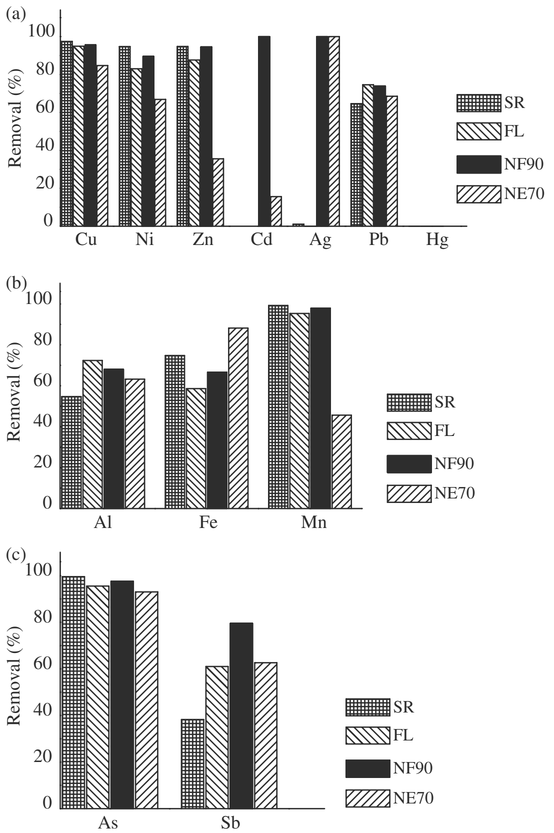

Fig. 2. Removal efficiencies of elements in effluent of wastewater treatment by NF and RO membranes: (a) group I; (b) group II; (c) group III.

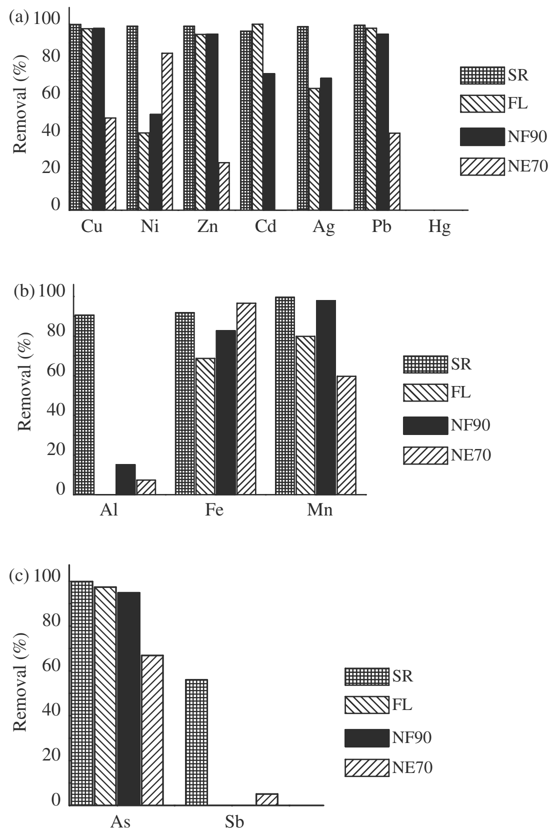

Fig. 3. Removal efficiencies of elements in seawater by NF and RO membranes: (a) group I; (b) group II; (c) group III.

Table 4
Conductivity and DOC levels for membrane feed and permeate samples

Water samples	Water quality	SWRO (SR)	Tight NF (FL)	Tight NF (NF90)	Loose NF (NE70)
Wastewater effluent	Conductivity of feed (μS/cm)	906			
	Conductivity of permeate (μS/cm)	18	106	64	723
	DOC of feed (mg/L)	5.54			
	DOC of permeate (mg/L)	1.78	1.96	0.74	4.62
Seawater	Conductivity of feed (μS/cm)	46,100			
	Conductivity of permeate (μS/cm)	1098	5320	4940	40,100
	DOC of feed (mg/L)	2.01			
	DOC of permeate (mg/L)	1.76	0.58	0.56	0.54

mechanisms for the trend of relatively low removals of the three species by the tight NF membranes has not been provided in this paper; this paper intended to provide facts from initial investigations, and to determine specific areas for further more detailed studies. *Thirdly*, with the loose NF membrane (i.e., NE70); the membrane exhibited fairly good removal efficiencies for the components of the wastewater effluent, with exceptions of Zn and Mn; however, in the case of seawater the removal efficiencies were poor compared to the tight NF membranes (see Table 3). For both the tight and loose NF membranes, the removals of Al and Sb were found to be difficult.

3.2. Organic matters aspects

As previously mentioned in this section, the SWRO membrane was poor in terms of DOC removals, even compared to the tight NF membranes. This was not thoroughly investigated; although, it can be supposed that most of organic matters in both the wastewater effluent and seawater would exhibit relatively low molecular weight distributions (i.e., low size exclusion), and are also comprised of relatively non-humic constituents (with low negative-ionizable functional groups) (i.e., low electrostatic repulsion), as measured by XAD-8/4 resins [11], in our other study (not included in this paper). Also, the pore size of the SWRO membrane (not shown in this paper) exhibited a wide distribution between 100 and 500; thus, even though this membrane can be categorized as an SWRO membrane, as fabricated for the very efficient remove of ions, it still has to allow low molecule weight organics (especially neutrals) to pass through its pores.

3.3. Toxicity aspects

Using the Microtox method, only the seawater sample treated by the loose NF membrane (i.e., NE70) was found to have a toxic unit close to 1.0, i.e., the EPA guideline for the control of wastewater effluent toxicity [14], which is in reasonably good accordance with the results obtained from the membrane experiments. All of the toxic units of the membrane treated wastewater effluent samples were unexpectedly high, as measured using *D. magna*. These high toxicities were believed not to have resulted from the influences of metals and/or metalloids, but from the unbalance of the ion distribution due to the membrane

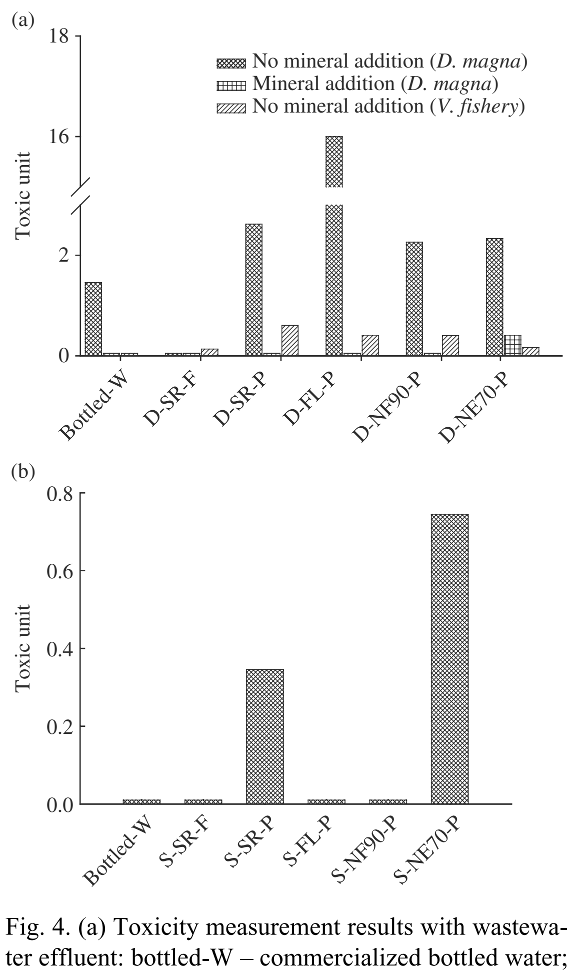

Fig. 4. (a) Toxicity measurement results with wastewater effluent: bottled-W – commercialized bottled water; D-SR-F – membrane feed water; SR, FL, NF90, NE70 – membrane codes; P – membrane permeate, (b) Toxicity measurement results with seawater: bottled-W – commercialized bottled water; S-SR-F – membrane feed water; SR, FL, NF90, NE70 – membrane codes; P – membrane permeate.

surface charge. With the addition of minerals, the previously high toxicity units were substantially reduced (Fig. 4).

4. Conclusions

The key goal of this work was to provide initial investigation for the removal trends of 12 different metals and metalloids from seawater, using RO and NF membranes for both wastewater reclamation and desalination. Therefore, robust conclusions or verification of specific mechanisms for membrane efficiencies cannot be given. However, general observations with regard to the transmission of metals and metalloids through membranes, and the corresponding toxicity changes, may be provided. From this works, the followings were observed: (1) the SWRO membrane tested exhibited greater performance in terms of metals and metalloids removals than the NF membranes tested; of the NF membranes, the two tight NF membranes, as expected, were proved better than the loose NF membrane, (2) there was no distinct difference in removal trends between the three metals and metalloids groups, but the effective removal of aluminum and antimony from seawater were observed to be difficult using both the tight and loose NF membranes, and (3) whether the results of both (1) and (2) are related to toxicity measurements results is uncertain, but the sample treated using the loose NF membrane provided the highest toxic unit value; however, this was still believed to be low.

Acknowledgements

This work was supported, in part, by a grant (No. R01-2006-000-10993-0) from the Basic Research Program of the Korea Science and Engineering Foundation (KOSEF), and also supported by the KOSEF through the Advanced Environmental Monitoring Research Center (ADEMRC) at GIST.

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