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INDEPENDENT REGULATORY
REVIEW COMMISSION

February 12, 2010

VIA EMAIL: RegComments@state.pa.us

Environmental Quality Board
P.O. Box 8477
Harrisburg, PA 17105-8477

Re: Proposed Chapter 95 Wastewater Treatment Rulemaking

Dear Environmental Quality Board members,

This letter is in response to the invitation for comment on the proposed revisions to Chapter 95 of the Pennsylvania Code noticed in the November 7, 2009 and November 14, 2009 editions of the Pennsylvania Bulletin.

As an organization whose mission is to protect the water quality of the Monongahela River, Allegheny River, Ohio River, and their respective watersheds through water sampling, discharge and use permit review, community engagement, and active investigation of all potential threats to water quality in the Three Rivers region, Three Rivers Waterkeeper strongly supports the Department of Environmental Protection's decision to propose changes to Chapter 95. We believe that these regulations will preserve and protect Pennsylvania's waters from the substantial harm caused by increased loadings of total dissolved solids (TDS), chlorides, sulfates, barium, and strontium.

Although Three Rivers Waterkeeper supports the proposed changes to Chapter 95, we urge the DEP to take the additional steps outlined in other letters submitted by the Campaign for Clean Water and the University of Pittsburgh Environmental Law Clinic on behalf of Clean Water Action. Three Rivers Waterkeeper was a signatory to both sets of comments and firmly believes that they are well reasoned, thoroughly researched, and cover several areas of regulation and policy that must be addressed to ensure that the DEP can adequately protect our water resources.

In particular, Three Rivers Waterkeeper respectfully requests that the DEP consider the following seven additions and modifications to the proposed Rule.

1. Provide a clear and concise basis for the numeric standards in the proposed Rule;

2. Present a clear and concise delineation between the wastewater-quality standard proposed and other types of limitations used in other regulations (e.g. technology-based standards, water-quality standards, etc.);
3. Expressly preserve the Best Professional Judgment analysis as part of the permitting process so that particular regional circumstances will still be considered;
4. List specific technologies the DEP considered and foresees as being viable options for compliance with the proposed Rule;
5. Review and / or conduct additional research on the ecological and human effects of exposure to the component ions of TDS including chloride, sulfate, and bromide;
6. Promulgate a numeric standard for bromide; and
7. Require all NPDES permit renewals to be subject to the proposed Rule.

Rather than be unduly repetitious, Three Rivers Waterkeeper incorporates by reference the full background and discussion of these seven points that are contained in the comments mentioned above.

Finally, Three Rivers Waterkeeper would like provide a preemptive rebuttal to any comment the DEP receives suggesting that the numeric limitations contained in the proposed Rule are not feasible. Simply put, treatment of high-TDS wastewater roughly classifies as desalination. Chemically speaking, TDS is a measure of numerous mineral salts in their charged ionic state. Not only have coastal regions worked with desalination processes extensively, other fossil fuel extraction industries have dealt with wastewater treatment issues. As a result, there is a thriving industry dedicated to industrial-scale desalination. Therefore, Three Rivers Waterkeeper believes that no technological barriers exist that would prevent achieving the numeric standards listed in the proposed Rule. In support of this position, we have attached four articles from professional trade journals that extensively discuss reverse osmosis, nanofiltration membranes, treatment costs, and facility design (attached as Exhibits 1 – 4).

In conclusion, Three Rivers Waterkeeper would like to commend the DEP for acting quickly and decisively to promulgate a rule that will prevent a bourgeoning environmental disaster. The proposed Rule is a fair and balanced approach to protecting the environment and promoting the local economy. Three Rivers Waterkeeper would like to thank the EQB, DEP, and all other who have given their time and effort into protecting our environment through this process.

Sincerely,

Ned M. Mulcahy, Esq.
Executive Director, Three Rivers Waterkeeper

Patrick Grenter, Esq.
Legal Director, Three Rivers Waterkeeper

Exhibit 1

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Desalination 225 (2008) 139–155

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Beneficial use of co-produced water through membrane treatment: technical-economic assessment

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Abstract

Large amounts of co-produced water are generated during natural gas production. This study investigated the viability and cost effectiveness of ultra-low pressure reverse osmosis (ULPRO) and nanofiltration (NF) membranes as potential techniques for beneficial use of produced water by meeting potable and irrigation water quality standards and concentrating iodide in the brine. A 2-stage laboratory-scale membrane testing unit was employed to examine rejection of various constituents of concern at a low and high recovery using produced water generated from sandstone aquifers. The performance of two ULPRO membranes TFC-ULP (Koch) and TMG10 (Toray America) and one NF membrane NF-90 (Dow/Filmtec) was compared to a conventional RO membrane (TFC-HR, Koch). These membranes were pre-selected during previous bench-scale experiments with regard to specific flux, fouling propensity, salts and organics rejection, and iodide recovery efficiency. Of the membranes tested, the NF-90 achieved the highest specific flux. The salt rejection and iodide recovery by the NF-90, however, were much lower than the RO and ULPRO membranes tested. The permeate quality of the NF-90 met USEPA National Primary Drinking Water Standards, but exceeded the Secondary Standards regarding chloride and total dissolved salts. The two ULPRO membranes TMG10 and TFC-ULP, exhibited a higher specific flux as compared to the TFC-HR while displaying a similar rejection, notably the TMG10 which showed a very stable rejection at low and high recoveries. Cost analysis showed that the ULPRO membrane system provided marginally lower overall O&M costs than RO for meeting drinking water standards. The ULPRO membrane operation resulted in even lower treatment cost than RO and NF for meeting irrigation water standards, especially at high energy cost. Findings from these studies indicated that ULPRO membranes can provide a viable and cost-effective solution to beneficial use of produced water from sandstone aquifers.

Keywords: Produced water; Nanofiltration; Ultra-low pressure reverse osmosis; Desalination; Water reuse; Iodide recovery

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1. Introduction

The accepted and applied methodology to produce methane gas from coal seams, sandstone and carbonate reservoirs is dewatering to lower the reservoir pressure in order to liberate trapped gas bubbles. As a by-product, this methane exploration method generates significant amounts of co-produced water. Co-production of methane gas in many cases represents a substantial risk to the natural environment due to the large amounts of brine that need to be disposed via surface discharge or deep well injection. These issues are especially of concern since methane co-production has become an increasingly important source of natural gas in the United States. Many regions in the US where methane exploration is underway are also characterized through a lack of water for drinking water supply and agricultural needs. Therefore, produced water is increasingly being considered as a way to supplement limited freshwater resources in many parts of the US as well as other countries. Methane co-produced water is commonly characterized by the presence of oil and grease, hydrocarbons, and high total dissolved solids (TDS) concentrations, which restricts beneficial use without proper treatment [1].

Decisions on selecting appropriate treatment processes (or trains) capable of achieving a desired end use quality are usually determined by produced water quality and treatment costs. In recent years, there have been studies of the feasibility and economics of treating produced water and reclaiming it for agricultural or forestry [2–5], industrial [5–7] or potable uses [2,3,8,9]. In general, de-oiling and demineralization are common steps toward beneficial use. Oil and grease can be removed by adsorption [5], air floatation [10], centrifugation [11], hydroclones [12], membrane filtration [13], and advanced oxidation [14]. In addition, biological treatment such as reed beds [4] and wetlands [15] have also been employed to further degrade suspended solids, residual organics, nutrients and metals from produced water. With regard to demineralization, the most promising technologies considered for removing dissolved salts from produced water are mechanical vapor compression [7] and reverse osmosis (RO) membranes [3,5,16–19]. The current demineralization technologies, however, are energy intensive and often cost prohibitive for beneficial use of produced water. The advent of ultra-low pressure RO (ULPRO) membranes and nanofiltration (NF) membranes with a high degree of salt removal offers a viable option for produced water treatment because they can be as effective as RO in removing certain solutes from water while requiring considerably less feed pressure [20,21].

Some methane gas reservoirs explored recently such as the Atlantis Project, Hill County (Montana) are also characterized by elevated concentrations of iodide exceeding 40 mg/L (ppm). Iodine is an essential and rare element with increasing demand in many industrial applications. The major end-uses of iodine include animal feed supplements, catalysts, inks and colorants, pharmaceuticals, photographic chemicals and films, sanitary and industrial disinfectants, and stabilizers [22]. Since the widely used pesticide methyl bromide was phased out on January 1, 2005 due to its ozone layer depletion potential, the USEPA and the State of California are both considering the registration of methyl iodide as a new chemical to replace methyl bromide for soil fumigant application. The registration of methyl iodide could create additional demand for iodine. In addition, the industrial uses of iodine are still increasing, and the areas of application are expanding beyond the established markets [23]. Recovery of iodine from produced water provides an additional economic benefit to produced water treatment by off-setting treatment costs. Membrane treatment will reduce the volume of the concentrate brine that needs to be disposed of, and create an opportunity for augmenting non-potable and potable water supplies in areas of severe water shortage.

This study is building upon a previous study which targeted the selection of appropriate NF and ULPRO membranes to treat produced water with respect to low fouling potential, high iodide recovery and water qualities suitable for non-potable and potable reuse [19]. The experimental results derived from our previous bench-scale testing were not suitable for scale-up and process design due to different hydrodynamic conditions and module geometry as compared to full-scale membrane configurations. Therefore, in this study a laboratory-scale 2-stage membrane testing unit employing two 4040 spiral wound elements was used to further investigate the treatment viability of produced water by membrane technology. Key elements of this investigation were operational performance of ULPRO/NF membranes, product water quality, and costs associated with installation and operation.

2. Materials and methods

2.1. Water quality

Water tested during this study was collected from a natural gas production site in Eastern Montana. A comprehensive water analysis was conducted to identify water quality constituents in produced water critical to membrane treatment and beneficial reuse. Analytical methods and sampling strategies followed protocols described in the Standard Methods [24] or published elsewhere [19]. Table 1 presents average concentrations of major constituents from twenty two grab samples collected over four years.

The produced water was characterized as a brackish groundwater of sodium chloride type with a pH of 8.45 ± 0.22. The TDS concentration was quantified as 5,520 ± 718 mg/L with a specific conductance of 10,510 ± 934 μS/cm. Besides sodium and chloride, major constituents with concentrations of less than 100 mg/L were calcium, magnesium, bromide, and iodide. The well water was relatively rich in iodide with a concentration of 50 ± 8 mg/L. The water was classified as hard (total hardness of 124 ± 23 mg/L as $CaCO_3$) with an alkalinity of 235 ± 20 mg/L as $CaCO_3$. Minor constituents with concentrations of less than 10 mg/L were aluminum, boron, barium, potassium, silicon and strontium. No other inorganic constituents were detected in the well water above the detection limit of the analytical methods.

The dissolved organic carbon (DOC) concentration in the well water was 1.75 ± 0.20 mg/L and organics were characterized by moderate to high aromaticity (specific UV absorbance (i.e., calculated as the ratio between UVA-254 and DOC) equals 4.0 ± 0.45 L/mg m). Oil and grease were detected at low concentrations. Hydrocarbons and BTEX compounds (benzene, toluene, ethylbenzene m, p-xylene, o-xylene), however, were not

Table 1
Water quality of produced water extracted from a natural gas production site

Analytes	pH	Conductivity	TDS	Total hardness	Alkalinity					
Conc.	8.45 ± 0.22	10,551 ± 934 μS/cm	5,520 ± 718 mg/L	124 ± 23 mg/L as $CaCO_3$	235 ± 20 mg/L as $CaCO_3$					
Cations	Al	B	Ba	Ca	K	Mg	Mn	Na	Si	Sr
Conc. (mg/L)	0.11 ± 0.21	3.8 ± 0.3	2.0 ± 0.5	29.5 ± 5.3	6.9 ± 1.1	11.1 ± 1.9	0.07 ± 0.03	2250 ± 327	2.7 ± 0.6	2.1 ± 0.5
Anions	Cl	Br	I							
Conc. (mg/L)	3,306 ± 854	51 ± 17	50 ± 8							
Organics	DOC	UVA-254	Oil and grease	Specific UVA						
Conc.	1.75 ± 0.20 mg/L	10.0 ± 4.3 m^{-1}	0.70 ± 0.41 mg/L	4.0 ± 0.45 L m^{-1} mg^{-1}						

detected in the well water samples provided during the course of this study. The radionuclides analysis indicated a very low level of radioactivity (combined radium 226 and radium 228 1.5 pCi/L) as compared to the Primary Maximum Contaminant Level (MCL) for radionuclides (combined radium 226 and radium 228 5.0 pCi/L) applied by USEPA to all community water systems.

2.2. Studied membranes

Four commercial thin-film composite polyamide membranes were selected for laboratory-scale testing and cost analysis. They included one RO membrane (TFC-HR, Koch Membrane Systems), two ULPRO membranes TFC-ULP (Koch) and TMG10 (Toray America), and one NF membrane NF-90 (Dow/Filmtec). The ULPRO and NF membranes were selected during previous research due to their favorable specific flux, product water quality and iodide recovery [19]. The conventional TFC-HR membrane served as the "benchmark" RO membrane in this study.

2.3. Membrane testing unit

A two-stage membrane laboratory-scale unit was employed for testing (Fig. 1). The membrane unit employed two single element (4040 spiral wound) vessels arranged in a two-stage array. A LabView (National Instruments) customized supervisory control and data acquisition (SCADA) system was used to acquire data for the following parameters: flow (feed, permeate and concentrate), conductivity (permeate and concentrate), pressure (feed and concentrate), and temperature (feed). Data collected by the SCADA system was used to compare operational performance among the tested membranes. A baffled stainless steel feed tank (200 L) was used to supply the feed water to the high-pressure pump. Before membrane per-

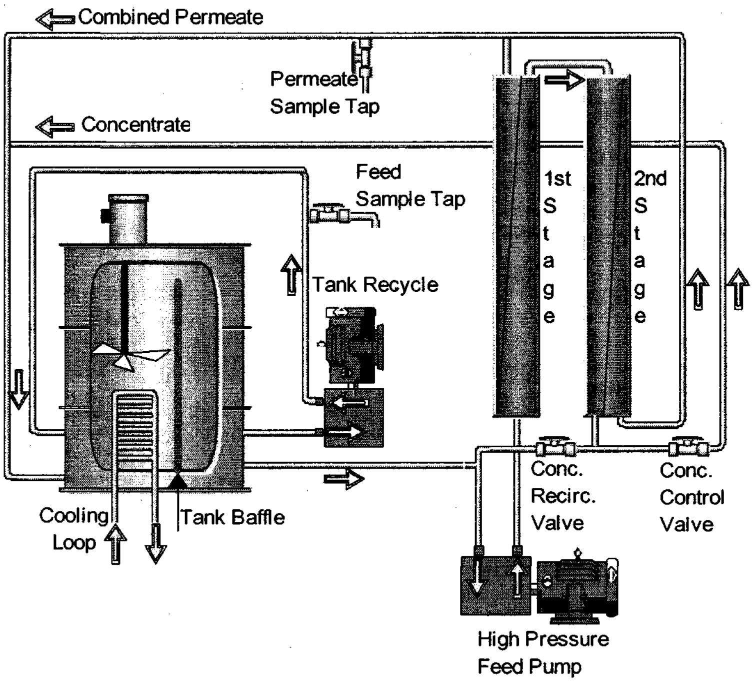

Fig. 1. Schematic of the two-stage membrane testing unit using 4040 spiral wound elements.

formance testing, spiral wound membrane specimens were tested in accordance to manufacturer specification sheets to validate element integrity and performance.

For all 2-stage membrane experiments a feed water pH of 6.0–6.1 was maintained using concentrated HCl. Produced water used for feed water was 0.45 μm microfiltered prior to membrane experiments. Antiscalant solution (Hypersperse MDC700 from GE Betz, Trevose, PA) was added to achieve a concentration of 3 mg/L. During all 2-stage membrane experiments, a vertical mixer and a tank recycle pump was used to insure proper mixing. During operation, combined permeate and concentrate flows from the membrane unit were recycled to the stainless steel tank. The return lines were situated so as to maximize mixing and hydraulic retention time before returning to the system feed. A stainless steel cooling loop was used to maintain a constant feed water temperature (about 22.5°C) during membrane experiments.

Membrane performance was evaluated during two flow regimes: flow-through and internal recycle. For all 2-stage membrane experiments, the overall feed flow was set around 34.1 L/min (9.0 gpm, i.e., gallons per minute). Flow through mode simulates the recovery of a lead element in the first stage of a membrane treatment array, with a system recovery (% of permeate flow rate to feed flow rate) of 15–23% total and a permeate flux of 0.48–0.79 m^3/(m^2·d) (12–19 gfd, i.e., gallons of permeate produced per day divided by the area of membrane (ft^2)). During the internal recycle mode, an internal concentrate recycle loop was used to simulate higher recoveries and bulk concentrations typically observed in the last stage of a full-scale membrane treatment array. When the internal recycle valve was open, a portion of the combined concentrate flow was diverted to the pump inlet and the system feed flow became a combination of flow from the feed container and combined concentrate flow. By reducing the feed flow (herein raw water flow) from the feed container and maintaining the permeate flow similar to flow through experiments, higher system recoveries could be simulated. During internal recycle experiments a system recovery between 50 and 69% was simulated which resulted in a permeate flux of 0.22–0.53 m^3/(m^2·d) (5–13 gfd). The operational conditions for each membrane are summarized in Table 2.

In this study, the membranes were operated

Table 2
Operational conditions of each membrane during flow through and internal recycle mode

Operating parameters	Operating mode	TFC-HR	TFC-ULP	TMG10	NF-90
Feed pressure, kPa	Flow through	1397	1397	1257	1257
	Internal recycle	1449	1367	1467	1467
Overall feed flow rate, L/min	Flow through	33.3	33.1	33.3	34.8
	Internal recycle	33.6	33.8	32.8	34.4
Raw water flow, L/min	Flow through	33.3	33.1	33.3	34.8
	Internal recycle	3.3	11.1	8.6	7.9
Concentrate flow, L/min	Flow through	26.5	25.5	25.2	26.7
	Internal recycle	1.0	5.6	3.0	2.5
Permeate flow, L/min	Flow through	4.9	7.6	8.1	8.1
	Internal recycle	2.3	5.5	5.6	5.4
Recovery, %*	Flow through	14.8	22.9	24.4	23.4
	Internal recycle	69.0	49.8	65.5	68.3

Note: *Recovery =(Permeate flow/raw water flow) ×100.
For flow through operation, overall feed flow =raw water flow.
For internal recycle operation, overall feed flow =raw water flow +internal recycle flow.

under different operating conditions. The rejection of a component of a feed solution is expressed as a brine rejection value which is given as (1)

$$\text{Rejection}\,(\%) = \left(1 - \frac{C_p}{C_c}\right) \times 100 \tag{1}$$

where C_p is the permeate concentration and C_c is the concentrate concentration. This value takes into account the increased concentration of a component during concentration polarization and offers a more useful comparison for two systems operated at different recoveries.

During membrane experiments, feed samples were withdrawn from the tank recycle line, and permeate and concentrate samples were taken from the permeate and concentrate lines prior to discharge into the feed tank. Membrane experiments were performed for 40 min in each flow regime before samples were collected for analysis.

3. Results and discussion

3.1. Membrane operation

The feed pressure and specific flux values obtained under different recoveries for the ULPRO and NF membranes and the "benchmark" RO membrane TFC-HR are presented in Figs. 2 and 3. Of the membranes tested during flow-through experiments (15–23% recovery), the TFC-HR required the highest feed pressure of 1,397 kPa (200 psi) and displayed the lowest specific permeate flux value of 0.34 L/(m^2·d·kPa) (i.e., 0.06 gfd/psi). The NF-90 had a significantly higher specific flux of 0.59 L/(m^2·d·kPa) (i.e., 0.1 gfd/psi) while operating at a similar pressure as the TMG10 between 1,260 and 1,290 kPa. The two ULPRO membranes TFC-ULP and TMG10 provided a similar specific flux 0.53 L/(m^2·d·kPa) (0.09 gfd/psi) while the TMG10 operated at a lower pressure than the TFC-HR and the TFC-ULP. In the internal recycle regime, the specific flux was much lower than in the flow through regime simulating low recoveries due to the high osmotic pressure as a result of higher feed concentrations. The operating performance of the tested membranes during simulation of higher recoveries followed a similar trend as observed during the flow through regime (Fig. 3). The TFC-ULP exhibited a higher specific flux and lower pressure than the TMG10, which was due to the lower recovery of the TFC-ULP (50% vs. 69% of the TMG10).

Fig. 4 presents the permeate conductivity and rejection of the tested membranes during differ-

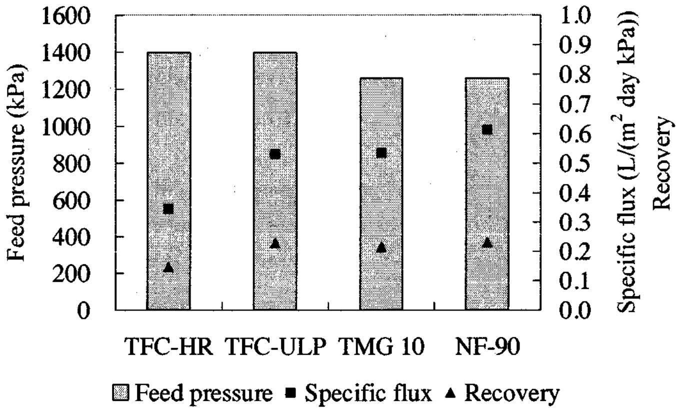

Fig. 2. Feed pressure, recovery and specific permeate flux of tested ULPRO and NF membranes versus the "benchmark" RO membrane TFC-HR during flow through experiments (error bars represent the standard deviation).

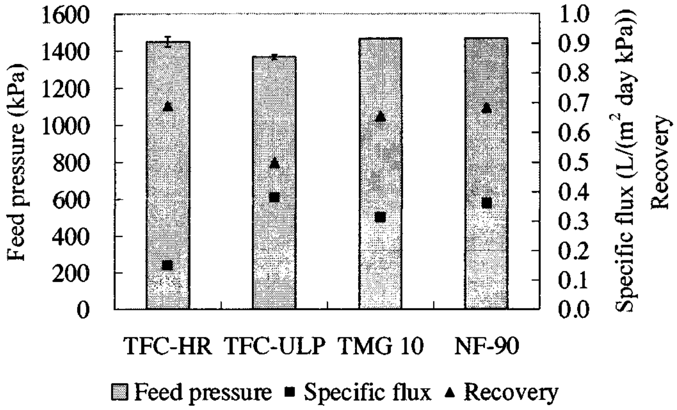

Fig. 3. Feed pressure, recovery and specific permeate flux of tested ULPRO and NF membranes versus the "benchmark" RO membrane TFC-HR during internal recycle experiments (error bars represent the standard deviation).

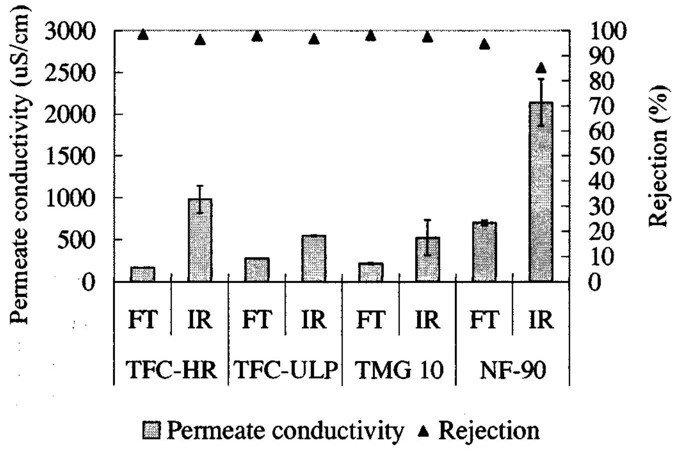

Fig. 4. Permeate conductivity and rejection of tested ULPRO and NF membranes vs. the "benchmark" RO membrane TFC-HR during flow through (FT, low recovery) and internal recycle (IR, high recovery) experiments (error bars represent the standard deviation).

ent recoveries experiments. Of the RO membranes, the TFC-HR exhibited the greatest salt rejection (96.5–98.6%) followed by the TMG10 (97.7–98.3%) and the TFC-ULP (96.8–97.9%). The NF-90, however, displayed the lowest salt rejection (85.3–94.9%). The tested membranes all displayed higher rejection in terms of conductivity at low recovery during flow through experiments than at high recovery during internal recycle.

3.2. Rejection performance

During membrane experiments in flow through and internal recycle flow regimes, samples were collected for TOC, iodide, UV absorbance, cation and anion analysis. The rejections for select constituents above the detection limits and at relatively high concentrations are reported in Figs. 5, 6 and 7.

The TOC concentration in permeate streams was below 200 μg/L for all four membranes at both recovery regimes, with the TFC-ULP and TMG10 exhibiting slightly higher rejection of TOC than TFC-HR and NF-90 (Fig. 5). The rejection of aromatic organics in terms of UV absorbance at 254 nm, however, was slightly higher by the TFC-HR than the other three membranes during flow through and internal recycle experiments (Fig. 5).

The divalent cations, such as Ba, Ca and Mg, exhibited very high rejection by the tested membranes, above 99.3, 98.5, 99.5, and 99.5% by the TFC-HR, NF-90, TFC-ULP, and TMG10, respectively, during flow through and internal recycle regimes (Fig. 6). Silica was also well rejected with rejection above 96.6, 96.2, 98.1, and 98.3% by the TFC-HR, NF-90, TFC-ULP, and TMG10, respectively, during flow through and internal recycle regimes. The TFC-HR, TFC-ULP and TMG10 achieved a higher rejection of sodium than the NF-90 (>96.0% vs. 91.1–93.3%), during flow through and internal recycle regimes. Boron showed the lowest rejection among the detected components for all of the tested membranes, between 36.0–58.4% during flow through regime and 30.4–55.6% during internal recycling regime.

Iodide exhibited a much lower rejection (62.7–

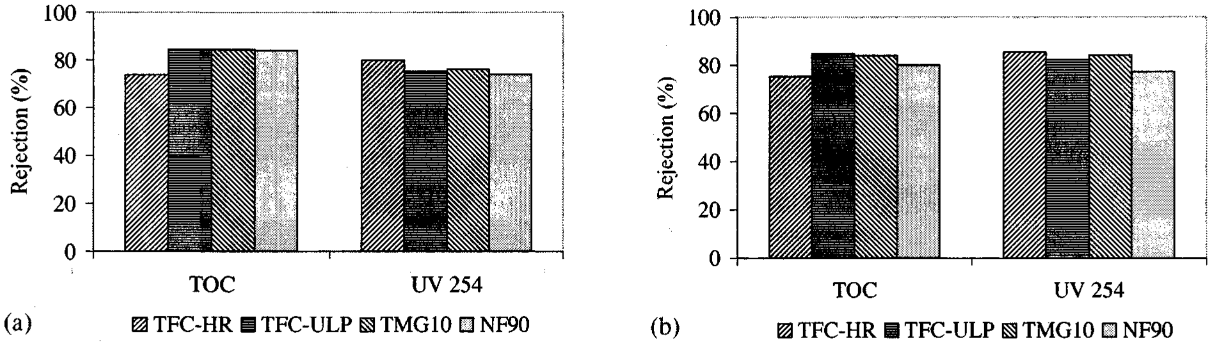

Fig. 5. Rejection of TOC and UV absorbance at 254 nm in (a) FT and (b) IR flow regimes.

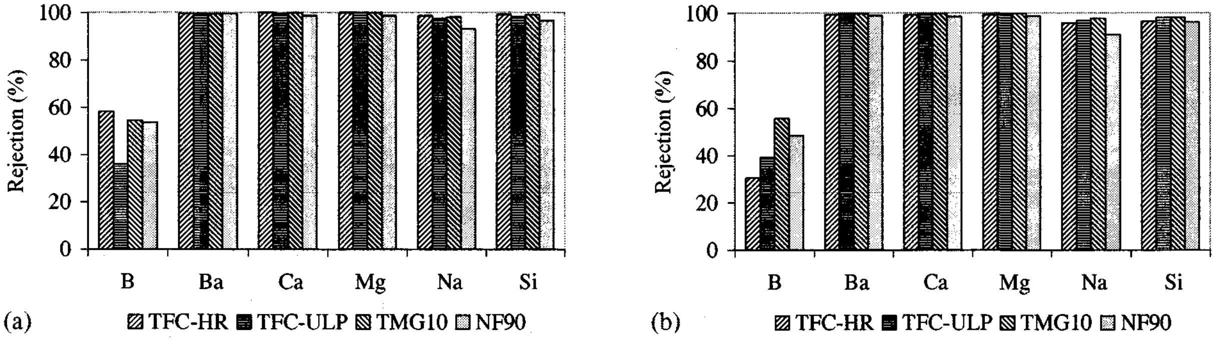

Fig. 6. Rejection of boron, barium, calcium, magnesium, sodium and silicon in (a) FT and (b) IR flow regimes.

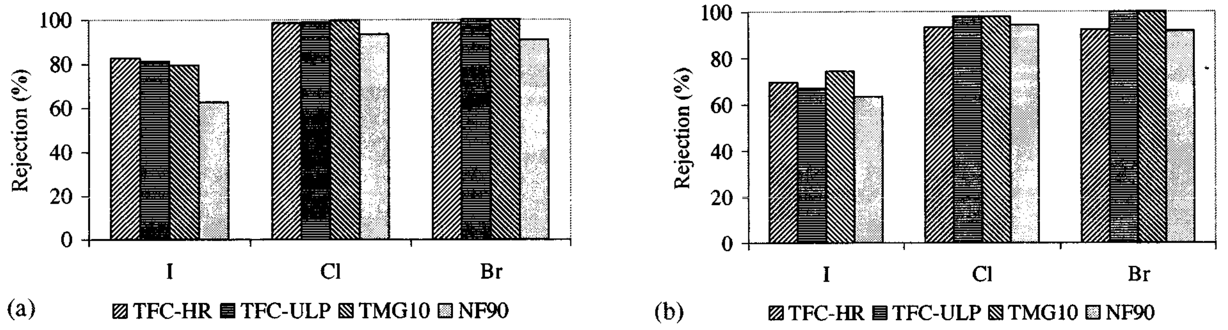

Fig. 7. Rejection of chloride, bromide and iodide in (a) FT and (b) IR flow regimes.

82.6%) by the four membranes as compared to chloride (93.1–99.6%) and bromide (90.7–>99.9%), while the NF-90 exhibited the lowest rejection of these constituents among the tested membranes (Fig. 7).

3.3 Membrane product water quality

A potential beneficial use of membrane treated produced water is for augmentation of potable water sources. Table 3 compares the key constituents of interest in membrane product water with USEPA National Primary and Secondary Drinking Water Regulations (primary standards and secondary standards). The constituents not listed in the table are those concentrations in the produced water below the detection limit or the drinking water standards. No trace pollutants of concern (such as arsenic, selenium, etc.) were detected in membrane treated water. The product water quality listed in Table 3 is the average value of permeates from flow through and internal recycle regimes simulating a composite final product quality.

The final product water from the RO and ULPRO membranes exhibited a quality which can meet USEPA primary and secondary drinking water standards. The permeate of the NF-90 could not meet USEPA secondary standards with regard to chloride and TDS.

Boron is another element of concern for applying treated produced water for beneficial use. Due to possible, despite controversial and inconclusive, toxic effects which impair growth in ani-

Table 3
Comparison of membrane final product water with water quality standards

Contaminant	Primary MCLs (mg/L)	Secondary MCLs (mg/L)	Average concentration (mg/L)			
			TFC-HR	TFC-ULP	TMG10	NF-90
Barium	2		0.01	0.03	0.01	0.02
Boron			2.5	1.9	1.9	2.6
Bromide			7.0	1.2	1.4	14.0
Chloride		250	190	74	78	372
Iodide			14.9	16.6	17.0	22.9
TDS		500	325	176	172	566
TOC			0.13	0.20	0.20	0.08

mals and cause nerve damage, the European Union regulates a 1 mg/L value for boron in the Drinking Water Directive [25]. In 1993 the WHO Guidelines for Drinking Water Quality proposed a 0.3 mg/L (later revised to 0.5 mg/L) standard for boron, while the United Kingdom established a standard of 2 mg/L for drinking water. In the United States, the USEPA included boron in the second Drinking Water Contaminant Candidate List (CCL) [26], and the California Department of Health Services (DHS) proposed 1 mg/L boron concentration as action level to provide guidance to drinking water systems for unregulated contaminants.

Boron is a naturally occurring element, usually prevalent in seawater and brackish ground water. The maximum concentration found in 1,546 samples of river and lake waters from various parts of the US was 5.0 mg/L, with a mean value of 0.1 mg/L [27]. Groundwaters could contain substantially higher concentrations at certain locations. The concentration in seawater is reported as 4–5 mg/L. Although boron is an essential element for plant growth, sensitive crops have shown toxic effects at 1.0 mg/L or less of boron. While the criterion of 750 μg/L is thought to protect sensitive crops such as citrus during long-term irrigation [27], most grasses are relatively tolerant at 2.0–10 mg/L of boron [28].

Boron often exists in the form of boric acid in aqueous solutions, which is a weak acid with a pKa of 9.2. Within the experimental pH range (6.0–6.1), boric acid exists primarily as the undissociated state (H_3BO_3), which resulted in the low rejection by RO and NF membranes. In this study, all the tested membranes exhibited a low rejection with the boron concentration in the final product water between 1.9 and 2.5 mg/L. Several options are available to achieve additional boron removal from the RO/NF product water.

(i) Increasing pH to above 9.5 (optimal at 10.5). Boron can be effectively removed by most thin film composite membranes. At this pH, membrane scaling, however, will be severe and frequent acid cleaning will be required. This will increase membrane operating cost and shorten membrane life time.
(ii) Two-pass membrane system. The permeate from the first membrane system flows into the second system with or without pH adjustment to remove boron. Membrane scaling associated with high pH operation is avoided and the operating pressure is low due to purer feed water quality entering the second pass. Currently, this is the most common practice to meet boron water quality specifications [29–32].
(iii) Using new commercial RO membranes which are effective for boron removal, such as the Hydranautics SWC4 RO membrane. These membranes can meet the WHO requirement in a single pass, but these are generally very tight membranes and reject boron by size exclusion [33,34]. Membranes are operated at very high pressure and scaling is an issue due to concentration polarization effects. Moreover, these techniques have not yet been adequately developed at the present time and will result in additional cost.
(iv) Using post-treatment by ion-exchange resin. However, this method is reported to be expensive [35].

Bromide and iodide are also of concern as the primary precursors to the formation of disinfection byproducts (DBPs) in drinking water. Although not regulated individually, CALFED, the California state and federal coalition that governs Delta water use, has the goal of achieving an average TOC concentration of 3 mg/L and bromide concentration of 50 μg/L or equivalent level of public health protection in their Drinking Water Quality Program [36]. Despite the relatively high concentration of bromide and iodide in the final product water (1.2–14 mg/L and 15–23 mg/L, respectively), the formation of DBPs is not problematic due to the low concentration of TOC (<200 μg/L). The effective removal of TOC by the RO and NF membranes significantly reduced the potential formation of DBPs.

The potential application of the membrane treated water for agricultural irrigation needs to consider the TDS level of the product water and the concentration of sodium, calcium, and magnesium ions. All of the tested membranes were capable of achieving an acceptable TDS concentration for irrigation (1,000 mg/L TDS). However due to the greater rejection of divalent ions than mono-valent ions, the final product water after membranes displayed a high sodium to calcium and magnesium ratio. High sodium concentrations not only reduce the clay-bearing soil's permeability, but also affect the soil structure. To estimate the degree to which sodium will be adsorbed by a soil from a given water, the sodium adsorption rate (SAR) has been developed (2)

$$\mathrm{SAR} = \frac{\mathrm{Na}^{+}(\mathrm{meq/L})}{\sqrt{\dfrac{(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+})(\mathrm{meq/L})}{2}}} \qquad (2)$$

For sensitive fruits, the tolerance limit of SAR value for irrigation water is about 4. For general crops a limit of 8–18 is generally considered within a usable range [28]. Therefore, without addition of calcium the membrane permeates would not be suitable for crop irrigation. Due to the low TDS of the product water, addition of a calcium source (e.g. calcium carbonate, gypsum, calcium chloride) can decrease SAR effectively. Compared to calcium carbonate and gypsum, addition of calcium chloride will result in higher concentrations of soluble calcium and should be the most effective way to lower irrigation water SAR. However, calcium chloride is considerably more expensive than calcium carbonate and calcium sulfate (gypsum).

3.4. Iodide recovery from membrane brine

Table 4 presents the iodide concentration in membrane brine during internal recycle operation.

Table 4
Iodide concentration in brine after membrane treatment

	TFC-HR	TFC-ULP	TMG10	NF-90
Iodide in raw feed (mg/L)	51	62	63	58
Iodide in brine (mg/L)	119	103	144	130

At the operating recoveries of 65 and 68%, the TMG10 displayed the greatest iodide recovery efficiency with 144 mg/L iodide in brine, followed by the NF-90 membranes with 130 mg/L iodide in the membrane concentrate. The TFC-ULP exhibited the lowest iodide concentration in brine of 103 mg/L due to the low operating recovery of 50%. Membrane treatment significantly increased iodide concentrations in brine, making commercial iodine recovery economically attractive.

Chile and Japan are the largest producers of iodine in the world and account for 99% of the US iodine import [23]. All domestic iodine production is from iodine-rich natural brines with concentrations exceeding 100 ppm in the deep subsurface of the Anadarko basin of northwestern Oklahoma [23]. The brine rich in iodide generated during membrane process can then be further treated by the methods commercially used to recover iodine from well brines, such as the chlorine-oxidation air-blowout method, activated carbon adsorption, copper wire precipitation, and ion exchange. Treatment efficiencies increase with elevated iodide concentrations in brines.

3.5. Cost analysis for membrane technology

Laboratory-scale experiments have demonstrated that the ULPRO membranes could provide product water of high quality and recover iodide at a comparable efficiency as the RO membrane. The ULPRO and NF membranes can be operated at the same flux as the TFC-HR, achieving a higher specific flux by requiring a much lower operating pressure. This means lower energy consumption and cost-saving from a practical standpoint. However, the tradeoff between treatment cost and water quality needs to be considered to better compare the ULPRO/NF with the RO membranes. Cost analysis for membrane technology was conducted for producing 1 mgd (million gallon per day) (3,785 m^3/d) of product water. Treatment to both the drinking water standard (500 mg/L TDS) and the irrigation water standard (1000 mg/L TDS) was evaluated. Permeate recovery was fixed at 75% for all calculations.

The proposed process schematic for a demonstration-scale membrane treatment is shown in Fig. 8. After degassing, produced water extracted from the gas production well is fed to a microfiltration unit using hollow fiber membranes to pre-treat the well water prior to NF/RO treatment. Pressure requirements for the MF are rather low around 210 kPa (~30 psi) and it is assumed that the MF can be operated with the head provided by the well extraction pump. The MF will operate at high recoveries (>95%) and needs to be regularly backwashed using MF filtrate. MF reject and backwash water can be disposed of through evaporation ponds. The MF is then followed by a single pass 2-stage RO or NF membrane system.

In this study, post-treatment of product water such as boron removal and SAR adjustment is not included in the cost analyses. The cost associated with membrane cleaning is also not included as part of the cost analyses. Because membrane concentrate will be potentially used for iodide recovery, brine disposal is eliminated from cost analyses.

3.5.1. *Water quality modeling and cost analysis for the Koch TFC-HR-400 and TFC-ULP-400 membranes*

Water quality modeling, considering an average quality as listed in Table 1, was performed with the ROPRO program, distributed by Koch, using the Koch TFC-HR-400 and TFC-ULP-400 membranes. We assumed that the water quality simulation and cost analysis would be the same for the TMG10 and the TFC-ULP because these two ULPRO membranes performed similarly during the laboratory testing. Blending with untreated water was considered to achieve the final product TDS to a goal of 450 mg/L for the drinking water standard or 900 mg/L for the irrigation water standard. This provides a safety factor of 10% under the regulations. Blending also increases the pH of the product water. Iodide, bromide and boron were added to the ROPRO database by including rejection values measured experimentally for the two specific membranes. Two-stage trains were configured by setting the flux at 0.65 $m^3/(m^2{\cdot}d)$ (16 gfd). Cost analysis was done using the COSTPRO program, using parameters listed in Table 5.

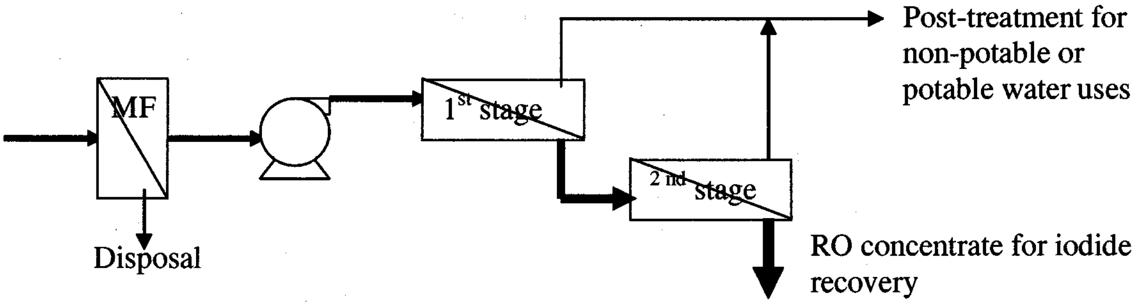

Fig. 8. Proposed MF and 2-stage RO or NF membrane treatment schematic for produced water.

Table 5
Values and sources of cost parameters

Parameter	Basis	Value	Source
Plant life		20 y	[20]
Interest rate		10%	
Capacity	Permeate	1 mgd	
Flux	Permeate	16 gfd	[20]
Remaining capital (in addition to initial membrane investment)	Permeate flow	\$549/mgd permeate	[20]
Membrane replacement	7 y membrane lifetime	\$795/element (TFC-HR) \$901 (TFC-ULP) \$900 (Dow NF-90)	Company software and vendor
Energy cost	Purchased from off-site	\$0.06/kWh	Local energy cost in Nov 2005
Pump efficiency	Overall efficiency	0.77	Hydranautics IMS design
Acid cost	37% HCl, including transportation to site	\$0.12/lb	DOW sales representative
Antiscalant dose	Concentration used in bench experiments	3.0 mg/L	[19]
Antiscalant cost	Bulk cost for 270 gallons including transportation	\$3.18/lb	GE Betz sales representative
Labor	1 mgd product	\$38,400/y	[20]

3.5.2. Water quality modeling and cost analysis for the NF-90 membrane

Water quality analysis for the Dow/Filmtec NF-90 membrane was simulated by using the Hydranautics ISE design program with the ESPA-3 membrane. The ESPA-3 was found to perform very similar to the NF-90 membrane with regard to operating pressure and product water quality. The NF-90 membrane was evaluated for meeting the irrigation water standard only because the permeate water quality exceeded the drinking water TDS level of 500 mg/L. Cost analysis was performed using the COSTPRO program, to be consistent with cost analysis of the other two membranes. The feed pressure, acid dosage, and number of elements required for the cost analysis were taken from the Hydranautics program output.

3.5.3. Determination of membrane configurations

For the NF-90 and for the Koch TFC ULP-400 treating to the drinking water standard, a two-stage 18×8 array with 6 elements per vessel provided the desired permeate flux near 16 gfd (0.65 $m^3/(m^2{\cdot}d)$). This represents a total of 156 8040 membranes for each system. For the other combinations, which included the ULP membrane treating to the irrigation water standard and the HR membrane treating to both standards, a 16×8 array using 144 elements fit the criteria. In these cases, the larger amount of water used for blending resulted in less feed water required.

3.5.4. Calculation of required acid dosages

Initial modeling showed that acidification was a large component of the total treatment costs.

Acid dose requirements were calculated by the ROPRO program using a target pH which was determined to be 0.2 pH units less than the pH value at which the Langelier index was greater than zero. Acid dosage was affected by membrane rejection; higher rejection corresponds to higher accumulation of ions in the concentrate, causing a high value for the Langelier index. For a membrane with lower rejection, precipitation of $CaCO_3$ can be avoided at a higher feed water pH. Acid dosages are independent of the water quality standard to be met.

A high proportion of the cost of treatment is due to acidification with HCl. Using sulfuric acid for pH adjustment was tested as an alternative. The total cost of treatment using acidification with sulfuric acid could be reduced by ~\$0.09/m^3 (\$0.33 per 1000 gallons of product) than using HCl. However, barium sulfate is supersaturated by a factor of 162 in the concentrate flow stream with sulfuric acid.

3.5.5. Neutralization of acid in product water

Product water pH is neutralized by two processes: carbon dioxide stripping and blending of raw feed water with the permeate. Permeate pH values before stripping or blending range from 4.85 to 5.34. After CO_2 stripping and blending, product water pH is increased to acceptable values, ranging between 6.88 and 7.34. Further acid neutralization of the product water with either caustic or lime should not be necessary.

3.5.6. Results of cost analysis

In comparing the costs associated with using the three different membranes, several cost advantages were apparent for both high and low salt rejection membranes. High rejection of salt led to increased blending flow. This results in a lesser flow rate of feed water to be pumped, and less water which must be treated with HCl and antiscalant. The feed flow rate factor which contributes to energy costs is also reduced. Low rejection of salt has the advantage of lower acid dosage. The TFC-ULP membrane array requires less pressure to operate than the TFC-HR system, but the NF-90 system requires very similar feed pressure as compared to the TFC-ULP.

The Koch TFC-ULP membrane system provides an overall cost of \$0.97 per 1000 gallons of product water to the drinking water standards. This is about 5% lower than the TFC-HR (Table 6). The TFC-ULP and NF-90 provided an identical cost for treating the average composition water to the irrigation water standard of \$0.89 per 1000 gallons, 6% lower than the TFC-HR. The treatment costs listed in Table 6 are based on an electricity cost of \$0.06/kWh, which is significantly lower than the cost in most parts of the country (\$0.10–\$0.15/kWh). Energy cost can remarkably impact the overall cost of treating produced water. Table 7 compares the total treatment cost at \$0.06, \$0.10, and \$0.15/kWh energy cost. In conclusion, the ULPRO membrane is much more cost effective in treating produced water than RO, and the ULPRO treatment cost is even lower than the NF membrane in meeting the irrigation standard with increasing energy cost.

The costs listed in Table 6 and 7 will likely increase by \$0.79 per 1000 gallons of product water due to MF pre-treatment [37]. The treatment costs in this study did not include the influence of membrane fouling during long-term operation. The treatment cost can increase significantly due to increased feed pressure to maintain constant permeate flux, clean-in-place, and shortened membrane life.

4. Conclusions

This research employed a 2-stage laboratory-scale membrane testing unit to examine the viability and cost-effectiveness of ULPRO/NF membranes for beneficial use of co-produced water in comparison with an RO membrane.

The NF-90 required the lowest pressure for producing a high permeate flux. The rejection of

Table 6
Results of cost analysis for the membrane systems designed for 1 mgd production (3,785 m^3/d)

System	Initial capital	Replace membranes	Chemical	Labor	Energy	Total costs	Total costs $\$/m^3$ ($ per 1000 gallons)
			$ per year				
Average water composition treating to the drinking water standard							
TFC-HR	55,000	16,300	162,800	38,400	99,600	372,100	0.27 (1.02)
TFC-ULP	59,400	20,100	155,600	38,400	79,000	352,500	0.26 (0.97)
Average water composition treating to the irrigation water standard							
HR	51,500	16,400	149,100	38,400	86,500	341,900	0.25 (0.94)
ULP	54,600	18,500	142,600	38,400	72,400	326,500	0.24 (0.89)
NF-90	59,200	20,100	128,200	38,400	80,000	325,900	0.24 (0.89)

Table 7
Total cost ($ per 1000 gallons of product water) at different energy costs

Energy cost ($/kWh)	0.06	0.10	0.15
Treating to the drinking water standard			
TFC-HR	1.02	1.20	1.43
TFC-ULP	0.97	1.11	1.29
Treating to the irrigation water standard			
TFC-HR	0.94	1.09	1.29
TFC-ULP	0.89	1.03	1.19
NF-90	0.89	1.04	1.22

the NF-90, however, was much lower in comparison with the TFC-HR, TFC-ULP and TMG10. The permeate of the NF-90 could not meet secondary drinking water standards in terms of TDS and chloride. The two ULPRO membranes exhibited a high permeate flux, displaying a similar rejection in comparison with the TFC-HR, notably the TMG10 which showed a very stable rejection at low and high recoveries. Calcium needs to be added in membrane product water to reduce SAR value prior to irrigation. All of the tested membranes exhibited a low rejection of boron which would require further treatment, if boron is regulated in drinking water standards or treated water is used for irrigation of sensitive crops. The TOC concentration in permeate of all tested membranes was below 200 μg/L, which reduces the DBPs formation associated with the presence of bromide and iodide in membrane product water. Membrane systems can recover 60–80% iodide from the produced water resulting in iodide concentration in the final concentrate exceeding 100 mg/L. Using membrane reject rich in iodide makes commercial iodine recovery economically attractive.

Cost analysis showed that the ULPRO membrane system provided marginally lower overall O&M costs than RO for meeting drinking water standards. The ULPRO membrane operation resulted in even lower treatment cost than RO and NF for meeting irrigation water standards, especially at high energy cost.

Multi-beneficial use of produced water can increase water supply, reduce the volume of the concentrate brine for disposal, lower environmental impacts from methane gas exploration, and therefore has a high potential to minimize crisis locally and regionally. The additional benefit of recovering iodide represents an important resource for the national economy besides methane gas and water production. The findings from the preliminary studies indicated that ULPRO membranes could provide a viable and cost-effective solution to beneficial use of produced water.

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Exhibit 2

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Brackish groundwater treatment by nanofiltration, reverse osmosis and electrodialysis in Tunisia: performance and cost comparison

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Abstract

The possibility of producing drinking water from brackish groundwater using nanofiltration (NF), reverse osmosis (RO) and electrodialysis (ED) processes was studied. Brackish groundwater samples were taken from the south of Tunisia (Gabes and Zarzis cities), and characterized in terms of pH, conductivity, hardness and inorganic matters. The results obtained in this work show that nanofiltration permits to reduce the concentrations of Ca^{2+}, Mg^{2+} and SO_4^{2-}, which are responsible for elevated sulfate hardness. The total dissolved salts of the produced water is equal to 1890 $mg.l^{-1}$. This is higher than the maximum value for drinking water fixed by the WHO at 500 $mg.l^{-1}$. Desalination of brackish groundwater by RO or ED might be technically and economically viable to cope with water scarcity and overcome the water deficit in Tunisia. The results showed that RO and ED were actually efficient since they highly reduced the content of inorganic matters present in raw waters. The treatment by RO or ED shows that the concentrations of ions in the obtained permeate (or the diluate) did not exceed the permissible WHO standards. ED seems to be the economical desalination process for Gabes water due to its low energy consumption whereas Zarzis water should be treated with the RO process.

Keywords: Brackish water; Desalination; Potable water; Nanofiltration; Reverse osmosis; Electrodialysis; Costs of processes

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1. Introduction

The 21st century is called the "century of water'' because of the coming water crisis due to the population increase and environmental destruction. Fresh water from rivers, lakes and groundwater totals only 0.01% of total water resources on earth [1]. Tunisia is characterized by an arid to semi-arid climate. With such a population growth rate (≈1.6%) and fast socio-economical development, water required and waste water production are steeply increasing, and the gap between water supply and demand is growing wider [2]. Tunisia has a water potential of about 4.3×10^9 m^3/y, of which 2.6×10^9 m^3/y represent surface water and the rest is distributed between subsoil and deep aquifers. The present use goes beyond 60% of surface water and 82% of underground water [3,4]. By the end of 2025, these resources will reach quantitative saturation, while the qualitative deficit has already been real for a long time [5].

Since the 1980s, Tunisia has resorted to the desalination of brackish water by membrane techniques to supply traditionally deficient regions with good-quality water and come up with a solution for industrial water utilities. Tunisia has more than 60 desalting units producing more than 95,000 m^3/d. Most of the desalination plants apply the reverse osmosis (RO) process (close to 80%) [6]. The National Drinking Water Agency was created to supply water to inhabitants and to operate desalination plants for drinking water. Right now, it owns and operates four RO plants with a total capacity of 56,000 m^3/d. Water desalination for urban supply in the Kerkennah islands started in 1983. Desalination activity has registered an important growth since 1995, when the RO plant of Gabes started to work with 22,500 m^3/d. Since 1999, two new RO plants in Djerba and Zarzis have been working appropriately. They have a production capacity of 15,000 m^3/d each [7–9]. All plants are fed by the water from a deep geothermal layer.

This study contributes to the development of efficient technologies to produce affordable drinking water in Mediterranean countries where the threat of water shortages is a severe problem. Membrane techniques are increasingly used for water treatment. In nanofiltration (NF), higher product water fluxes can be achieved at lower pressure than RO membranes. Electrodialysis (ED) is an electrochemical process for the separation of ions across charged membranes from a solution to another under the influence of electrical potential difference. As mentioned before, the RO technique is the most widely used in Tunisia for water desalination. The aim of this study is to compare the performances and the economical costs of three techniques (NF, RO and ED) applied to two brackish waters from the south of Tunisia.

2. Materials and methods

2.1. Brackish groundwater

Brackish groundwater samples were collected from the Gabes and Zarzis desalination plants located in the south of Tunisia. The water samples were pre-treated through a ventilated sand filter to reduce its contents in iron and to eliminate suspended matter. There are presented in Table 1. A common alternative method is to utilise the electrical conductivity reading and multiply by a standard factor (ranging from 0.50 to 0.70) to obtain the required total dissolved salts (TDS) result [10].The Gabes desalination plant treats mixed waters of Chott El Fejij's eight deep wells with an average of 2600 mg.l^{-1} on TDS. The TDS of Zarzis water is twice as high as that of Gabes, which is in keeping with conductivity values. The conventionally pretreated groundwaters have high concentrations of calcium, sulfate, chloride, sodium and elevated hardness (117°F for Gabes water and 123°F for Zarzis water). They do not show signs of pollution (roughly measured by NO_3^-) due to over-

Table 1
Physicochemical analysis of Gabes and Zarzis brackish groundwaters and the standards for drinking water fixed by the WHO [12]

	Gabes water	Zarzis water	Standards
pH	7.60	7.80	6.50–8.50
Turbiduty (NTU)	1.6	1.8	5
Conductivity (μS.cm^{-1})	4188	8400	—
TDS (mg.l^{-1})	2633	5292	500
Hardness (°F)	117	123	50
Alkalinity (°F)	10	14	—
Ca^{2+} (mg.l^{-1})	365	320	—
Mg^{2+} (mg.l^{-1})	64	106	—
Na^{+} (mg.l^{-1})	409	1430	250
K^{+} (mg.l^{-1})	42	55	—
Fe^{3+} (mg.l^{-1})	0.2	0.01	0.3
HCO_3^- (mg.l^{-1})	120	167	—
SO_4^{2-} (mg.l^{-1})	1040	1450	400
Cl^- (mg.l^{-1})	674	1900	250
NO_3^- (mg.l^{-1})	2	12	44
F^- (mg.l^{-1})	1.28	1.2	1.5

exploitation (leading to aquifer salinisation) but they present a major risk to users in different sectors (domestic or industrial) [11]. The NF test was performed with only Gabes water; RO and ED experiments were established with Gabes and Zarzis waters.

2.2. Equipment and membranes

2.2.1. NF and RO experiments

NF experiments were established in a Microlab 40 plant (Fig. 1) equipped with a tubular membrane from Gamma Filtration (MPT 03) which has the following characteristics: material in polyamide and polyethersulfone, molecular weight cut-off 200 Dalton, permeability in deionized water 87 l.h^{-1}.m^{-2} (measured at 20 bars and 30°C), length 0.82 m, diameter 127×10^{-4} m and surface membrane used (0.033 m^2). We have adopted the following experimental conditions: natural pH, pressure 20 bars, room temperature 25°C and circulation speed 2.5 m.s^{-1}.

For RO, a pilot plant was equipped with a Filmtec RO spiral membrane (Nanomax 95) which has the following material characteristics: polyamide, length 30.5 cm, and membrane surface used, 0.4 m^2. RO tests were established at 15 bars, 25°C, natural pH and VRF = 3 for Gabes water and VRF= 2 for Zarzis water.

2.2.2. Electrodialysis

In a typical ED cell, a series of anion- and cation-exchange membranes are arranged in an alternating pattern between an anode and a cathode to form individual cells. At the end of ED tests, ion concentrations increase in alternating compartments, with a simultaneous decrease of ions in other compartments [13]. Aqualyser P1 (Corning, EIVS, France) equipment was employed for ED experimental studies. A schematic view of the experimental set-up is shown in Fig. 2 [14]. The equipment contains a stack with 20 pairs of CMV cationic membranes and AMV anionic membranes with 0.27 m^2 area. A rectifier is provided to supply a DC power at constant voltage (max. 30 V) or constant current (max. 3 A). The pilot consists of three hydraulic circuits:

- a circuit for the solution to process which impoverishes selectively an ion is called the "diluate" circuit.
- a circuit of concentration which salinity increases vs. time, called the "concentrate" circuit.
- a circuit for electrode rinsing.

Three solution tanks are used for holding the diluate, the concentrated and the electrode rinse solutions. Volumes of solutions contained in three circuits are measured equally (1 L each). Three pumps were used: pumps stake in step and the current established. For the ED experiments, 25 V of DC potential were fixed. Concentrate and

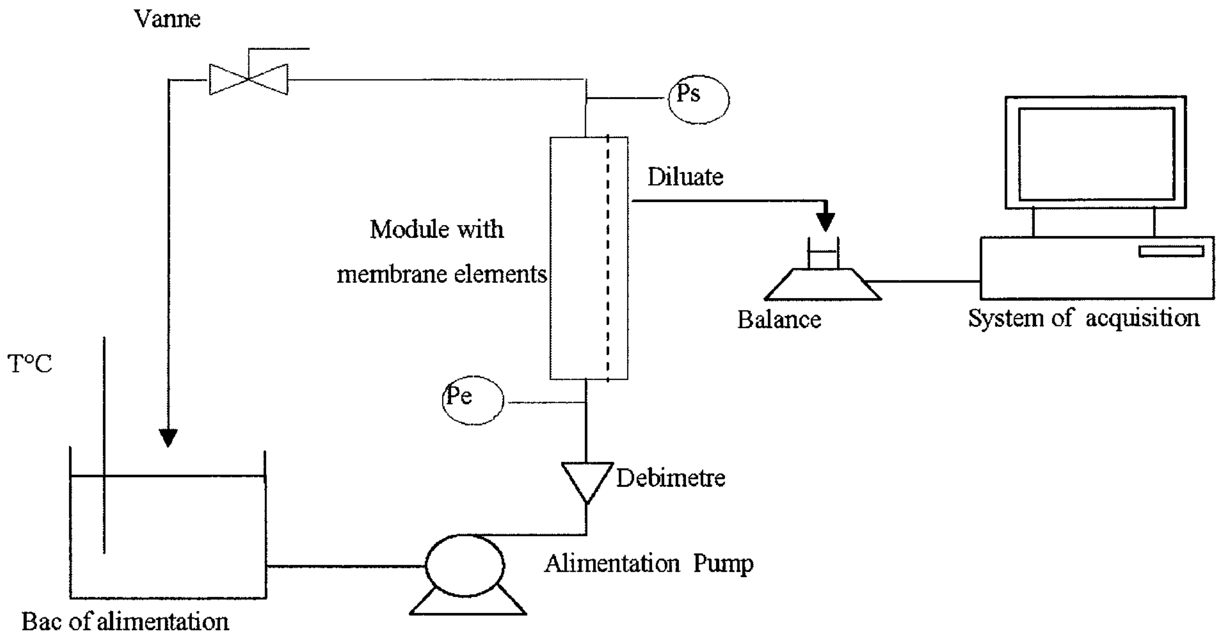

Fig. 1. Scheme of the NF set-up.

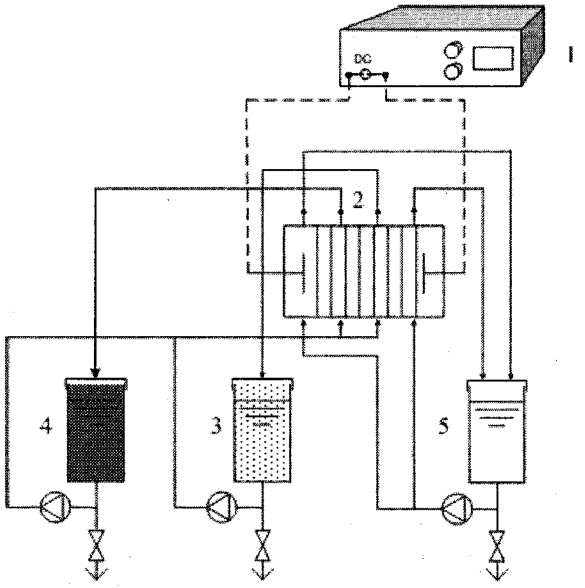

Fig. 2. Schematic representation of electrodialysis pilot. 1 power supply, 2 membrane cell, 3 diluate compartment, 4 concentrate compartment, 5 rinsing electrode compartment.

rinsing circuits can be filled with a solution of 10 $g.l^{-1}$ NaCl. Each test, carried out batchwise, lasts 12 min for Gabes water and 18 min for Zarzis water. Diluate samples were taken for analysis every 2 min for Gabes water (3 min for Zarzis water).

2.3. Analysis

Concentrations of Na^+, Ca^{2+}, Mg^{2+}, Cl^- and SO_4^{2-} are determined by ionic chromatography (Dionex DX 120) equipped with a CS 12 A column for cations and an AS 12 A column for anions. Alkalinity was obtained by titration to a fixed pH while conductivities were measured by a conductimeter (Consort K911).

Following through concentrations in the diluate allows to calculate the rejection rate using the following relation:

$$TR\ (\%) = (1 - C_{pi}/C_{oi}) \times 100$$

where C_{oi} and C_{pi} are the initial and final concentrations of the considered species.

The measure of solution volumes of concentrate and permeate at the end of treatment (by RO or NF) allows to calculate the volumic reduction factor (*VRF*), the water recovery ratio (*Y*) and to establish the mass balance using the relations:

$$VRF = V_i/V_r;\ Y(\%) = V_p/V_i \times 100$$

and

$$\text{mass balance} = C_iV_i = C_pV_p + C_rV_r$$

where V_i, V_p and V_r represent the initial, permeate and concentrate volume, respectively. C_i, C_p and C_r represent the concentration of cations or anions in raw water, permeate and concentrate, respectively.

3. Results and discussion

3.1. Results obtained by NF

Fig. 3 shows the evolution during 30 min of the concentration flux which is constant (around 100 l.h^{-1}.m^{-2}) during the NF test of Gabes water. The plugging phenomenon could be neglected until the volumic reduction factor reaches 3. In fact, from 3 L of Gabes water to desalination, we obtained 2 L of permeate and 1 L of concentrate. Table 2 shows the results of the chemical analysis of the Gabes raw water, the concentrate and the permeate ones.

The NF treatment allows a partial improvement of the quality of the desalination Gabes water. The results obtained in this research have shown the possibility to reduce the Ca^{2+}, Mg^{2+}, and SO_4^{2-} concentrations which are responsible for sulfate hardness. Na^+ and Cl^-, which are responsible for the salinity, were not significantly retained with this process. The rejection rate for Cl^- ions is extremely low because the membrane is negatively charged [15]. SO_4^{2-} could be an impermeable ion while Cl^- could transfer far more easily. Sulphate ions are almost retained while Na^+ can pass through the membrane, leading to an excess of positive charge on the permeate side. This excess generates an electrostatic force which increases anion transfer, particularly of Cl^- because SO_4^{2-} cannot cross the membrane. The electrostaic force also reduces cation transfer (Na^+) and therefore increases the Na^+ rejection rate. Anions and cations cannot permeate independently, but permeate the membrane while maintaining electroneutrality [16]. This phenomenon is called the Donnan effect [17]. The diffusion effect can be an additional reason for

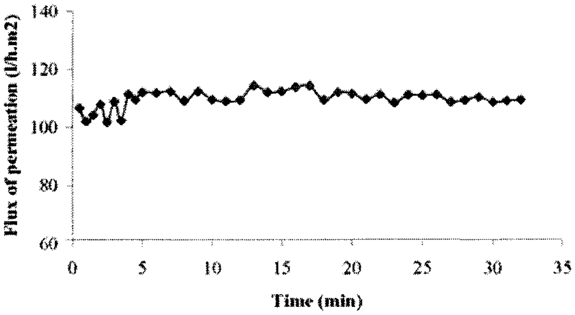

Fig. 3. Variation of flux vs. time. Membrane: MPT 03, pressure: 20 bars; temperature: 25°C; circulation speed: 2.5 m.s^{-1}.

Table 2
Chemical analysis of Gabes raw water, permeate and concentrate

	Raw water	Permeate	Conc.	*TR* (%)
Conductivity (µS.cm^{-1})	4180	3000	5550	—
TDS (mg.l^{-1})	2633	1890	3496	—
Ca^{2+} (mg.l^{-1})	365	210	665	42.5
Mg^{2+} (mg.l^{-1})	64	39.5	136	38.3
Na^+ (mg.l^{-1})	409	316	613	22.7
Cl^- (mg.l^{-1})	677	674	681	≈0
SO_4^{2-} (mg.l^{-1})	1040	342	2321	67.1

Table 3
Cation and anion mass balance

	C_iV_i	$C_pV_p + C_rV_r$	Error (%)
Ca^{2+}	1095	1085	0.9
Mg^{2+}	201	215	6.7
Na^+	1227	1245	1.4
Cl^-	2022	2039	0.8
SO_4^{2-}	3120	3005	3.7

ion removal. Ions with the lowest diffusion coefficient characterized the highest retention whereas ions with the highest diffusion coefficient had the lowest retention of Cl^- [18].

The obtained permeate has a TDS of 1890 mg.l^{-1}, which in this case could not be considered as drinking water quality. The maximum value of TDS for drinking water given by the WHO is fixed at 500 mg.l^{-1} [12]. We calculated the mass balance (Table 3). The result shows that the mass balance was respected. After treatment by the NF process, the membrane was washed with demineralized water. Results show that after rinsing, the membrane had the same initial permeability.

The Zarzis water is richer in chloride and sodium than the Gabes water. By NF and with Gabes water, Na^+ and Cl^- were not retained. In this case, the possibility of producing drinking water from the Zarzis sample using NF under the same conditions is very difficult.

3.2. Results obtained with the RO process

The experimental conditions were determined to obtain a permeate with low salinity acceptable for human consumption (high retention of monovalent and bivalent ions), with reasonable flow and low energy consumption. To satisfy these conditions, we demonstrated that the pressure must be equal to 15 bars and the VRF to 3 for Gabes water and VRF to 2 for Zarzis water. With Gabes water, the TDS of the permeate is lower (≈330 mg.l^{-1}) than the WHO standard while it is slightly higher than Zarzis water. Tables 4 and 5 show that RO is efficient to remove the inorganic content matter from the Gabes and Zarzis brackish groundwaters, converting them into drinking water suitable for human consumption. The concentrations of ions in the permeate did not exceed the permissible WHO standards except that the chloride concentration in the permeate obtained from Zarzis water slightly exceeded the WHO standards but not the Tunisian Drinking Waters Standards (the maximum allowable limit for TDS value and chloride concentration were 800 and 400 mg.l^{-1}, respectively). For Gabes water, the quality of drinking water treated this way would be above the water quality aimed for at the water treatment plant. A blend of RO water and conventionally treated water could still satisfy the water standards and exceed the current quality of drinking water of the water treatment plant.

The retention of bivalent ions was higher than that of monovalent ones. The difference of retention can be attributed to the difference of energy hydration of the latter (Table 6); the more hydrated these ions, the more difficult their transfer across the membrane [19]. Consequently, SO_4^{2-} ions, which are more strongly hydrated than Cl^- ions, become difficult to permeate through the membrane. We note that the rejection rates of anions or cations for Zarzis water are higher than those of Gabes water. The rejection rates increase with the salinity of water.

3.3. Results obtained with the ED process

In the ED experiments, 25 V DC potential was fixed for two samples of brackish water: Gabes and Zarzis waters. In Fig. 4 the variation of conductivity of Gabes water vs. ED time is plotted. The figure shows a decrease of the conductivity of diluate during the electrodialysis process, which is in agreement with the decrease of global mineralisation. The conductivity around 1000 µS.

Table 4
Chemical analysis of Gabes raw water, permeate and concentrate (VRF = 3)

	Raw water	Permeate	Concentrate	TR (%)
Conductivity (μS.cm^{-1})	4250	598	8590	—
TDS (mg.l^{-1})	2677	328	5411	—
[Ca^{2+}] (mg.l^{-1})	365	25	1027	93.1
[Mg^{2+}] (mg.l^{-1})	70	5	165	92.8
[Na^{+}] (mg.l^{-1})	409	74	1046	81.9
[Cl^{-}] (mg.l^{-1})	674	150	1545	81.8
[SO_4^{2-}] (mg.l^{-1})	1040	80	2950	95.00

Table 5
Chemical analysis of Zarzis raw water, permeate and concentrate (VRF= 2)

	Raw water	Permeate	Concentrate	TR (%)
Conductivity (μS.cm^{-1})	8400	1160	12460	—
TDS (mg.l^{-1})	5292	638	7850	—
[Ca^{2+}] (mg.l^{-1})	320	10	528	96.8
[Mg^{2+}] (mg.l^{-1})	106	3.4	175	96.8
[Na^{+}] (mg.l^{-1})	1430	183.5	2216.5	87.2
[Cl^{-}] (mg.l^{-1})	1900	284	2722.5	851
[SO_4^{2-}] (mg.l^{-1})	1450	61	2190	95.7

Table 6
Ionic radius, hydrated ionic radius and hydration energy for studied ions [19]

Ion	Ionic radius (nm)	Hydrated ionic radius (nm)	Hydration energy (KJ.mol^{-1})
Na^{+}	0.095	0.365	407
Mg^{2+}	0.074	0.429	1921
Ca^{2+}	0.099	0.349	1584
Cl^{-}	0.181	0.347	376
SO_4^{2-}	0.230	0.380	1138

cm^{-1} (TDS ≈500 mg.l^{-1}) was obtained after 10 min of ED for the Gabes water. The evolution of anion concentration in the diluate compartment during the ED test of the Gabes water is illustrated in Fig. 5. One observes that the contents of

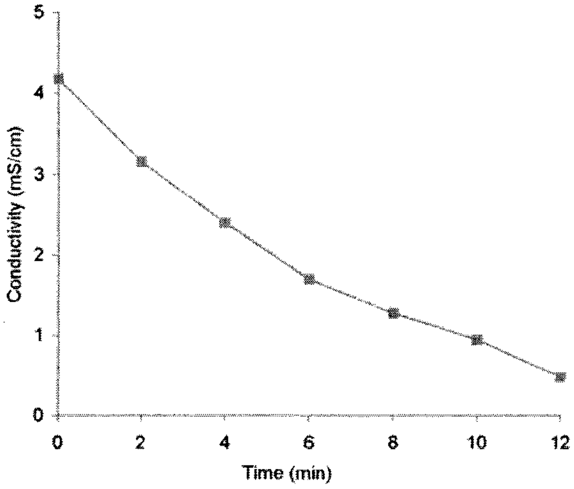

Fig. 4. Variation of conductivity of Gabes water vs. ED time.

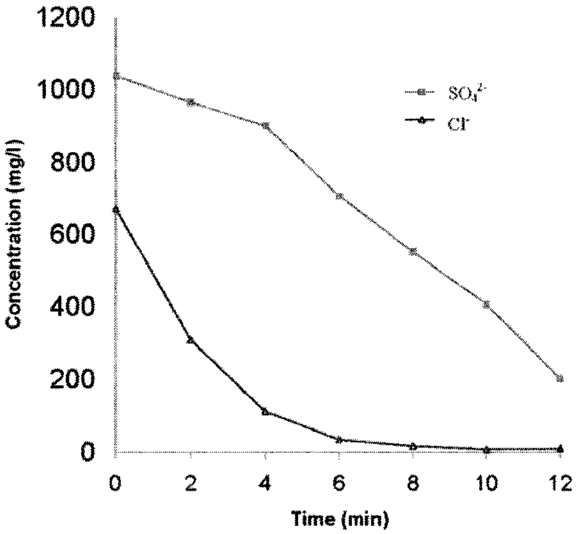

Fig. 5. Evolution of anions concentration vs. time of ED (Gabes water).

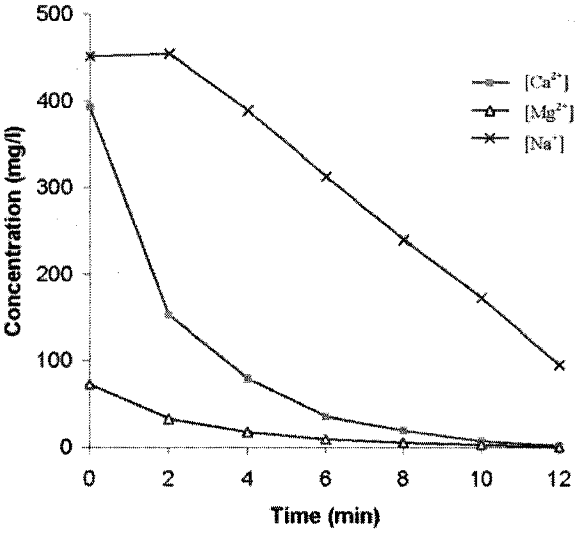

Fig. 6. Evolution of cations concentration vs. time of ED (Gabes water).

chloride in the diluate compartment decrease far more than the contents in sulfate. The SO_4^{2-} ions, which are strongly hydrated, are less removed from the diluate compartment to the concentrate compartment.

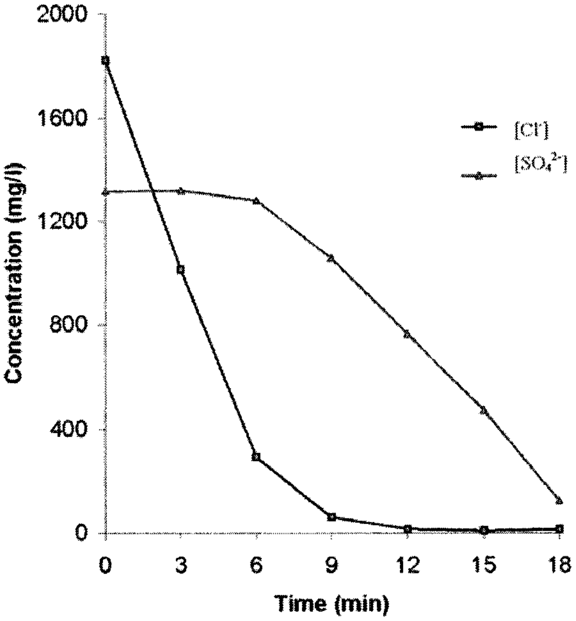

Fig. 7. Evolution of anions concentration vs. time of ED (Zarzis water).

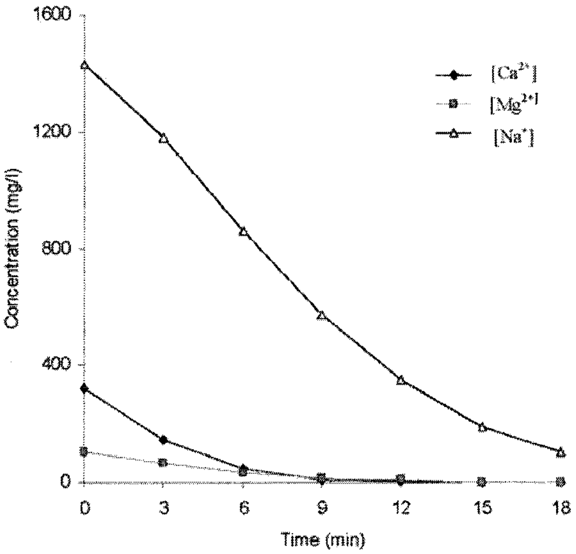

Fig. 8. Evolution of cations concentration vs. time of ED (Zarzis water).

The evolution of the concentration of cations (Ca^{2+}, Mg^{2+} and Na^+) in the diluate compartment is illustrated in Fig. 6, which indicates that cations cross the membranes with various velocities. This is due to their characteristics, especially hydration energy. The divalent ones, which are strongly hydrated, are less removed from the diluate. Besides energy hydration, the hydrated ionic size of cations and anions (Table 6) may have an additional effect [20]. The bulkier the ion, the more it is retained by the membrane. The same results are obtained with the Zarzis water sample; the TDS value around 500 mg.l^{-1} was obtained after 15 minutes of ED (Figs. 7 and 8).

All figures clearly show that it is necessary to avoid making the ED longer than 10 min for the Gabes and 15 min for the Zarzis waters because the escape of anions and cations then increases considerably.

4. Economic evaluation

The complete economic evaluation should take into account the initial cost and the maintenance cost. The initial investment (including building construction, pumps, piping energy cabling and transformers, electronic components, automation, membrane, filters, plant design and assembling) is assumed as proportional to membrane area and it is depreciated linearly over 20 years without considering the interest on investment. The cost of maintenance, which corresponds to the control of the operating condition of the installations and the loads of investment due to the change of faulty equipment and consumable, varies between 5 to 10% per year from the cost of the installation [21,22].

In this study, the economic evaluation was based only on the energy consumption calculation during RO and ED techniques which are used to desalinate the two samples of brackish groundwater from the south of Tunisia. The energy consumption was calculated in the experimental conditions (batch mode in ED and one pass in RO) using the models of Strathmann [23] for ED and of Maurel [24] for RO.

4.1. Energy requirements in a pratical ED desalination process

The total energy requirement in a practical ED process is the addition of four terms [23]:

- the energy required to transport ions from a feed to a concentration solution,
- the energy necessary to pump the solution through the stack from a feed solution reservoir to the product tank and brine disposal,
- the energy consumed by the electrode reactions and,
- the energy required to operate various process controls and measuring instruments.

The specific energy required in the ED desalination process is given by [23]:

$$E_{prac/spec} = \frac{N_{cell}}{A_{prac}Q_{prac}}\left[\frac{\Delta \ln \dfrac{C_s^{fd}C_s^{c}}{C_s^{fc}}}{\Lambda_s\left(C_s^{fd}-C_s^{d}\right)}+r^{am}+r^{cm}\right]\left[\frac{Q_{prac}F\left(C_s^{fd}-C_s^{d}\right)}{N_{cell}\xi}\right]^2$$

Here $E_{prac/spec}$ is the desalination cost in ED per unit product, N_{cell} is the number of cell pairs in a stack, C_s^{fd} and C_s^{fc} are the equivalent concentrations of the diluate and the concentrate at the cell inlet, C_s^{d} and C_s^{c} are the concentrations of the diluate and the concentrate at the cell outlet. Λ_s is the equivalent conductivity of the salt solution, r^{am} and r^{cm} are the area resistance of the anion- and the cation-exchange membrane, Δ is the thickness, ξ is the current utilization, Q_{prac} is the diluate flow stream of the entire stack and A_{prac} is the practically used cell pair area.

The energy needed to pump represents approximatively 20% of the energy required to transport ions [23]. Pumping energy requirement was independent of the feed solution concentration.

The energy consumed by the electrode reaction and required for operation of the control and measuring instruments is generally neglected or taken as a fixed item which is between 1 and 3% of the energy used for ion transfer and pumping of the solutions [23]. The total energy requirements in a practical ED process increase strongly with the feed solution concentration when the product concentration and all other parameters are kept constant.

4.2. Specific energy required in a practical RO desalination process

The specific energy required (water transport energy across the membrane and the pumping transport energy) in a practical RO desalination process is given by [24]:

$$W = P.d/36.7.\eta_p.Y$$

where P is the repulsing pressure, d the density of water, η_p the output pump and Y the water recovery ratio (%).

The ratio of pumping transport energy in the system against the water transport energy across the membrane is equal to 1.4 [25]. In the majority of the current RO installations, the circuit of concentration is reduced in pressure throuth a valve. The energy contained in the high pressure fluid can be recouped either by means of turbine or by means of a system with pistons. The recuperated energy is given by:

$$W_{tur} = \frac{1}{36.7}(P - \Delta P).\eta_{tur}.\left(\frac{1}{Y} - 1\right)$$

where P is a loss of pressure and η_{tur} is the output turbine. In this case the real consumed energy is thus the difference between energy of pumping and the energy recovered by the turbine:

$$W = \left(\frac{P.d}{36.7.\eta_p.Y}\right) - \frac{1}{36.7}(P - \Delta P).\eta_{tur}.\left(\frac{1}{Y} - 1\right)$$

Table 7
Consumption energy for Gabes and Zarzis water desalination with RO and ED processes

	Energy consumption ($kWh.m^{-3}$)	
	RO process	ED process
Gabes water	0.81	0.53
Zarzis water	1.09	1.50

If the pressure recovery process is integrated in the RO process, the energy consumption might be decreased. However, in our case, the saving of energy would be only about 15% (calculated according to the last relation ($\eta_{tur} = \eta_p$) and it would be necessary to hold account of an important additional investment.

The parameters used in the calculation of the required energy for Gabes and Zarzis waters are given in the Appendix. The results of the calculation of energy consumption to produce 1 m^3 of desalinated water are shown in Table 7. They show that the energy consumption increase with increasing feed solution concentration. This case is valid for either RO or ED treatment processes because this energy is proportional to the quantity of salt to eliminate. For Gabes brackish groundwater, ED appears the more economic desalination process because of its low energy consumption, whereas the Zarzis water would be treated with the RO process. The obtained results are in accordance with other calculations for RO for drinking water purposes [22, 24, 26].

5. Conclusions

The possibilities of producing drinking water from brackish water collected from the south of Tunisia using NF, RO and ED processes were studied. We conclude from this study that:

- NF could ensure the reduction of bivalent ions. The NF process was insufficient to obtain drinking water from the Gabes water sample: the TDS of the permeate obtained with this process was superior to the standard value authorized by the WHO.

- RO is actually efficient since it sharply reduced the content of inorganic matters present in raw waters (rejections >80%). After treatment, the obtained permeate has a low value of TDS, which is accepted by WHO because this salinity is necessary for human consumption of drinking water.
- ED tests lasted 10 min for Gabes water and 15 min for Zarzis water. They obtained a diluate which has a lower value of TDS, beyond 500 mg.l^{-1}.
- ED appears the economic desalination process for Gabes brackish groundwater because of its low energy consumption, whereas the Zarzis water would be treated with the RO process.

Acknowledgement

We thank Mr. Courfia K. Diawara, University Cheikh Anta Diop, and Dakar Fann, Senegal, for their observations. We wish to thank Mrs. Maryse Derouiniot, Centre of Research and Transfer of Technologies (CRTT), Nantes, France, for assistance in experiments.

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Appendix
Parameters used in the calculation of required energy for Gabes and Zarzis waters

A.1. Using the ED process

		Gabes Water	Zarzis Water
Number of cells	N_{cell}	20	20
Total area of membrane	A_{prac}	0.27 m^2	0.27 m^2
Concentration feed inlet	C_s^{fd}	84.10^{-3} keq.m^{-3}	170×10^{-3} keq.m^{-3}
Concentration diluate outlet	C_s^d	7×10^{-3} keq.m^{-3}	10×10^{-3} keq.m^{-3}
Equivalent conductance of solution	Λ	7.5 S m^2 keq^{-1}	7.5 S m^2 keq^{-1}
Cell thickness	Δ	1.1×10^{-3} m	1.1×10^{-3} m
Faraday constant	F	9.65×10^7 As keq^{-1}	9.65×10^7 As keq^{-1}
Total area resistance of membranes	r^{am}, r^{cm}	0.0007 Ω.m^2	0.0007 Ω.m^2
Concentration concentrate inlet	C_s^{fc}	170×10^{-3} keq.m^{-3}	170×10^{-3} keq.m^{-3}
Concentration concentrate outlet	C_s^c	247×10^{-3} keq.m^{-3}	330×10^{-3} keq.m^{-3}
Current efficiency	ξ	0.8	0.8

A.2. Using the RO process

Pressure	P	15 bars
Water density	d	1
Output pump	η_p	0.8
Water recovery ratio	Y	66.6% for Gabes water and 50% for Zarzis water

Exhibit 3

Desalination 250 (2010) 1016–1018

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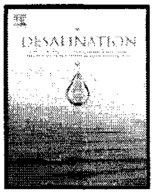

Advanced performance evaluation of a reverse osmosis treatment for oilfield produced water aiming reuse☆

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Produced water
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ABSTRACT

Technology advancements and the increasing need for fresh water resources have created the potential for desalination of oil field brine (produced water) to be a cost-effective fresh water resource for beneficial reuse. At the mature oil and gas production areas in the northeast of Brazil, the majority of wells produce a substantial amount of water in comparison with oil production (more than 90%). At these fields, the produced water has to be treated on site only for oil and solids removal aiming re-injection. The aim of this work is to assess the quality of the produced water stream after a reverse osmosis desalination process in terms of physicochemical characteristics influencing reuse of the water for irrigation or other beneficial uses.

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1. Introduction

The water scarcity in the world has already been forecast figuring one of the greatest challenges of the 21st Century, and disclosures the need for water reuse, which represents a potential possibility for sustainable development. From an industrial point of view, two other questions also related to the utilization of water must also be taken into consideration: costs with the input itself, and the steps required to achieve each industry particular specifications and volume of generated effluents, which shall represent added costs with water disposal and/or treatment. The current regulating agencies trend is to charge water impounding and disposal, thus, increasing industrial costs.

Moreover, in what concerns oil industry, produced water reuse is getting more important as oilfields are reaching their mid-life or maturity of production, and water generation associated with oil production is growing considerably and may reduce the sustainability factor of oilfields drastically [1]. Besides, the growing demand for water in industrial processes may affect the local environment in a significant way. Likewise, water scarcity, especially in the semi-arid northeast of Brazil, makes water reuse a factor of high priority and attractiveness.

The objectives of this study were (1) to determine the efficacy of a pilot-scale reverse osmosis (RO) and nanofiltration (NF) system for treatment aiming reuse of produced waters from a specific oil field, and (2) to assess the quality of treated water in terms of physicochemical characteristics influencing reuse of the water for irrigation or other beneficial uses. For the field experiments, the actual produced water was used from a PETROBRAS production site in order to evaluate the performance of the system in terms of rejection of inorganic and organic compounds, which are considered important for irrigation purposes.

2. Materials and methods

2.1. Experimental set-up

The experimental set-up of the system used during the field experiments is showed in Fig. 1 and the characteristics of the pilot-scale RO/NF unit are summarized in Table 1. A series of pretreatment steps was initially performed at the produced water treatment full scale plant before applying it to the RO/NF membrane. Pretreatment includes basically passage through oil/water separator, warm softener, sand filters, ion exchange softener and cartridge filter (1.0 μm).

After the pretreatment, the produced water was continuously fed to a high-pressure multi-stage centrifugal pump in order to provide the necessary flow (3.5 m^3/h) and pressure (up to 15 bar) for efficient membrane operation. It is important to note here that the primary objective of this study was not to optimize the efficiency of the membrane system, but to decrease the concentration of salt and other organic pollutants in the produced water aiming beneficial purposes.

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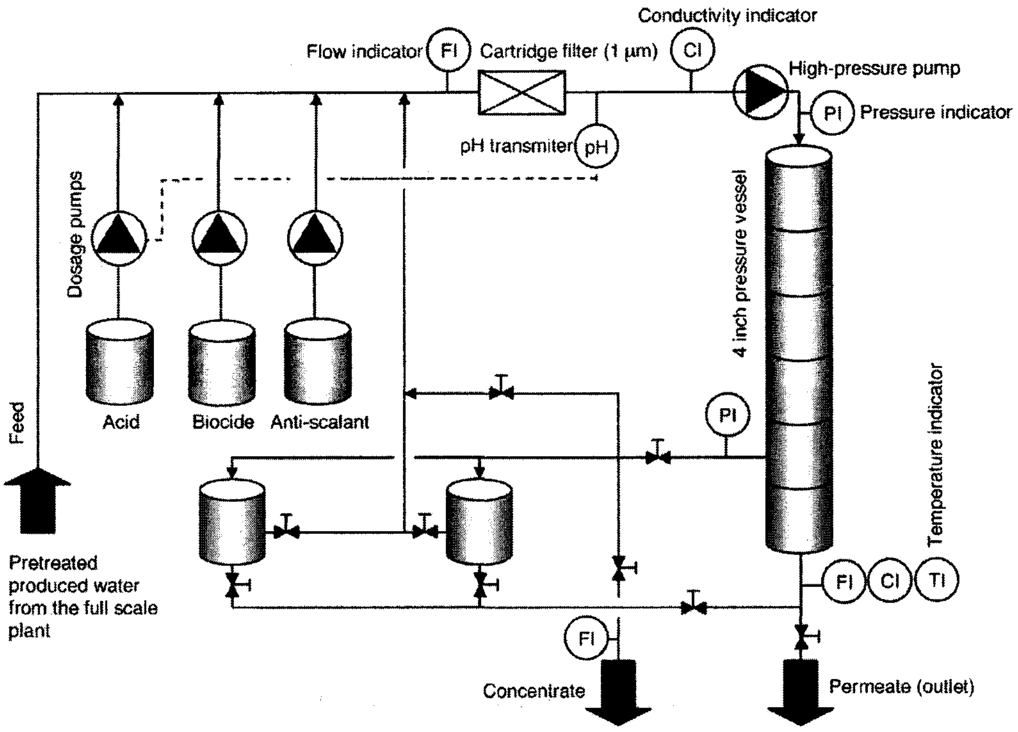

Fig. 1. Experimental set-up.

3. Results and discussions

The results for produced water characteristics prior to treatment and after treatment with RO and NF membranes operated with pH of 7.0 and 9.5 are presented in Table 2.

It is important to note, considering the analysis showed in Table 2, that the quality of the produced water before the membrane treatment is very good indicating its big potential for reuse for beneficial purposes.

Furthermore, both RO and NF treatment systems transformed the raw produced water from oil wells, that was unsuitable for discharge, into a very good quality water, suitable for surface water disposal or for reuse purposes. On the other hand, additional considerations when meeting water quality guidelines for irrigation may include toxicity.

In addition, due to the fact that the membranes tend to remove the majority of the salts from the raw produced water, it will be necessary to add some elements in the water in order to use it for irrigation, such as calcium, magnesium, and other nutrients.

Table 1
Specifications for the pilot-scale RO/NF unit.

Parameter	Reverse osmosis	Nanofiltration
Membrane size	9.75 × 100 cm spiral-wound cross-flow	
Total surface area	7.6 m^2	
Material	Polyamide	
Operating temperature	40 °C	
Operating pressure	15 bar	10 bar
Operating flow rate	2.5 m^3/h	

4. Conclusions

The important findings from this work are summarized as follows:

- The pilot-scale RO/NF unit effectively decreased conductivity and TDS in the considered produced water and reduced the concentration of several water quality parameters considered important for beneficial reuse.
- The treatment of the studied produced water using membrane processes met the overall objective of this study, which was to achieve water suitable for beneficial use.
- Additional considerations when meeting water quality guidelines for irrigation should include toxicity. Furthermore, it is also important to investigate the influence of this water on the soil and its effects on the crop yields. All these studies are being carried out in order to implement the produced water reuse for irrigation purposes in the northeast of Brazil.

Reference

[1] T. Pedenaud, TOTAL experience to reduce discharge of hydrocarbons through produced water, SPE International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production, 2006.

Table 2
Constituent concentrations in produced water after and before the RO and NF treatment for pH values of 7.0 and 9.5.

Parameter	Goal[a]	Reverse osmosis				Nanofiltration			
		pH = 7.0		pH = 9.5		pH = 7.0		pH = 9.5	
		Feed	Outlet	Feed	Outlet	Feed	Outlet	Feed	Outlet
Alkalinity	mg/L[b]	188	24	185	30	158	28	376	39
Aluminum	<0.05 mg/L	0.01	0.01	0.01	0.01	0.012	0.045	0.01	0.01
Ammonia	<0.50 mg/L	0.8	0.5	0.8	0.3	2	0.3	0.02	0.02
Antimony	<5 µg/L	2	2	2	0.2	2	2	5	5
Barium	<0.7 mg/L	0.01	0.01	0.1	0.1	0.018	0.01	0.028	0.01
Benzene	<1 µg/L	<5	<5	<5	<5	1.3	<1	<5	<5
Bicarbonate	mg/L[b]	162	32	159	30	138	38	–	–
Boron	<0.5 mg/L	0.252	0.125	0.475	0.071	0.262	0.284	0.449	0.563
Bromate	<0.01 mg/L	0.01	0.01	0.01	0.01	0.01	0.01	0.05	0.005
Calcium	<250 mg/L	0.7	0.1	0.66	0.1	0.59	0.1	2	0.5
Carbonate	mg/L[b]	28	10	24	10	10	10	–	–
Chlorine	<250 mg/L	753	18	790	28	583	23	617	12.9
Conductivity	<2500 µS/cm 20 °C	2020	133	2010	51	1899	97	3900	270
Chlorine dioxide	<0.8 mg/L	0.5	0.5	0.5	0.5	0.5	0.5	–	–
Hardness	<500 mg/L	33	7.6	25	5	83	5	11	5
Strontium	mg/L[b]	0.08	0.01	0.08	0.01	0.075	0.001	0.07	0.01
Iron	<200 µg/L	39	10	85	10	105	26	0.476	0.01
Glutaraldeid Biocide	mg/L[b]	0.01	0.198	0.151	0.01	3.19	0.517	–	–
Gution® Herbicide	<0.005 µg/L	1	0.001	1	1	1	1	1	0.004
Lithium	<2.5 mg/L	0.321	0.013	0.8	0.01	0.304	0.01	0.173	0.01
Magnesium	mg/L[b]	135	100	501	100	190	100	2	0.5
Manganese	<50 µg/L	17	10	10	10	10	10	0.01	0.01
Naphthalene	mg/L[b]	1.5	1	0.01	0.01	7.37	0.03	1	1
Nickel	20 µg/L	10	1	15	10	10	10	0.01	0.01
DO	>6 mg/L	3.6	4.7	4.4	4.7	3.2	4.7	0.2	1.2
Potassium	mg/L[b]	17.5	3	31.3	0.3	20.3	2	37.7	1.5
Radium 226	0.6 Bq/L	0.006	0.002	0.006	0.002	0.011	0.003	–	–
Salinity	[b]	625	18	1176	17,2	782	44	0.010	0.010
Sodium	<200 mg/L	245	1.93	462	6.8	307.5	17.3	171	22.3
TDS	<500 mg/L	816	33	954	29	631	35	1978	98
Total Solids	mg/L[b]	907	58	1013	42	718	43	2332	120
Toluene	<2.0 µg/L	<2	<2	<2	<2	<2	<2	2.8	<2
Turbidity	0.1 NTU	2.21	0.11	1.92	0.11	1.08	0.22	4.2	0.4
Xylene	<0.3 mg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	0.17	0.04
Zinc	<0.18 mg/L	0.03	0.01	0.01	0.01	0.01	0.01	0.052	0.034

DO: dissolved oxygen; TDS: total dissolved solids.

[a] PETROBRAS requirements.

[b] Under study.

Exhibit 4

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Produced water treatment by nanofiltration and reverse osmosis membranes

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ABSTRACT

Produced water, water that is co-produced during oil and gas manufacturing, represents the largest source of oily wastewaters. Given high oil and gas prices, oil and gas production from non-conventional sources such as tar sands, oil shale and coal bed methane will continue to expand resulting in large quantities of impaired produced water. Treatment of this produced water could improve the economic viability of these oil and gas fields and lead to a new source of water for beneficial use.

Two nanofiltration and one low-pressure reverse osmosis membrane have been tested using three produced waters from Colorado, USA. The membranes were analyzed before and after produced water filtration using field emission scanning electron microscopy (FESEM), attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS). In addition, membrane–water contact angles have been measured. XPS data indicate adsorption of organic and inorganic species during filtration. FESEM and ATR-FTIR data support theses findings. Water contact angles indicate the effect of membrane hydrophilicity on fouling. Our results highlight the value of using multiple surface characterization methods with different depths of penetration in order to determine membrane fouling. Depending on the quality of the produced water and the water quality requirements for the beneficial uses being considered, nanofiltration may be a viable process for produced water treatment.

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1. Introduction

Wastewaters containing dispersed oils and suspended particles are produced as a consequence of general metal manufacturing, food processing, transportation and oil and gas production [1]. The largest source of oily wastewaters is due to on shore and off shore oil and gas production. These 'produced waters' (PWs) constitute the single largest waste stream from oil and gas exploration and production activities.

Given high oil and gas prices, production of oil and gas from non-traditional sources such as tar sands, oil shale and coal bed methane will continue to expand. Coal bed methane (CBM) refers to methane obtained from coal seams [2]. In the case of CBM, in 1987 there were only a few producing wells in Wyoming's Powder River Basin, however in 2004, there were over 13,600. Unlike conventional oil and gas wells, production of oil and gas from non-traditional sources is usually accompanied by the co-production of large quantities of water. For example, the Wellington oilfield in Wellington, CO, produces about 98% water and 2% oil [3]. In Wyoming, from 1987 to 2004, 380,000 acre-feet (2.9 billion barrels) of water were produced while recovering 1.5 trillion cubic feet of CBM. The total volume of PW in Wyoming, if all known reserves of recoverable CBM were extracted, is estimated to be 7 million acre-feet (55.5 billion barrels) [4].

The quality of PWs varies greatly. The total dissolved solids (TDS), generally defined as material that can pass through a 2 μm filter, can be as high as 170,000 mg L^{-1} [5]. The recommended TDS for potable water is less than 500 mg L^{-1} and 1000–2000 mg L^{-1} for other beneficial uses such as stock ponds or irrigation. By comparison, average sea water has a TDS of 35,000 mg L^{-1}. The TDS of a PW depends strongly on the depth of the coal bed, and the origin of the water entering the coal beds.

Management of PWs has become a major factor in the feasibility of gas field development [6]. Today more than 60% of the PWs are reinjected into wells that are geologically isolated from underground sources of drinking water. Reinjection costs vary from $0.40 to $1.75 per barrel, while installation costs vary from $400,000 to $3,000,000 per well [7]. Surface discharge of large volumes of PWs has already had many adverse environmental affects such as stream bank erosion, change in natural vegetation, and salt deposition [8].

Development of economical treatment processes for PWs is vital for two reasons:

- Regions where CBM and other non-conventional oil and gas exploration are occurring in the western USA lack drinking and irrigation water. Currently much of the PW in the US is treated

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Table 1
Common components in PW

Organic compounds	Inorganic components	Production chemicals
Aliphatic, aromatic, polar compounds, e.g., fatty acids, oil, grease, benzene, phenol	Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, $SO_4{}^{2-}$, $CO_3{}^{2-}$, silicates (H_4SiO_2), borates (H_3BO_3)	Emulsion breakers to improve separation of oil and water, corrosion inhibitors

as waste yet PW could provide a vital source of new water for beneficial use.

- Economical and environmentally friendly methods of disposal of PWs are vital in order to prevent serious environmental damage.

The composition of PWs varies widely since they originate from different geological formations. Table 1 gives some typical species that may be present. Often bio-fouling by microbial growth is also a major concern.

Conventional treatment of PWs has included gravity separation and skimming, dissolved air flotation, de-emulsification, coagulation and flocculation [9–12]. However, there are numerous disadvantages associated with these unit operations. For example, gravity separation may not produce effluents that meet discharge limits; use of chemical emulsion breakers requires customization for each site to determine the types and quantities of chemicals needed; large volumes of sludge are often produced; and operation costs can be high.

The use of membrane filtration processes such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis offer many advantages for the treatment of PWs:

- The technology is more widely applicable across a range of industries (e.g., off shore and on shore oil exploration).
- The membrane is a positive barrier to rejected components, thus the variation in feed water quality will have a minimal impact on permeate quality.
- No addition of chemicals is required.
- Membranes can be used in process to allow recycling of selected waste streams.
- Membrane equipment has a smaller footprint, energy costs are often lower and the plant can be highly automated.

Both polymeric and ceramic membranes have been used for PW treatment [13]. Here we focus on the use of polymeric nanofiltration and low-pressure reverse osmosis thin film composite (TFC) membranes for treatment of PWs for the following reasons:

- While polymeric membranes are generally cheaper than ceramic membranes, they cannot be used at temperatures much above 50 °C. Though PW could be obtained at temperatures above 50 °C, the temperature of the PW is likely to be less than 50 °C by the time it reaches the membrane treatment step.
- A number of previous investigators have considered the use of microfiltration [1,14–17] and ultrafiltration [1,18–20]. However, far fewer investigators have considered the use of nanofiltration [6,21] and reverse osmosis [22] membranes for treatment of PWs.
- For PWs salt removal is often essential. Thus nanofiltration and low-pressure reverse osmosis membranes will be required.

Two commercially available nanofiltration membranes: NF 270 and NF 90 and a low-pressure reverse osmosis membrane, BW 30 all from FilmTec Corporation, Dow Chemical Company, Edina, MN have been tested using three different PWs from Colorado. The membranes have different surface roughness and rejection behav-

Table 2
Properties of membranes tested at 30 L m^{-2} h^{-1}, 2000 ppm solute, 25 °C, pH 7–8 and 10% recovery

Membrane	Type[a]	Contact angle (°)	Feed pressure[a] (kPa/psi)	Rejection[a] (%)	Zeta potential[b] (mV)		Root mean square roughness[b] (nm)	Comments
					pH 4.5	pH 7		
NF 270	Semi aromatic	42.7	345/50	NaCl 80; $CaCl_2$ 50; $MgSO_4$ 99.3	−12.1	−32.6	9.0 ± 4.2	MWCO between 200 and 400 Da, NF 270 has higher MWCO
NF 90	Fully aromatic	54.6	480/70	NaCl 90–96	17.5	−26.5	129.5 ± 23.4	
BW 30	Fully aromatic	60.8	1035/150	NaCl 99.4; $CaCl_2$ 99.4; $MgSO_4$ 99.7	−12.1	−5.2	68.3 ± 12.5	Brackish water treatment membrane operates at lower pressure than salt water treatment membranes

[a] Manufacturers data.
[b] See Ref. [24].

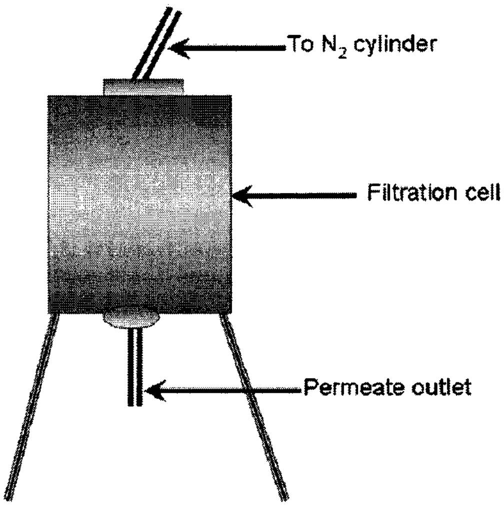

Fig. 1. Schematic diagram of filtration system.

ior for salts. The variation of permeate flux with time during dead end filtration has been determined. Recovery of permeate flux after cleaning has also been investigated. Water contact angles have also been measured. Membrane surfaces have been studied using field emission scanning electron microscopy (FESEM), attenuated total reflection Fourier transform (ATR-FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS). The utility of these techniques in identifying membrane fouling and adsorption of organic and inorganic compounds present in the PWs is discussed.

2. Experimental

Three PWs, labeled PW1, PW2 and PW3 were obtained from three sources in Colorado. The PWs used in these experiments were not kept in an oxygen-free environment as it is likely that treatment of PW for beneficial use will occur well after it is brought into contact with the atmosphere. PW1 and PW2 were co-produced from CBM manufacturing facilities in Walsenburg, southern Colorado. PW3 was obtained from Wellington in northern Colorado and is associated with oil production. The PWs were characterized using inductively coupled plasma atomic emission spectroscopy (ICP AES). In addition, total organic carbon (TOC) and TDS were also determined.

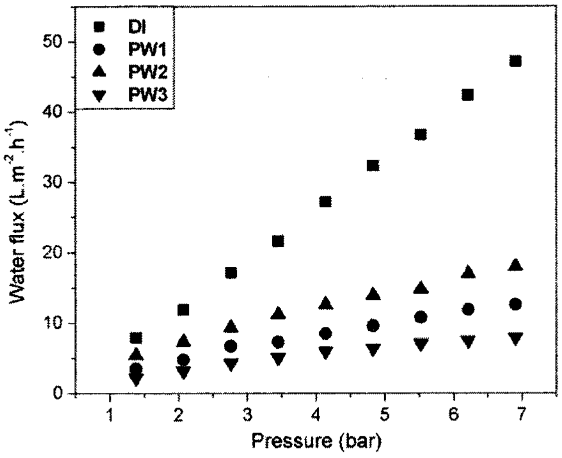

Fig. 3. Permeate fluxes for NF 90 membrane; DI refers to DI water flux.

The three FilmTec membranes that were tested consist of three layers: a polyester support web, a microporous polysulphone interlayer and an ultra thin polyamide barrier layer on the top surface. Table 2 gives information on the three membranes tested here. NF 270 is a piperazine-based semi-aromatic polyamide thin film composite membrane while NF 90 and BW 30 are fully aromatic polyamide thin film composite membranes [23,24]. Zeta potential and root mean square roughness of the membranes as measured by Tang et al. [24] are also given in Table 2.

Prior to use, membranes were washed with a 1:10:9 (volume basis) mixture of sulphuric acid/ethanol/de-ionized (DI) water (water free of charged species) for 12 h as described by Kulkarni et al. [25]. Membranes that were washed using this procedure are referred to as pretreated membranes. Deadend filtration experiments were conducted using an YT30 142 HW, Millipore Corp, Bedford, MA filtration cell. The membrane diameter was 140 mm. The feed was pressurized using a nitrogen cylinder attached to the feed reservoir. The feed volume was 500 mL. All experiments were conducted at room temperature. The experimental set-up is shown in Fig. 1.

Initial experiments consisted of testing the membranes at increasing pressures between 1.4 and 7 bar. Once the system reached the required pressure, the pressure was held for 2 min to ensure equilibrium. Next the permeate was collected for 5 min

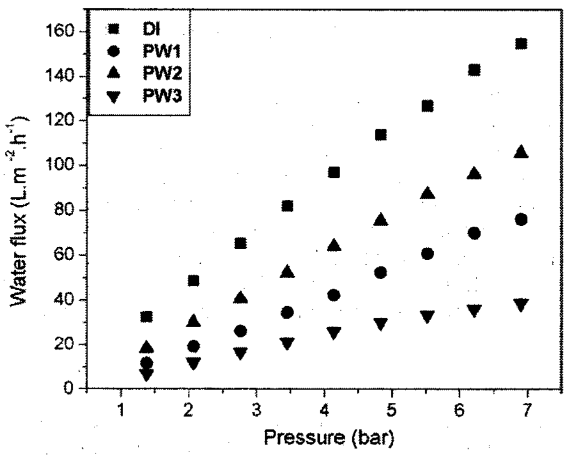

Fig. 2. Permeate fluxes for NF 270 membrane; DI refers to DI water flux.

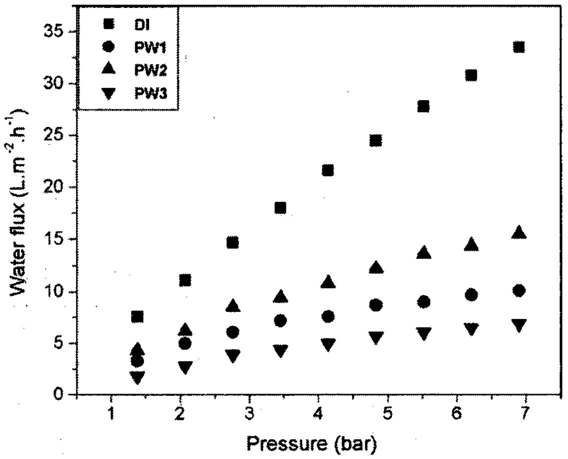

Fig. 4. Permeate fluxes for BW 30 membrane; DI refers to DI water flux.

Table 3
Chemical analysis of PWs

Sample	Component concentration (mg L^{-1})						pH	Conductivity (μS)	TDS (ppm)
	ICP AES analysis					TOC			
	Ca	Mg	Na	K	Si				
PW1	1.7	0.01	314	1.2	7.4	68.8	8.52	1448	722
PW2	2.4	0.01	250	1.3	10.1	47.7	8.41	1175	588
PW3	11.0	1.3	782	10.5	14.4	136.4	8.70	4190	2090

and weighed. Then the pressure was set to the next value and the procedure was repeated. Each run took about 90 min. In order to determine the effect of cleaning using DI water, some membranes were then used to filter DI water after PW filtration at a feed pressure of 1.4–7 bar.

In the second series of experiments the variation of the apparent salt rejection (as measured by conductivity of the permeate) with time at a constant pressure of 5.5 bar was determined. The permeate was collected for 20 min and the TDS and conductivity were determined using a handheld conductivity/TDS/temperature meter, Oakton Instruments, Vernon Hills, IL. TOC for PW3 permeate from all three membranes was also determined. Apparent salt rejection (ASR) was calculated using the following expression:

$$\mathrm{ASR}(\%) = \frac{C_{f_1} - C_{f_2}}{C_{f_1}} \times 100 \qquad (1)$$

where C_{f_1} is the initial conductivity of the feed and C_{f_2} is the conductivity of the permeate.

Static water contact angles were determined for all three virgin membranes (prior to pretreatment) by the sessile drop method using a contact angle goniometer (Model 100, Ramé-Hart Instrument Co., Netcong, NJ). Measurements were made at ambient temperature, using DI water 20 s after a 2 μL drop was applied to the surface and the needle tip removed from the surface. Each contact angle represents the average of a number of runs. Contact angles were calculated using the circle fitting method.

Three surface characterization methods were used to analyze the membranes. Pretreated membranes before and after PW filtration were inspected using FESEM, JSM 6500F, JOEL Ltd., Tokyo, Japan equipped with an in-lens thermal field emission electron gun. All membranes were imaged at a voltage of 15 kV and a magnification of 25,000 times. FESEM provides qualitative information on surface roughness and deposition of foulants on the membrane. In order to prevent collapse of the pores during sample preparation, all membranes were immersed in ethanol for 4 h. Next the ethanol was displaced by supercritical CO_2.

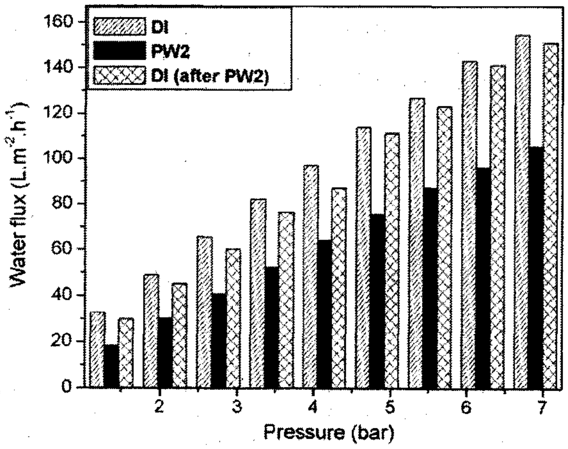

Fig. 5. Average DI water flux for the NF 270 membrane before and after 90 min filtration with PW2 as a function of feed pressure.

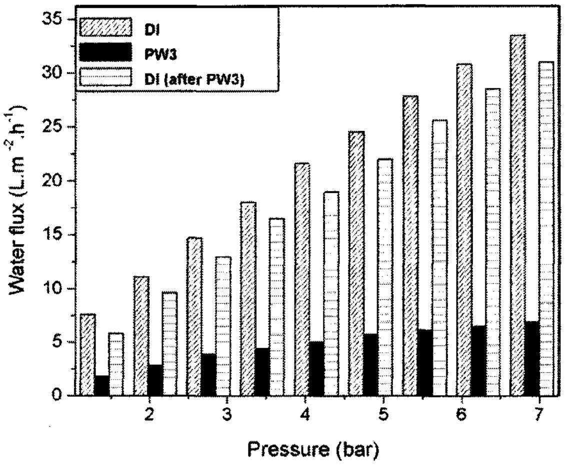

Fig. 6. Average DI water flux for the BW 30 membrane before and after 90 min filtration with PW3 as a function of feed pressure.

Pretreated membranes before and after PW filtration were examined using ATR-FTIR spectroscopy. A Nicolet Magna 760 FTIR spectrometer, Thermo Electron Corp., Madison, WI, equipped with a mercury–cadmium–tellurium (MCT) detector with a resolution of 4 cm^{-1} was used. ATR-FTIR spectroscopy provides qualitative information on the types of functional groups present at depths between 200 nm and 1 μm. The fouled membranes were rinsed with DI water for 10 min, in order to remove unbound foulants. The membranes were then dried at room temperature for 24 h prior to analysis. ATR-FTIR spectra were recorded at room temperature. A total of 512 scans were averaged for each spectral measurement. The internal reflection element was a zinc selenide (ZnSe) crystal plate with an incidence angle of 45°. An XT-KBr beam splitter was used. All the samples were scanned over the range of 600–4000 cm^{-1}.

XPS is a surface sensitive technique that measures elemental composition (except for H) and provides chemical binding information for the top 1–10 nm from the surface. Virgin (membrane prior to pretreatment) and pretreated membranes before and after PW filtration were analyzed. Virgin membranes were analyzed as supplied by the manufacturer. After PW filtration, membranes were washed with DI water for 10 min in order to remove unbound foulants and dried at room temperature for 24 h prior to XPS analysis using a Physical Electron 5800 ultra-high vacuum XPS-Auger spectrometer (Chanhassen, MN). For each measurement, 10 survey scans over the range 0–1100 eV with a resolution of 1 eV were averaged. For all scans, a spot size of 250 μm × 1000 μm was used.

3. Results

Table 2 gives DI water contact angles for the three membranes. NF 270 has the lowest contact angle indicating it is the most

Table 4
Permeate quality, experimental conditions: 24.5 ± 0.5 °C and 5.5 bar for 20 min

Membrane	PW1			PW2			PW3			
	Conductivity (μS)	TDS (ppm)	Recovery (%)	Conductivity (μS)	TDS (ppm)	Recovery (%)	Conductivity (μS)	TDS (ppm)	TOC (mg L^{-1})	Recovery (%)
NF 270	1164	585	84	997	500	62	3580	1780	98.1	31
NF 90	762	381	13	655	335	10	2610	1340	89.7	8
BW 30	736	370	13	630	310	10	2210	1090	45.2	6

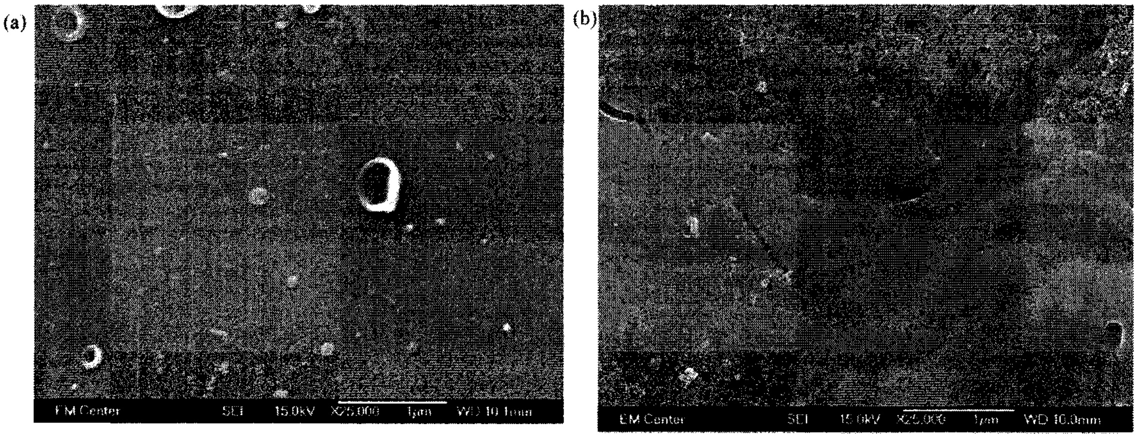

Fig. 7. FESEM images of pretreated NF 270 membranes: (a) before and (b) after filtration of PW1 for 90 min.

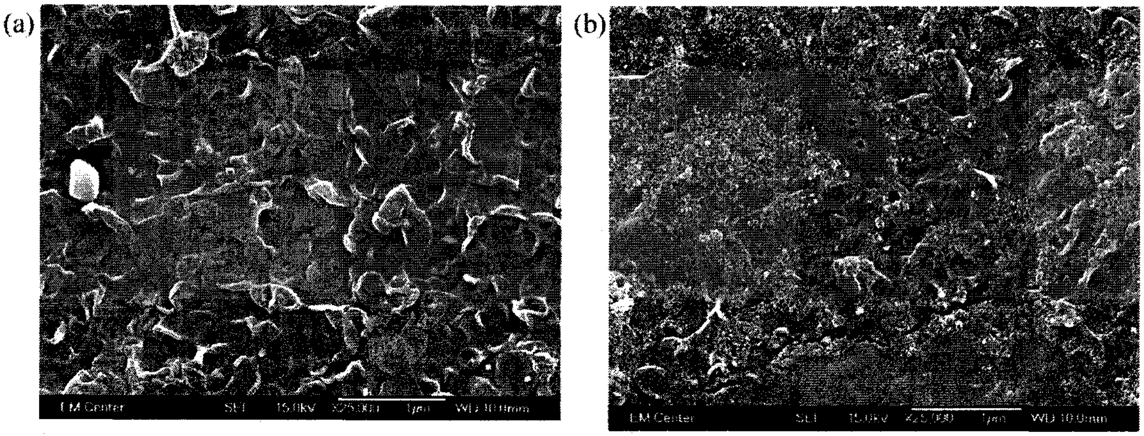

Fig. 8. FESEM images of pretreated NF 90 membranes: (a) before and (b) after filtration of PW1 for 90 min.

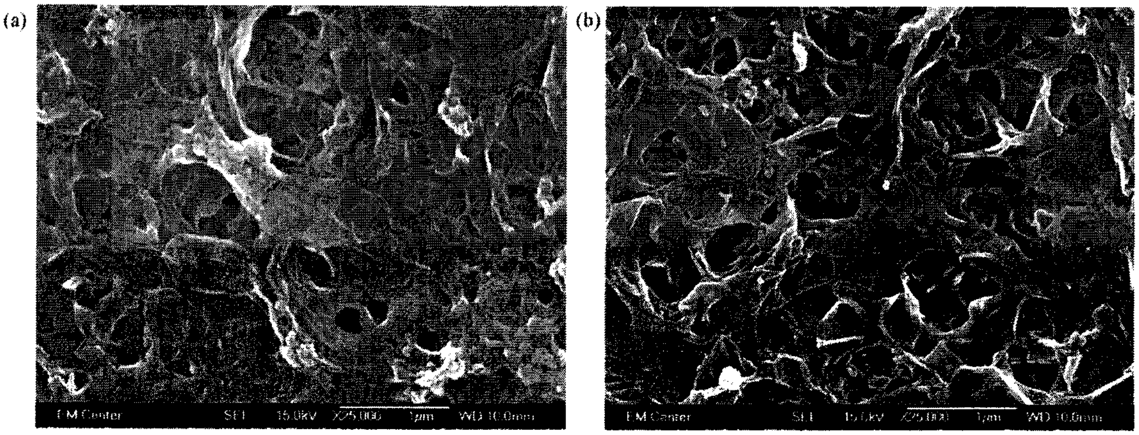

Fig. 9. FESEM images of pretreated BW 30 membranes: (a) before and (b) after filtration of PW1 for 90 min.

hydrophilic of the three membranes. The composition of the three PWs is given in Table 3. As can be seen the concentration of inorganic ionic species and consequently the conductivity as well as the TOC and TDS is highest for PW3, the PW obtained from the Wellington oil field. PW2 had the lowest concentration of ionic species, TOC and TDS.

Figs. 2–4 give the variation of permeate flux with pressure for the NF 270, NF 90 and BW 30 membranes, respectively, for all three PWs. The DI water flux for each membrane is also given. As expected the DI water flux is higher than the flux for each of the PWs at a given pressure for all three membranes. The DI and PW fluxes for all three membranes vary linearly with applied pressure. At a given pressure the permeate flux for DI water and the three PWs is highest for the NF 270 membrane and lowest for the BW 30 membrane.

Since the highest PW flux was obtained for PW2 using the NF 270 membrane this system was studied in more detail. Fig. 5 shows the change in average permeate flux over two cycles. The first bar for each pressure represents the average DI water flux over 90 min. Next PW2 was filtered for another 90 min. The average PW2 flux is given by the black solid bars. Finally DI water was again run though the membrane. The average DI water flux is given by the third bar for each pressure. The results show that the average DI water flux for the second run is lower than the first run indicating fouling of the membrane.

Fig. 6 is analogous to Fig. 5. However this time the BW 30 membrane was tested using PW3. Figs. 2–4 indicate that the lowest PW flux was obtained for the BW 30 membrane using PW3. The first bar for each pressure gives the average initial DI water flux. Next PW3 was filtered. The black solid bars give the average PW3 flux. Finally DI water was again run through the membrane. The average DI water flux is given by the third bar for each pressure. Like Fig. 5, the average DI water flux for the second run is lower than the first run indicating membrane fouling. Though not shown here, other combinations of membranes and PWs resulted in a decrease in the average permeate flux of the DI water in the second cycle. Further the PW flux was always much less than the DI water flux at a given pressure.

Table 4 provides the permeate quality after filtration for 20 min at 5.5 bar. For all three PWs the conductivity and TDS of the permeate were determined. For PW3 the TOC was also determined. The smaller the molecular weight cut-off of the membrane, the lower the conductivity, TDS and TOC of the permeate. Further, for a given membrane the permeate quality is worst for PW3, the PW that has the highest TOC and TDS.

Figs. 7–9 give FESEM images for pretreated membranes before and after filtering PW1. For all three membranes after filtering PW1, deposition of particulate matter can be seen. Further there appears to be a coating of rejected solutes on the membrane surface.

Figs. 10–12 give ATR-FTIR spectra for the NF 270, NF 90 and BW 30 membranes, respectively. Each figure gives the spectrum for the pretreated membrane before and after filtering each of the PWs for 90 min. Pretreating the membranes with sulphuric acid/ethanol/DI water did not change the base membrane spectrum. The thickness of the active layer of these membranes is a few hundred nanometre [26]. Thus the effect of pretreating the membrane is probably swamped by the signal from the microporous polysulphone interlayer.

All samples were scanned from 600 to 4000 cm^{-1}. Figs. 10–12 give the spectra from 600 to 2000 cm^{-1}. Characteristic peaks observed for the base membrane in the range of 2000–4000 cm^{-1} are in agreement with previous studies [27]. The main peaks were at 2800–3000 cm^{-1} and a broad peak centred at 3330 cm^{-1}. The peaks in the range of 2800–3000 cm^{-1} may be assigned to aromatic =C–H stretching and aliphatic C–H stretching [28]. Tang et al. [27] indicate that the membranes are coated with an O rich layer such as polyvinyl alcohol. The broad peak centred at 3300 cm^{-1} is due to overlapping of stretching vibration of N–H and carboxylic groups in the polyamide layer and groups such as O–H from the coating.

Over the wave number range 2000–4000 cm^{-1} little change in the spectra of the base membrane was observed after PW water filtration. Thus Figs. 10–12 give results only for wave numbers between 600 and 2000 cm^{-1}. Figs. 10–12 indicated that the peak heights associated with the base membrane are reduced after filtration. The y-axis scale for all spectra is the same. The level of reduction is least for the NF 270 membrane.

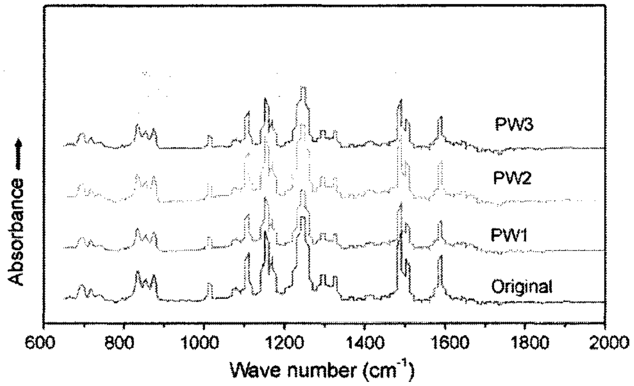

Fig. 10. ATR-FTIR spectra of petreated NF 270 membrane before and after PW filtration for 90 min.

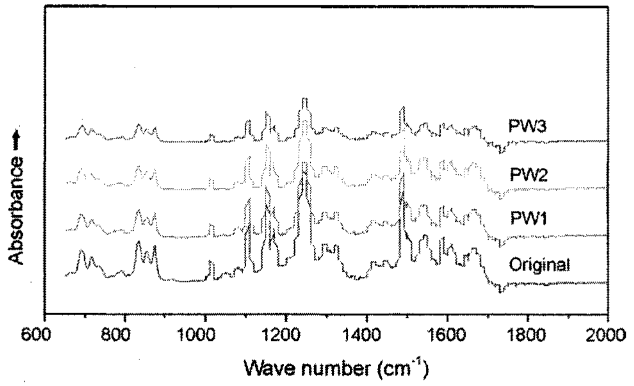

Fig. 11. ATR-FTIR spectra of petreated NF 90 membrane before and after PW filtration for 90 min.

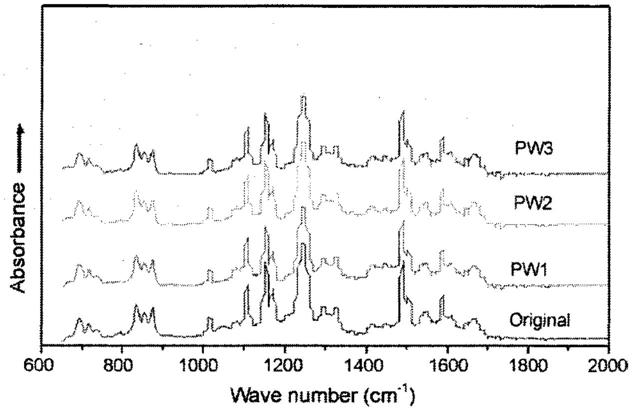

Fig. 12. ATR-FTIR spectra of petreated BW 30 membrane before and after PW filtration for 90 min.

Table 5
XPS surface elemental analysis (in at.%)

Membrane	C	O	N	C:O:N ratio	S	Na	Cl	Si
NF 270 (V)	64.4	22.3	7.5	8.6: 3.0:1.0	1.1	3.7	0.9	–
NF 270 (P)	65.6	20.9	10.1	6.5: 2.1:1.0	2.7	0.5	0.3	–
NF 270 (PW1)	74.9	15.7	4.3	17.4: 3.7:1.0	–	4.3	0.4	–
NF 270 (PW2)	63.4	21.6	7.7	8.2: 2.8:1.0	1.7	4.7	0.5	0.4
NF 270 (PW3)	70.6	18.4	5.6	12.6: 3.2:1.0	–	4.7	0.4	0.3
NF 90 (V)	71.0	16.4	11.1	6.4: 1.5:1.0	0.8	0.5	0.2	–
NF 90 (P)	70.4	17.2	9.7	7.3: 1.8:1.0	1.1	0.8	0.8	–
NF 90 (PW1)	72.0	17.5	7.2	10.0: 2.4:1.0	–	3.0	0.3	–
NF 90 (PW2)	67.7	20.8	7.5	9.0: 2.8:1.0	–	1.2	1.2	1.2
NF 90 (PW3)	65.9	21.3	8.1	8.1: 2.6:1.0	–	3.7	0.5	0.5
BW 30 (V)	70.7	22.2	6.1	11.6: 3.6:1.0	–	0.5	0.5	–
BW 30 (P)	69.4	25.2	4.9	14.2: 5.1:1.0	0.9	–	–	–
BW 30 (PW1)	74.8	19.2	1.1	68.0:17.5:1.0	–	4.2	0.3	0.3
BW 30 (PW2)	69.2	26.2	2.7	25.7: 9.7:1.0	–	1.9	0.1	–
BW 30 (PW3)	70.7	23.8	2.6	27.2: 9.1:1.0	–	2.5	0.1	0.2

V: virgin membrane; P: pretreated membrane; PW1, PW2, PW3 membranes after filtering PW1, PW2 and PW3, respectively.

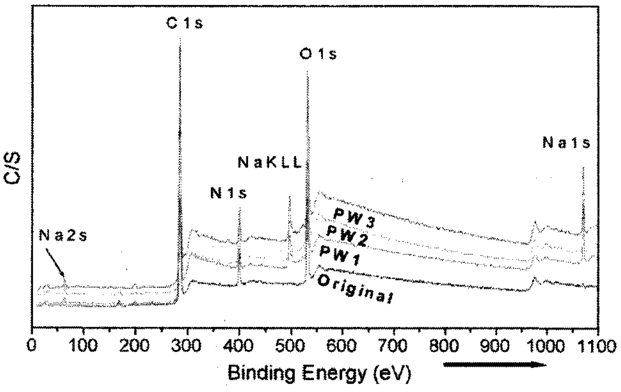

Fig. 13. XPS spectra of pretreated NF 270 membrane before and after PW filtration for 90 min.

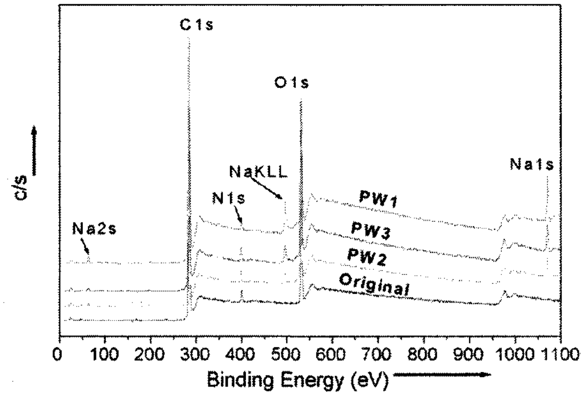

Fig. 15. XPS spectra of pretreated BW 30 membrane before and after PW filtration for 90 min.

XPS spectra are given in Figs. 13–15 for pretreated membranes before and after PW filtration. The pretreated membranes show peaks corresponding to elements present in the polyamide thin film: C(1s), N(1s) and O(1s). Qualitatively filtration of PWs leads to a change in the peak heights for C, N and O. The C and O peaks increase in height while the peak for N decreases slightly. Further several new peaks corresponding to Na appear: Na(2s) and Na(1s) representing Na 2s and 1s electrons as well as NaKLL representing Auger emission. Table 5 gives elemental compositions for the virgin and pretreated membranes before and after filtering each of the PWs. The C:O:N ratio is also given. In addition small amounts of Cl, Na, S, and Si are often detected. Table 5 indicates that pretreating the membranes with sulphuric acid/ethanol/DI water does lead to changes in the elemental composition of the polyamide layer. These results are discussed in detail in the next section.

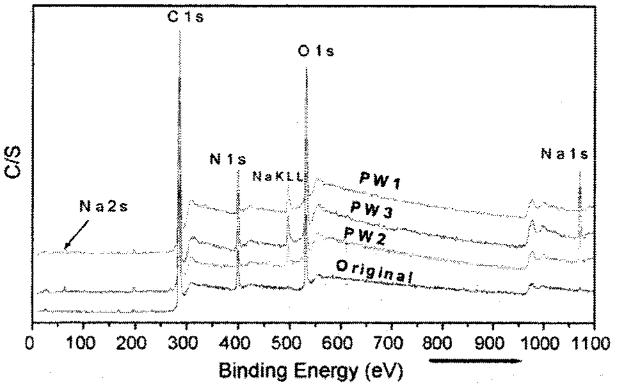

Fig. 14. XPS spectra of pretreated NF 90 membrane before and after PW filtration for 90 min.

4. Discussion

The BW 30 membrane is a fully aromatic polyamide composite membrane [27]. The theoretical O:N ratio is expected to be 1.0 when the polyamide layer is fully cross-linked and 2 for a linear polyamide when there is no cross-linking. Table 5 indicates that the virgin BW 30 membrane has an O:N ratio of 3.6:1.0. Tang et al. [27] also observed a very high O:N ratio for the BW 30 membrane. They indicate that the abundance of oxygen is most likely due to either proprietary modifications to the basic interfacial polymerization reaction or the presence of a coating such as polyvinyl alcohol. After pretreatment with sulphuric acid/ethanol/DI water a small amount of sulphur is detected.

Kulkarni et al. [25] indicate that sulphuric acid may be used to hydrophilize polyamide thin film composite membranes. By carefully controlling the hydrophilization conditions, the permeate flux may be increased and fouling decreased without loss in the rejection behavior of the membrane. Using hydrofluoric acid, Mukherjee et al. [29] obtained improved membrane performance. XPS analysis indicated fluorine concentrations of 0.7–1.5% depending on the processing conditions. Here we obtain about 0.9% sulphur suggesting partial hydrophilization of the membrane surface. In addition the ratio of C to N and O to N also increases as expected.

The virgin NF 90 and NF 270 membranes indicate the presence of small amounts of sulphur. This could be due to different manufacturing conditions [30]. Pretreatment of the membrane leads to an increase in the sulphur content. All three virgin and pretreated membranes indicate the presence of small amounts of Na and Cl. Virgin membranes were tested as received. The presence of very small amounts of Na and Cl in the pretreated membranes could be due to slight contamination of the DI water used to rinse the membranes prior to analysis.

For all three pretreated membranes, PW filtration leads to a change in the C:O:N ratio. The amount of C present increases significantly, indicating adsorption of organic foulants. Though the TOC is highest for PW3, for all three membranes, the C:N ratio increases most for PW1. Further, for all three PWs the increase in C:N ratio is greatest for the BW 30 membrane. The increase in the C peaks in Figs. 13–15 reflect these changes.

Table 5 indicates the greatest increases in the ratios of C:N and O:N occurring for the BW 30 membrane for all three produced waters. Table 4 indicates that the permeate quality is highest for the BW 30 membrane. This is expected as the BW 30 membrane has the lowest MWCO (see Table 1). Comparing all three membranes, Table 4 indicates that the permeate quality for the NF 90 and BW 30 membranes are closer than the permeate quality for the NF 270 and NF 90 membranes. Nevertheless the increase in the C:N and O:N ratios after PW filtration are similar for the NF 270 and NF 90 membranes but much larger for the BW 30 membrane. Table 2 indicates that membrane hydrophobicity increases in the order NF 270, NF 90 and BW 30 while surface roughness increase in the order NF 270, BW 30 and NF 90. Since increasing surface roughness and hydrophobicity lead to increased fouling, the much higher adsorption of organic compounds as evidenced by the much higher C:N and O:N ratios for the BW 30 membrane is most likely due to a combination of its low MWCO, hydrophobicity and surface roughness.

The ATR-FTIR spectra for all three membranes contain peaks at 694, 1151, 1487, 1503 and 1584 cm^{-1} [6,31] that indicate the presence of the polysulphone interlayer. Figs. 11 and 12 indicate the presence of the amide I peak at 1650 cm^{-1} for the NF 90 and BW 30 membranes, respectively. A rather broad and less distinct amide I peak is also present of the NF 270 membrane (Fig. 10). Figs. 11 and 12 also indicate the presence of the amide II peak at 1541 cm^{-1} for the NF 90 and BW 30 membranes. However the amide II peak is missing for the NF 270 membrane. The NF 270 membrane is made from piperazine, a secondary amine where as the NF 90 and BW 30 membranes are made from *m*-phenylene diamine, a primary amine.

Though PW filtration leads to a decrease in polyamide and polysulphone associated peak heights no new peaks are detected. In an earlier study Xu and Drewes [6] observed a similar result for PW filtration using a NF 90 membrane. The absence of peaks representing organic foulants is most likely due to the fact that the peaks associated with polysulphone and polyamide swamp any small peaks that represent adsorbed organic species. Though Xu and Drewes suggest, that organic fouling may not be a major mechanism for flux decline during PW filtration, our XPS data indicate significant fouling by organic species. Further the XPS peaks in Figs. 13–15 and the results of elemental analysis in Table 5 suggest that for the PWs studied here fouling by inorganic species also occurred. Further, Figs. 5 and 6 indicate significant decreases in the DI water flux after PW filtration. These findings are also supported by the FESEM images. Our results indicate the importance of using multiple surface analysis methods with different depths of penetration in order to characterize membrane fouling.

Membrane fouling results from interactions between dissolved and suspended solutes in the feed and the membrane surface. The FESEM data for filtration of PW1 indicate adsorption of contaminants onto the membrane surface. The permeate flux for PW3 at the same operating conditions was always lower than for PW1 and PW2 in agreement with the fact TDS and TOC is highest for PW3 (Table 3). Nevertheless both ATR-FTIR and XPS data indicate that PW1 causes significant membrane fouling. Table 5 indicates that the greatest increase in the C:N and O:N ratios for all three membranes occurred after filtration of PW1 indicating the importance of foulant properties such as charge and hydrophobicity as well as membrane properties in determining the level of fouling.

Membrane properties such as hydrophobicity, charge and roughness also affect the degree of adsorption of dissolved species. There are significant differences between the three polyamide thin film composite membranes tested here. Table 2 indicates that NF 270 has the smoothest surface, largest pore size, is the most hydrophilic and is the most negatively charged at the operating pH. Previous studies have indicated that fouling decreases with decreasing surface roughness [32–34]. Our results support these findings. The decrease in PW flux compared to DI water flux, as given by the ratio of the PW flux to the DI water flux, at the same pressure is always least for the NF 270 membrane. However since NF 270 has the largest membrane pore size, the conductivity, TDS and TOC of the permeate is the highest.

Table 3 indicates that the most abundant ionic species present is Na. Consequently we can approximate Na rejection by comparing the conductivity in the feed and permeate. Table 4 gives the % recovery (permeate volume removed/initial feed volume × 100) after 20 min of operation. Comparing Tables 2 and 4 it can be seen that even when the percentage recovery is less than 10%, the Na rejection is less for PW than specified by the manufacturer. It is however important to realize that the manufacturer's rejection data applies to the specific test conditions and ideal solutions. For real PWs lower rejection values are most likely due to the presence of a complex mixture of solutes.

The recommended TDS for beneficial uses such as water for stock ponds and irrigation is 1000–2000 ppm. Though in actual practice tangential flow filtration rather than dead end filtration will be used, the results obtained here may be used to screen the three membranes. Table 4 indicates that a TDS of less than 1000–2000 ppm is easily obtainable for PW1 and PW2 using the NF 270 membrane with very high water recoveries. Thus nanofiltration of PW1 and PW2 appears feasible. The economic viability of the process will depend on the frequency of membrane cleaning and the value of the treated water. Treatment of PW3, however, is likely to require multiple steps given the high TOC and TDS. Nanofiltration may be viable as a final polishing step.

5. Conclusions

Three commercially available membranes, NF 270, NF 90 and BW 30, have been tested using three PWs. The membranes have been analyzed using FESEM, ATR-FTIR and XPS. Our results indicate the value of using multiple surface characterization techniques with different depths of penetration when assessing membrane fouling. Significant fouling by organic compounds present in the PWs was detected. The NF 270 membrane which has the largest pore size, smoothest and most hydrophilic surface displayed the least reduction in permeate flux after testing with PWs. However the BW 30 membrane produced the highest quality permeate. In a practical application the choice of membrane will depend on the water quality requirements for the particular beneficial use being considered. Further the degree of membrane fouling during operation will affect the frequency of cleaning and hence the cost of the process. Our results indicate that membrane filtration could be a viable process for PW treatment.

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