



Membrane-based hybrid processes for high water recovery and selective inorganic pollutant separation

S.M.C. Ritchie¹, D. Bhattacharyya*

Department of Chemical and Materials Engineering, University of Kentucky, 177 Anderson Hall, Lexington, KY 40506-0046, USA

Abstract

The removal of heavy metals (e.g. Pb(II), Cd(II), Cu(II), etc.) and oxyanions (e.g. nitrate, As(III), V), Cr(VI), etc.) is of immense interest for treatment of groundwater and other dilute aqueous systems. However, the presence of non-toxic components, such as hardness (Ca, Mg) and sulfate, can interfere with the separation of toxic species. For example, pressure-driven membrane processes, such as reverse osmosis (RO), have been limited for water treatment due to problems that these extraneous components cause with water recovery and ionic strength (osmotic pressure) of the retentate. In addition, nitrate rejection by RO is considerably lower than NaCl rejection, resulting in permeate concentrations that may be too high for groundwater recharging. Other separation systems that rely solely on sorption of toxic species (e.g. ion exchange resins) may not have sufficient selectivity for efficient use in the presence of competing ions. Hence, implementation of pressure-driven membrane separations and high capacity sorbents in hybrid processes shows much promise for remedying these difficulties. For example, selective separation of nitrate may be achieved by combining nanofiltration (NF) for sulfate removal, followed by RO or ion exchange for nitrate removal (see example 1). When small concentrations of toxic metals are present, the large retentate volumes of RO processes may be reduced by selective removal of toxic species with a high capacity sorbent, thus permitting disposal of a lower volume, non-toxic stream (see example 2). The use of microfiltration membrane-based sorbents containing multiple polymeric functional groups is a novel technique to achieve high metal sorption capacity under convective flow conditions. These sorbents are formed by the attachment of various polyamino acids (MW: 2500–10,000), such as polyaspartic acid (cation sorption), polyarginine (oxyanion sorption), and polycysteine (chelation exchange), directly on the membrane pore surfaces. Since these sorbents have also been found to

*Corresponding author. Tel.: +1-859-257-2794; fax: +1-859-323-1929.

E-mail address: db@engr.uky.edu (D. Bhattacharyya).

¹Present address: Department of Chemical Engineering, University of Alabama, Box 870203, Tuscaloosa, AL 35487-0203, USA.

have high selectivity over non-toxic metals, such as calcium, they are ideal candidates for hybrid processing with RO/NF. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Hybrid processes; Membranes; Sorption; Inorganics

1. Introduction

The treatment of groundwater and other aqueous streams is often complicated as composition can vary widely. Toxic contaminants may include heavy metals such as Pb(II), Cd(II), and Cu(II) and oxyanions such as nitrate, As(III, V), and Cr(VI). The concentrations of these components may be small, such that metal removal by precipitation is complicated by solubility limits [1]. Removal by conventional ion exchange may also be affected by the presence of nontoxic species, such as hardness (Ca^{2+} , Mg^{2+}) and sulfate, which compete for the limited ion exchange sorption capacity. Pressure-driven membrane processes, such as reverse osmosis (RO) and nanofiltration (NF) can give high rejection of most of these species, though osmotic pressure, fouling, and insufficient rejection of nitrate must be considered. RO processes range from seawater desalination to brackish water treatment to ultra-low pressure (<14 bar) operation. NF and ultra-low pressure RO membranes are particularly useful for dilute systems because of low energy consumption. Excellent reviews of RO technology and theory may be found elsewhere [2,3]. In addition, recent developments in the areas of low-pressure RO and NF, including some cost evaluations compared to conventional brackish water membranes, have been discussed by several researchers [4–7]. The retentate stream also presents a challenge, as its disposal is not trivial, and osmotic pressure may not allow for sufficient water recovery (large retentate volume) [8]. Combination of the above processes, plus addition of new sorbent technologies in hybrid processes, may allow for successful treatment of these multiple contaminant containing waters. Sikdar et al. [9] have provided an excellent discussion of membrane-based environmental applications ranging from VOC to metals separation.

2. Background

The intent of this paper is to examine pressure-driven membrane processes and how these may be incorporated into hybrid processes to achieve desired separations. As alluded to in the introduction, these membrane processes include RO, NF, ultrafiltration (UF), and microfiltration (MF). Since UF is primarily used for size exclusion, it is not particularly useful for removal of inorganic ions from solution (exception polymer-enhanced UF which is not focus of this paper). RO and charged NF are ideally suited, and MF is considered for pretreatment and as a substrate for polyamino acid attachment, thus creating an effective MF sorbent material. The benefits and drawbacks of each process will briefly be discussed.

All membrane processes generally produce two streams, one that is more concentrated in one or more species and the other that is depleted of the same species. For pressure-driven membrane processes, the stream which passes through the membrane is called the permeate and the second stream is called the retentate. Process parameters [10,11] which are used

to characterize membrane separations for pressure-driven (RO/NF/UF/MF) processes are permeate (water) flux (J_w), rejection (R), and water recovery (r). The water flux, J_w , is defined as permeate volumetric flow rate per unit membrane area with units such as, m^3/m^2 per day, $\text{l}/\text{m}^2 \text{ h}$, and $\text{US gal}/\text{ft}^2$ per day. Rejection, R , is typically defined as: $R = 1 - (\text{permeate concentration}/\text{feed concentration})$. Typical NaCl rejections for RO membranes range from 99 to 99.8% and have permeabilities ranging from $2\text{--}36 \times 10^{-2} \text{ m}^3/\text{m}^2$ per day MPa ($6\text{--}90 \times 10^{-2} \text{ US gal}/\text{ft}^2$ per day bar) at 1–10 MPa (10–100 bar). The typical operating feed pressure ranges are: 15–50 bar for RO (for brackish water membranes), 7–30 bar for NF, 2–7 bar for UF, and 0.3–3 bar for MF. Water recovery is the fraction of influent water recovered in the permeate.

NF membranes are often referred to as “loose RO” membranes. In general, NF membranes can achieve higher water fluxes at lower transmembrane pressure, though with generally lower rejection than RO membranes. NF membranes are composed of polymeric materials (similar to RO membrane) that often contain negatively charged surface groups (i.e. carboxyl and sulfonate). Therefore, separation proceeds not only by diffusion, but also by repulsion between anions (Donnan exclusion) in solution and the surface groups. Thus, one would expect rejection to follow the trend: $\text{Na}_2\text{SO}_4 \gg \text{NaCl} > \text{NaNO}_3$. As has been alluded to earlier, RO and NF work very well for separating inorganics from solution. From 1987 [12] to 1995 [13], cellulosic and highly cross-linked polyamide membranes have been replaced with improved polyamide TFC membranes for nitrate removal, with corresponding increases in rejection from 70–97 to consistently 97% rejection. It should also be noted that for NF membranes, nitrate rejection is much lower (about 40%) due to nitrate hydration and charge shielding [14]. Oxyanions, such as nitrate and arsenate, need special consideration in drinking water treatment as they are toxic at very low concentrations. A summary of nitrate rejections for various RO and NF membranes is given in Table 1.

Traditionally, MF membrane separations have been performed on the basis of size exclusion and are typically used for filtration of suspended solids, bacteria, viruses, etc. However, the functionalization of MF membrane pores with appropriate chelation groups allows for dissolved heavy metal removal for water treatment at low pressure and high throughput rates. The introduction of single reactive groups into a MF matrix has been accomplished by irradiation of polyethylene/polypropylene hollow fiber membranes and subsequent reaction [16–18]. These reactive groups, such as iminodiacetic acid and amidoxime groups, provide sites for metal sorption, though all groups were located on the membrane pore surface. The advantage of MF membrane-based sorbents is that functional groups can be attached to membrane pores as polymeric ligands, rather than as monomeric surface functional groups. Accessibility and solute contact is thus enhanced since functional groups are in the flow path where contaminated solutions are channeled through the porous structure. Interactions between these groups and the heavy metal ions are very rapid, and since sorption proceeds under convective flow, transport resistance is minimized. Substrates for the sorbents can vary widely over a range of inexpensive, commercially available cellulosic and silica membrane materials that are easily functionalized with polymeric ligands. Typical polymeric ligands include polyaspartic acid (cation sorption), polyarginine (anion sorption), and polycysteine (chelation). An overview of this technology is shown in Fig. 1, and has been described in detail by the authors elsewhere [19,20].

Table 1
Nitrate rejections (10–200 mg/l feed ranges) of various RO and NF membranes^a

Membrane material and commercial name	Manufacturer	Test conditions	Flux (m ³ /m ² per day) (US gal/ft ² per day)	Nitrate rejection (%)	Reference
Commercial polyamide RO membranes	Hydranautics, Fluids Systems, and Dow-FilmTec	1.6 MPa (16 bar), $r = 80\%$	0.6 (14)	About 97	[13]
Cellulose triacetate RO 5K	Dow	1.9 MPa (19 bar), $r = 59\%$	[23 l/min (8700 US gal per day)]	85	[12]
Polyamide RO B-9 (0440-42)	DuPont	2.6 MPa (26 bar), $r = 50\%$	[17 l/min (6400 US gal per day)]	94	[12]
FT-30	FilmTec	2.8 MPa (28 bar), $r = 0\%$	1.17 (29.2)	92	[15]
Crosslinked TFC	Toray	2.8 MPa (28 bar), $r = 0\%$	1.25 (31.2)	97	[15]
RO cellulose acetate SS10	Osmonics	2.8 MPa (28 bar), $r = 0\%$	0.56 (13.9)	76	[8]
NF cellulose acetate SX10	Osmonics	1.4 MPa (14 bar), $r = 0\%$	0.45 (11.3)	32	[8]
NTR-729HF	Nitto-Denko	0.3 MPa (3 bar), $r = 0\%$	0.48 (12.0)	70	[5]
TFC-NF DS-5	Desal	2.8 MPa (28 bar), $r = 0\%$	2.6 (65.1)	40	[15]
PVA-NF	Hydranautics	2.8 MPa (28 bar), $r = 0\%$	2.7 (66.6)	43	[15]

^a TFC: thin film composite; PVA: poly-vinyl alcohol.

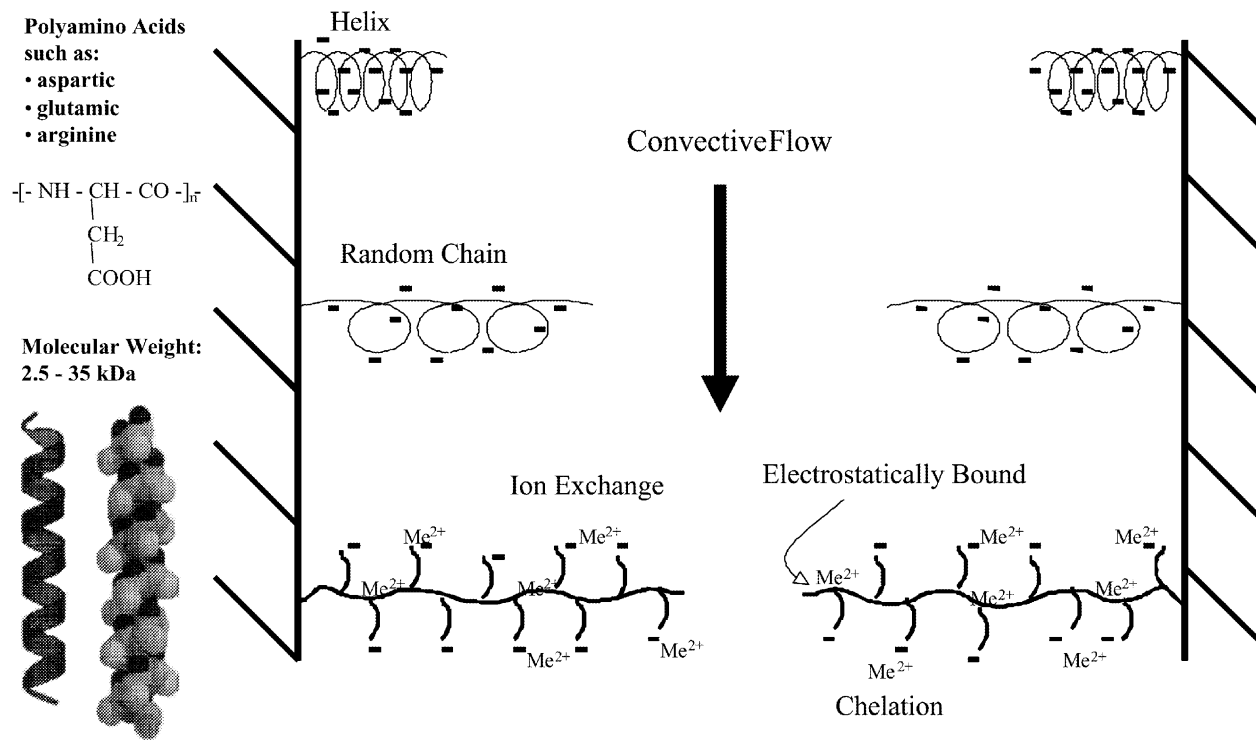


Fig. 1. Schematic of metal sorption mechanisms and helix formation for polyamino acid functionalized MF membrane sorbents.

3. Discussion

Hybrid processes provide flexibility in terms of integration of conventional (i.e. ion exchange, traditional RO) and emerging (i.e. ultra-low pressure RO, functionalized membranes) technologies. These processes are also dependent on the separation needs, and finding the niche for each process is critical. This paper will focus on membrane-based hybrid processes, specifically for water treatment. The processes examined include RO, NF, and MF sorbents. Characteristics of these membrane processes are given in Table 2. In general, traditional RO is very effective, with excellent rejection of almost all ionic species, including non-toxic components. For high TDS solutions this can result in high osmotic pressure. The overall efficiency of the process is also reduced as selective separation of toxic-species (from Ca^{2+} , Mg^{2+}) cannot be achieved. NF can allow for some selective separation (i.e. sulfate > nitrate) and partial water softening, as well as higher throughput at lower pressure, though it often does not reject contaminants to a sufficient degree, and thus may limit the feed concentration level that can be treated.

Removal of specific components is possible with MF sorbents, though finite capacity requires that the sorbents be regenerated. Species are sequestered via interactions with functional groups on the membrane. These may be tailored to achieve the desired selectivity. High capacity is achieved by attaching polymeric ligands, such that multiple functional sites are available for each respective surface site. Regeneration of the membranes can be accomplished by a simple acid wash. Regulation of the throughput rate is required, however, as sufficient contact time between the membrane and the solution is necessary, as with any sorbent. Membranes are inherently modular, and hence for large throughput applications supplemental modules operating in parallel may be utilized.

Hybrid membrane processes are applicable to a variety of separations, though only two cases will be examined in this paper. It should be noted, however, that analogous cases, such as the removal of arsenate (sulfate interference) could be approached in a similar manner. In addition, NF/RO hybrid systems have been used extensively for water softening

Table 2
Characteristics of membrane processes for removal of inorganic contaminants from aqueous solution

	Reverse osmosis	Nanofiltration	Microfiltration sorbent
Description	Dense polymeric thin film membrane	Charged polymeric thin film membrane	Microfiltration membrane containing polyfunctional ligands
Separation mechanism	Solution–diffusion	Solution–diffusion and Donnan exclusion	Ion exchange and chelation
Strengths	Excellent rejection of all ionic solutes	Excellent rejection of divalent solutes Lower pressure than RO Selective separation possible	Selective ion sorption Low pressure Passive separation of particles
Weaknesses	Higher energy requirement Large retentate volume Pretreatment	Low rejection of some monovalent solutes Limited to dilute solutions Pretreatment	Finite capacity Emerging technology

and desalination [21]. The cases examined here, however, will focus on the removal of very specific target constituents, such as nitrate or heavy metals, and how this can be achieved when other components are present. The first separation of interest regards the removal of nitrate from sulfate-containing waters. This separation is complicated, as nearly all sorbent techniques will selectively remove sulfate (higher valency). Since sulfate is not a contaminant, and is often present at much higher concentration than nitrate, it represents a significant interference to nitrate removal. The second example is the removal of toxic heavy metals from high hardness streams. This case is of particular interest for groundwater treatment, when calcium is an ever-present component. Again, since the concentration of calcium is generally much higher than that for any toxic species, it represents an interference to separation by conventional ion exchange technology. RO can be used to separate the toxic metal though calcium will also be concentrated in the retentate. Selective removal of the toxic metal from this retentate stream will be examined in the second example.

4. Example 1: Nitrate-hardness-organic removal from sulfate-containing potable waters

Nitrate separation from groundwater is an interesting problem, as this anion is highly hydrated, and charge shielding limits electrostatic interactions. However, ion exchange is still the most commonly used separation technique for nitrate. Since nitrate is monovalent, divalent sulfate has been found to be a strong interferent by conventional ion exchange. Modification of exchanger functional groups is required to add selectivity to the resin. An excellent review of efforts in this area has been provided by Guter [22]. It was found that the addition of steric hindrances to quaternary amines enhanced nitrate selectivity. For example, tributyl-substituted amines (Sybron Chemicals, Ionac SR6) was found to have a nitrate/sulfate selectivity of 15,000 and a capacity of 1.5 meq/g [22]. These resins are rather expensive, and regeneration is required. Regeneration generates a high TDS stream, and disposal of this stream can be cost prohibitive [23]. The cost for an 8×10^6 l per day (2.1 MGD (million gallons/day)) unit with nitrate levels ranging from 80 to 130 mg/l is about US\$ 850,000. Typical operating costs range between US\$ 0.02 and 0.10/1000l.

An alternative to this technology may be hybrid membrane processes. Recall that NF selectively rejects sulfate versus nitrate. The effectiveness of RO for the removal of most inorganic ions is well established in the literature [24]. Hence, operation of these two processes sequentially should allow for selective nitrate removal, and good water recovery. An example scheme is given in Fig. 2. The overall process consists of three operations. First, the influent is treated by NF, as it is very effective for the removal of natural organic material (NOM) [25], and does an excellent job rejecting sulfate. This is critical as NOM may affect ion exchange performance, and sulfate will compete strongly with nitrate for exchange sites. Since sulfate is effectively removed, conventional ion exchange can be used for nitrate removal after NF treatment. Hence, the use of expensive selective resins can be avoided. Regeneration of the bed is still needed, however, and thus MF sorbents with amine groups may be more desirable. Regeneration of MF sorbents is easier than ion exchange resins, as there is no microporous structure (<10 nm) from which ions must diffuse. Recall from Fig. 1 that functionalized polyamino acids (in this case, polyarginine)

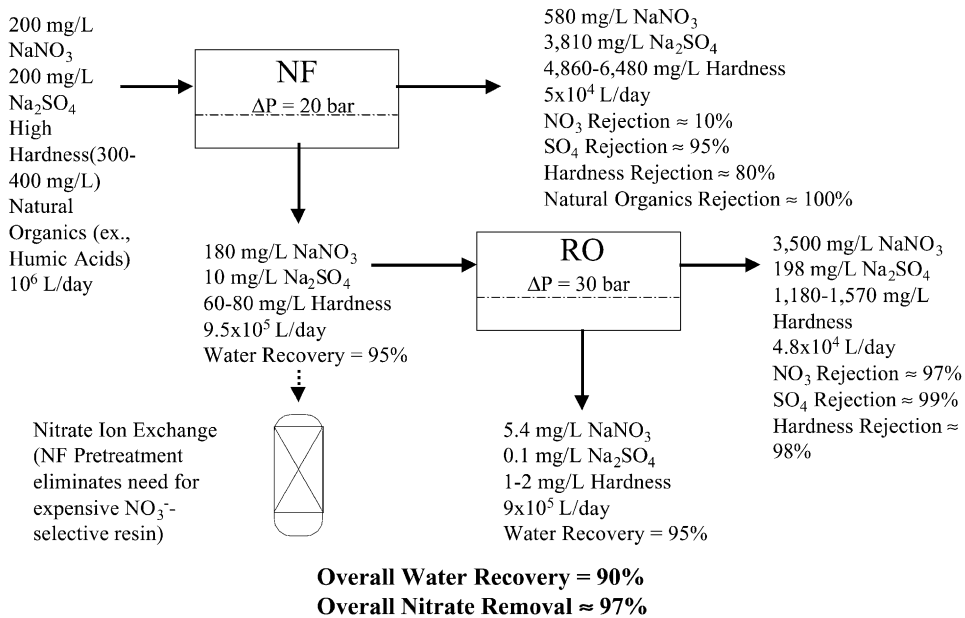


Fig. 2. Example scheme for nitrate removal from sulfate and other natural constituents containing waters by membrane-based hybrid processes.

containing multiple amine groups are pendent in the membrane pores (~100 nm), and are in the flow path. Hence, there is excellent contact between the nitrate containing stream and the subsequent regeneration stream in convective flow [26]. Thus, more mild regeneration solutions may be used, and the final solution will have a lower concentration of TDS.

The other alternative for secondary treatment is RO. It is well known that NF rejects hardness constituents (e.g. Ca²⁺, Mg²⁺) significantly, and thus fouling of the RO membrane will be lessened greatly [8]. Also, osmotic pressure buildup on the feed side (during feed concentration) will be less severe. Overall water recovery in this case is 90% as potable water. Further treatment of the RO and NF retentate by evaporation becomes more feasible since the salt concentrations are higher, and the volume is less than 5% of the total influent. The product water stream has excellent quality with low sulfate concentration, and a nitrate concentration below the drinking water maximum concentration limit (MCL).

The economics for NF/RO hybrid facilities match or are comparable to those for an ion exchange plant. For example, treatment of a 1300 mg/l TDS brackish water (from groundwater) at 24 × 10⁶ l per day (6.3 MGD) would require plant capital costs of US\$ 2,180,000. Operating costs would be about US\$ 525,000 per year. With amortization of capital over 10 years, the product water (with 36.5% blend of feed water) cost would be US\$ 0.09/1000l [7]. Removal of nitrate would take place simultaneously with TDS removal for this system. When adjusted for a direct comparison with ion exchange, capital cost is 15% lower for NF/RO hybrid systems, with similar operating costs. Additional work in this area has also been presented by Bohdziewicz et al. [8]. It should be noted that NF

and RO membranes also work well (up to 99.4% rejection) for the removal of arsenic [27,28], with excellent flux of $1.3 \text{ m}^3/\text{m}^2$ per day (up to 32 gfd (gallons/ft²-day)). Hence, the same system configuration could be used for sulfate removal (sulfate–arsenate systems), followed by arsenic sorption (by polyarginine-functionalized MF sorbents) or removal by RO. In addition, subsequent RO treatment effectively removes disinfection by-products [25] and bacteria and viruses [29]. These latter effects are particularly important for the production of potable water.

5. Example 2: Waste volume reduction and heavy metal recovery from RO retentate streams

A second example of interest is the selective recovery of heavy metals from RO retentate streams and retentate reduction. Recall from Fig. 2 that typically 95% of the RO influent can be recovered in the permeate. The retentate stream will thus contain 5% of the influent volume. For large-scale processes, this is significant, and hence disposal of this stream is a major challenge. For example, for water softening purposes, the retentate stream is concentrated in hardness. Since the concentrations of other components are very small, the retentate may be safely disposed of in the sewer. However, when trace quantities of heavy metals are in the influent, these will be concentrated in the retentate, and may be higher than permissible discharge limits. Selective removal of the heavy metal from the retentate would then be very useful. Hybridization of RO and selective sorption of toxic heavy metals by functionalized MF sorbents (containing multiple polymeric ligands) should be an excellent solution for this problem. For example, our work with polyglutamic acid functionalized MF membranes has shown $\text{Pb}^{2+}/\text{Ca}^{2+}$ selectivity greater than 15 [19]. Conventional ion exchange typically provides a selectivity of ~ 2 for Pb over Ca.

The recovery of valuable metals from multi-component waste streams is also a problem of interest. Concentration by RO is difficult due to the presence of high hardness, and conventional ion exchange is complicated by competitive sorption of Ca^{2+} and Mg^{2+} . Limited capacity and pressure drop associated with large column operation also makes ion exchange an unattractive option for this separation. Obtaining a concentrated regenerate, particularly for industrially relevant feeds, is also a concern. Again, a hybrid system for recovery of the valuable metal would be useful.

A hybrid process consisting of MF sorbent treatment of a RO retentate stream is shown in Fig. 3. For simplification, anions are not shown in the figure. The feed stream contains high hardness, but also an impurity of 10 mg/l Cd. The presence of metal, such as Cd^{2+} , in the retentate stream makes disposal much more costly. Separation of the Cd would then be highly desirable. First, RO is used to reduce the volume that must be treated by the MF sorbent. This is useful, as it allows for improved contact time between the solution and the sorbent. Also, it eliminates the need for a large number of membrane modules in parallel. Cd^{2+} , Ca^{2+} , and Mg^{2+} are all rejected ($>98\%$) by the RO membranes, and only 10% of the influent passes through the MF sorbent.

The MF sorbent can be functionalized with a variety of polyamino acids. Since the stability constants for Cd^{2+} with carboxylic acids are much higher than for Ca^{2+} and Mg^{2+} , polyaspartic acid and polyglutamic acid would work well. Our work with MF sorbents

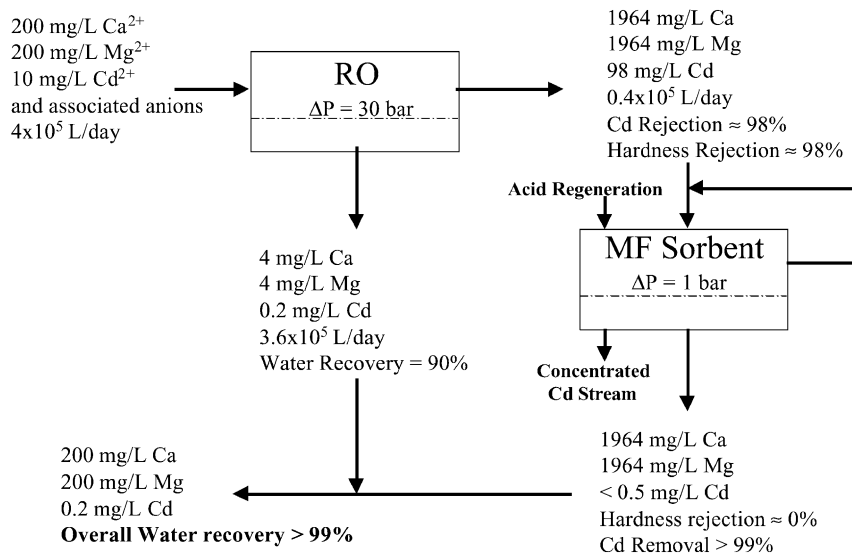


Fig. 3. Example scheme for cadmium removal from hardness containing waters by membrane-based hybrid process.

functionalized with polyglutamic and polyaspartic acids has shown excellent sorption of Cd²⁺, with capacities of around 1 mg/cm² external membrane area [20]. It should be noted that chelation exchangers (containing thiol or IDA groups) would also work well for the selective sorption of Cd²⁺ from these types of systems. However, polyamino acid functionalized MF membranes allow for convective flow (low mass transfer resistance) and higher capacity (polymeric ligands). We have found Cd²⁺ sorption on polycysteine functionalized membranes to be comparable to polyglutamic acid functionalized membranes [30]. Since polycysteine contains thiol groups, it has essentially no affinity for Ca, and is only regenerated with acid [31]. In the case of polycysteine functionalized membranes, complete regeneration was achieved with 0.1 N HNO₃ [30]. Cd can then be selectively removed from the RO retentate, and the remaining solution (after MF sorbent step) can be blended with the RO permeate stream. Notice that water recovery is >99% (very difficult for RO alone) and that only 10% of the feed stream must be treated with the sorbent. The product water is of sufficient quality for discharge or reuse, and the regenerant volume has been reduced. In addition, overall metal recovery is considerably higher than for RO alone. Hence, the advantages of each technology have been utilized.

6. Conclusions

The removal of toxic inorganics, such as nitrates and heavy metals, from groundwater and aqueous streams is often complicated by the presence of non-toxic components such as sulfate and hardness. Conventional ion exchange and RO, which normally work very well for relatively clean streams, become less effective if selective removal or high water recovery

is desired. Combination of these techniques, including NF, into hybrid processes can help to overcome some of these problems. NF works very well for the separation of divalent anions, and hence can be used effectively as a pretreatment step when sulfate selectivity \gg nitrate (such as in ion exchange processes). MF sorbents also work well when combined with NF, as more conventional ion exchange groups can be utilized for separations. Selective recovery of heavy metals is also possible with MF sorbents since the enhanced stabilities of heavy metal complexes over those with alkaline metals can be utilized [30]. Combination of the above processes, plus addition of new sorbent technologies in hybrid processes, offers tremendous flexibility for the treatment of multi-pollutant streams (including NOM removal). Future areas of membrane research including enhancement of water recovery (to 98%), and improved As(III) and nitrate rejections to $>95\%$ will be of immense value.

Acknowledgements

The authors would like to recognize the US EPA for partial support of the metal sorbent work and the NSF-IGERT program. The authors would also like to acknowledge the technical contributions of Dr. S.K. Sikdar of US EPA for the metal sorbent project.

References

- [1] J.A. Dyer, N.C. Scrivner, S.K. Dentel, *Environ. Prog.* 17 (1998) 1.
- [2] B. Parekh, *Reverse Osmosis Technology*, Marcel Dekker, New York, 1988.
- [3] S. Sourirajan, T. Matsuura, *Reverse Osmosis/Ultrafiltration Principles*, National Research Council of Canada, Ottawa, Ont., 1985.
- [4] R. Gerard, H. Hachisuka, M. Hirose, *Desalination* 119 (1998) 47.
- [5] C. Ratanatamskul, T. Urase, K. Yamamoto, *Water Sci. Tech.* 38 (1998) 453.
- [6] K.H. Ahn, K.G. Song, H.Y. Cha, I.T. Yeom, *Desalination* 122 (1999) 77.
- [7] G. Filteau, P. Moss, *Desalination* 113 (1997) 147.
- [8] J. Bohdziewicz, M. Bodzek, E. Wasik, *Desalination* 121 (1999) 139.
- [9] S.K. Sikdar, J. Burckle, J. Ragut, *Environ. Prog.* 20 (2001) 1.
- [10] D. Bhattacharyya, W.C. Mangum, M.E. Williams, in: R.A. Myers (Ed.), *Encyclopedia of Environmental Analysis and Remediation*, Wiley, New York, 1998, p. 4149.
- [11] W.S.W. Ho, K.K. Sirkar (Eds.), *Membrane Handbook*, Chapman & Hall, New York, 1992.
- [12] M.R. Huxstep, T.J. Sorg, Full report: reverse osmosis treatment to remove inorganic contaminants from drinking water, US EPA, PB88-147780, December 1987.
- [13] J.N. Cevall, W.B. Suratt, J.E. Burke, *Desalination* 103 (1995) 101.
- [14] K. Linde, A.S. Jonsson, *Desalination* 103 (1995) 223.
- [15] F.T. Awadalla, C. Striez, K. Lamb, *Sep. Sci. Tech.* 29 (1994) 483.
- [16] K. Saito, M. Ito, H. Yamagishi, S. Furusaki, T. Sugo, J. Okamoto, *Ind. Eng. Chem. Res.* 28 (1989) 1808.
- [17] S. Tsuneda, K. Saito, S. Furusaki, T. Sugo, J. Okamoto, *J. Membr. Sci.* 58 (1991) 221.
- [18] S. Konishi, K. Saito, S. Furusaki, S. Takanobu, *J. Membr. Sci.* 111 (1996) 1.
- [19] D. Bhattacharyya, J.A. Hestekin, P. Brushaber, L. Cullen, L.G. Bachas, S.K. Sikdar, *J. Membr. Sci.* 141 (1998) 121.
- [20] S.M.C. Ritchie, T. Olin, S.K. Sikdar, L.G. Bachas, D. Bhattacharyya, *Langmuir* 15 (1999) 6346.
- [21] V. Mavrov, H. Chmiel, B. Heitele, F. Rogener, *Desalination* 123 (1999) 33.
- [22] G.A. Guter, in: A.K. Sengupta (Ed.), *Ion Exchange Technology*, Technomic Publishing Co., Lancaster, PA, 1995, p. 61.
- [23] C.J. Martin, E.O. Kartinen, J. Condon Jr., *Desalination* 102 (1995) 35.

- [24] K. Scott, *Handbook of Industrial Membranes*, Elsevier, New York, 1995.
- [25] M. Siddiqui, G. Amy, J. Ryan, W. Odem, *Water Res.* 34 (2000) 3355.
- [26] J.A. Hestekin, L.G. Bachas, D. Bhattacharyya, *Ind. Eng. Chem. Res.* 40 (2001) 2668.
- [27] T. Urase, M. Saleqzaman, S. Kobayashi, T. Matsuo, K. Yamamoto, N. Suzuki, *Water Sci. Tech.* 36 (1997) 349.
- [28] J.J. Waypa, M. Elimelech, J.G. Hering, *JAWWA* 89 (1997) 102.
- [29] S.B. Sadr Ghayeni, S.S. Madaeni, A.G. Fane, R.P. Schneider, *Desalination* 106 (1996) 25.
- [30] S.M.C. Ritchie, K.E. Kissick, L.G. Bachas, S.K. Sikdar, C. Parikh, D. Bhattacharyya, *Environ. Sci. Tech.* 35 (2001) 3252.
- [31] H.A. Jurbergs, J.A. Holcombe, *Anal. Chem.* 69 (1997) 1893.