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Boron removal by membrane processes

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ABSTRACT

Boron has been widely distributed in the environment, in most cases at low concentrations. Due to its detrimental effect on the reproducibility of living organisms, the European Union stipulates the maximum admissible value for the concentration of boron at 1 ppm and the World Health Organisation at 0.3 ppm as the non-observed effect level (NOEL) for drinking water. The aim of this work is the boron removal by membrane processes, in particularly the evaluation of the effect of nanofiltration and reverse osmosis membranes, as their coupling was also studied on the elimination of boron. The RO and NF tests were carried out with the use of an Osmonics spiral module equipped with AG 2514 TF and HL 2514T membranes respectively. Using conventional membranes, significant removal of boron has been observed only in its ionic form. Our experimental results indicated that boron rejection mostly depends upon membrane type, pH level, and to a lesser extent on the recovery. More detailed analysis of the above-mentioned results showed that boron can be effectively removed only at a pH shifted feed water close to 11. Initial data on coupling of the two RO/NF membranes are discussed.

Keywords: Boron removal; Reverse osmosis; Nanofiltration

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1. Introduction

Due to the rise of water demand, both potable and for irrigation, coupled with a decrease in suitable water sources, suppliers have to turn to alternatives. Seawater desalination or treatment of high saline, eventually contaminated surface waters have become standard [1]. By using those alternative sources more trace contaminants such as boron may appear in the final product.

Boron is widely distributed in the environment mainly in the form of boric acid or borate salts. The main sources of boron in surface and ground waters are urban wastewater with detergents and cleaning products, industrial effluents from a great number of industrial activities and diverse chemical products used in agriculture [2].

Water boron contamination is a serious environmental problem. In aqueous solutions boron exists as boric acid, $B(OH)_3$ or borate anion, $B(OH)_4^-$ depending on the pH of the solution. Boron has virulence for reproduction and contaminates the nervous system. Therefore, removal of hazardous boron from wastewater is important for environment control [3].

Recently boron has been classified by the European Union (EU) as a pollutant of drinking water in national and international drinking water directives (EU Council Directive 98/83/EC: 1 mg L^{-1}). Moreover, boron is a

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unique micronutrient in which overdose and under-dose of boron supply cause toxicity and deficiency symptoms in plants, respectively. The level of boron in irrigation water exceeding 1 mg L^{-1} can affect the yield of sensitive crops (e.g., avocado, citrus fruits) [4]. A very low boron content is required in irrigation water for certain metabolic activities. Referring to Nable et al. [5], safe concentrations of boron in irrigation water are 0.3 mg L^{-1}.

Removing boron from water is difficult and can be prohibitively expensive and impractical. The widespread characteristics of water known to have a high content of boron and toxicity of its compounds both create a pressing need for investigations aimed at developing effective methods to remove this element from aqueous solutions [6]. The existent accepted methods for boron removal are ion exchange by resin, which is expensive as a consequence of regeneration and physicochemical treatments of flocculation–precipitation, also with very high costs due to the use of flocculants. Nevertheless, there have been a number of studies focusing on boron removal in drinking water treatment using membrane technology. However, most of these studies used RO membranes.

In areas where the shortage of water is a concern, processes have been developed to obtain water from seawater and brackish waters by means of reverse osmosis (RO) processes. These processes present salt elimination percentages superior in most cases to 98%. However, due to the boron chemistry, at normal operation pH of these plants, the boron is under molecular form and elimination diminishes to values around 43% [6].

It is well known that boron compounds in seawater do not dissociate to ions at low or natural pH. Therefore, boron rejection in NF and RO desalination systems is low and the process is not adequate to produce permeate complying with the required quality standards (0.4–1.0 mg/L boron). At elevated pH, the rejection increases up to 98–99% at pH 11 [7,8]. However, at high pH potential precipitation of calcium carbonate and magnesium hydroxide must be avoided. Boron rejection by RO membranes is affected by pH, permeate flux and temperature. The boron rejection of the currently applied SWRO systems, at nominal test conditions, is 85–90%. This corresponds to about 78–80% boron rejection in operation of commercial SWRO systems [9].

Glueckstern et al. [10] reported that boron removal in seawater RO desalination systems is usually done by a second desalination pass, operating at high pH (pH ≥10). This method is not economical for reduction of boron content in permeates of brackish water desalination. The most suitable method for this purpose would be through boron selective ion-exchange (IX) resins. Alternatively, especially for brackish sources with boron content too high for reduction to the required low concentration (<0.5 mg/L) by seawater RO membranes alone, a combination of high boron rejection seawater membranes and an IX system can applied.

Koseoglu et al. [11] determined the impact of dissolved solids in seawater and pH on boron rejection and permeate flux. Much higher boron rejections were obtained in model solutions than seawater at a pH of 8.2, while boron rejection >98% was consistently achieved at pH 10.5 by both membranes in model solutions and seawater. Consistent for both pH levels, lower permeate flux values were observed in seawater than model solutions at constant conditions due to much higher osmotic pressures in seawater. Increasing pH from 8.2 to 10.5 increased the flux values in seawater at constant membrane pressure, mainly due to membrane fouling and enhanced scale formation by Mg and Ca compounds. As the pressure was increased from 41.3 to 55.2 bar higher boron rejections were observed in seawater. High salinity levels in seawater reduced the rejection of boron by SWRO membranes compared to rejection of boron as single solute.

Dydo et al. [12] investigated the removal of boron from chemical landfill leachate of 25.4 mg/L boron content by means of NF and RO. The BW-30, TW-30, NF-90 and NF-45 (Filmtec) membranes, working at maximum permissible operating pressure, were applied. Their experimental results indicated that boron rejection mostly depends on membrane type and leachate pH level while it is almost recovery independent. A more detailed analysis of the above-mentioned results showed that boron can be effectively removed only at a shifted feed water pH, close to 11, that is the highest value for long-term operation of RO membranes. The highest boron rejection (close to 99%), and the low enough permeate boron content (<1 ppm) were observed in the case of the BW-30 membrane up to 50% recovery only. Thus a two-stage RO system operated under alkaline conditions was proposed to efficiently remove the boron from such leachate.

The objective of this study is to investigate the boron removal by membrane processes; in particular, the evaluation of the effect of NF and RO as well as their coupling.

2. Chemistry of boron

Boron is usually present in water as boric acid, a weak acid which dissociates according to:

$$H_3BO_3 + H_2O \rightleftharpoons H_2BO \;\; + H_3O^+ \qquad pK_a = 9.14 \qquad (1)$$

$$H_2BO + H_2O \rightleftharpoons HBO_3^{2-} + H_3O^+ \qquad pK_a = 12.74 \qquad (2)$$

$$HBO_3^{2-} + H_2O \rightleftharpoons BO_3^{3-} + H_3O^+ \qquad pK_a = 13.80 \qquad (3)$$

Its concentration is usually expressed as “total boron” [B],

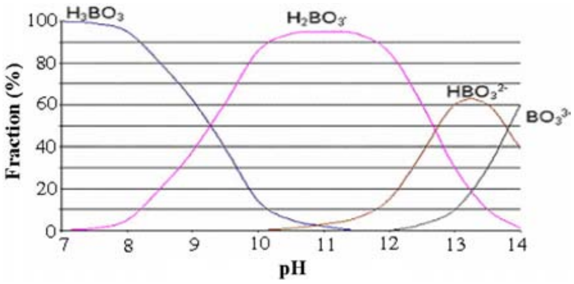

Fig. 1. Distribution of H_3BO_3 as a function of pH.

which includes all species and is expressed in terms of the molecular weight of the boron atom.

$$[B] = [H_3BO_3] + [H_2BO_3^-] + [HBO_3^{2-}] + [BO_3^3] \quad \text{as mg B /L} \tag{4}$$

In the usual pH operating range of RO elements, Eq. (1) is the one with the highest importance. We thus have a presence of both dissociated and non-dissociated boric acid species in the water as shown in Fig. 1. At lower pH the major species is boric acid in molecular form. Due to the absence of ionic charges, the hydration of the molecule cannot enhance those charges and is less strong. This results in a smaller size and less rejection of the molecule by a membrane. The dissociated form, on the other hand, will be fully hydrated, resulting in a larger radius and an enhancement of the ion negatively charged. This in turn results in higher rejection, both by exclusion and repulsion by the negatively charged membrane.

3. Experimental

The experiments were performed on the pilot plant equipped with NF and RO modules in order to investigate boron removal. The RO and NF tests were carried out with the use of an Osmonics spiral module equipped with AG 2514 TF and HL 2514 T membranes, respectively. The NF and RO membranes had an active membrane area of 0.6 m^2 and nominal permeate flow rates of 3.8 and 2.6 m^3/d at 10 and 55.2 bars respectively. The set-up has been presented previously [13].

The batch tests were carried out with H_3BO_3 solutions prepared in distilled water using various pH and at different recovery. pH was adjusted to the desired level with 0.1M NaOH or 0.1M HCl solutions.

Boron concentration in solutions was examined using the azomethine-H spectrophotometric method which is in common use due to its sensitivity, selectivity, accuracy and also due to the fact that it is simpler than other methods. The absorbance of the boron–azomethine-H complex at a wavelength of 420 nm was measured using a Pharmacia Biotech Novaspec II model spectrophotometer. The precision of this method was ±2.0%.

The amount of boron removed (R %) is given as:

$$R\% = 100.\left(1 - \frac{C_f}{C_0}\right)$$

where C_0 and C_f are the initial and residual boron concentration in the solution.

4. Results and discussion

4.1. Effect of pH

The effect of the pH on the elimination of boron by RO and NF membranes as well as their coupling was studied. The pressure of the feed and the recovery rate were maintained constant. Boron concentrations were analyzed in the feed and permeate for values of pH ranging between 7 and 12.

As shown in Fig. 2, the elimination of boron depends strongly on the pH. The RO membrane rejected about 46% and 77% of boron at pH values of 8 and 9 respectively. On the other hand, the rejection for the NF membranes was 30% and 60 % respectively under the same values of pH. At pH = 11, the percentage of elimination of boron reaches its maximum, and values of 96% and 70% were obtained respectively for RO and NF membranes.

Indeed, the boric acid is a weak acid with $pK_a = 9.15$; in addition, boric acid is neutral and is not hydrated in the aqueous solution. Consequently, this specie can pass through the membranes of RO and NF easily because of its small size.

At pH <9.15, boron exists mainly in solutions in the form of neutral boric acid, and at pH > ,15 the ionic forms predominate. At pH = 11 all the bore is in the form of $H_2BO_3^-$, and consequently we obtain the maximum elimination of boron with the RO and NF membranes. In the case of desalination of seawater and brackish water it is not possible to increase the pH of the solution in order to reach the maximum boron removal by the membrane process because of the problem of salt formation and deposits, leading to fouling of the membranes.

Some studies propose the use of a second or third desalination stage for RO in which the permeate obtained in the first stage is used. In this stage most salts are rejected except boron compounds, with the second or the third stages avoiding salt deposition and increasing the pH of the feed water. In our study, we propose a coupling based on the re-injection of NF permeate in feed water before passing through the RO module as indicated in previous work [13].

Fig. 2 shows the NF/RO coupling improves boron elimination for the studied range of pH. For pH = 11, the

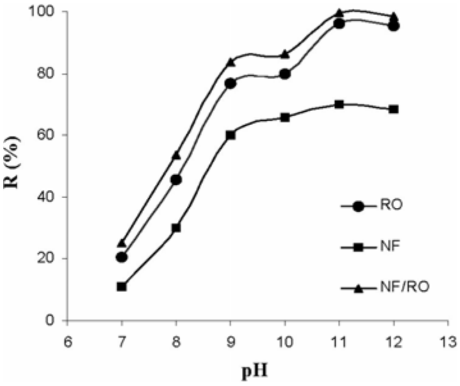

Fig. 2. Effect of pH on boron removal.

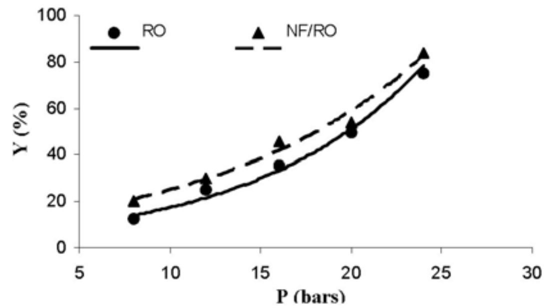

Fig. 4. Recovery factor vs. pressure for RO/NF parallel coupling with recirculation.

maximum of elimination reached 99.8%. This result can be explained by the fact that the recirculation of the NF permeate leads to a decrease of the osmotic pressure of RO feed water. At pH = 9, the elimination rate reached 80%, which corresponds to a concentration of 0.81 mg/L of boron in the permeate (Fig. 3). This is in agreement with the guidelines of WHO for drinking water quality.

4.2. *Effect of recovery*

The RO–NF parallel coupling with re-circulation experiments was realized under the following conditions: feed water pressure fixed in the range of 8–24 bar, feed water temperature maintained at 25°C and the studied sample of water containing 5 mg/L of boron. The results in Fig. 4 show a substantial improvement of the RO permeate flux. In fact, the recirculation of NF permeates permits a decrease of the feed water osmotic pressure. According to the transfer mechanism of RO, the flux increases linearly. This coupling also improved the recovery factor compared to RO alone.

Fig. 5 shows that for the same pressure, an increase in the recovery rate leads to a reduction of the retention rate. This is the consequence of the reduction of the speed of tangential circulation and appearance of a layer of polarization at the strong recovery rates.

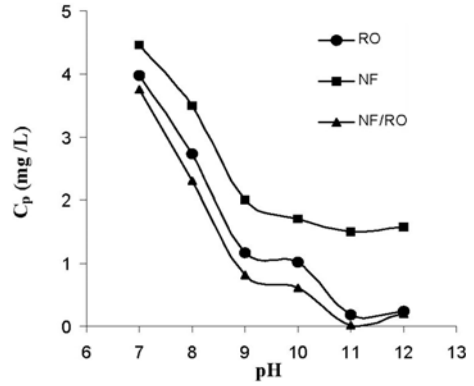

Fig. 3. Boron permeates concentration vs. pH.

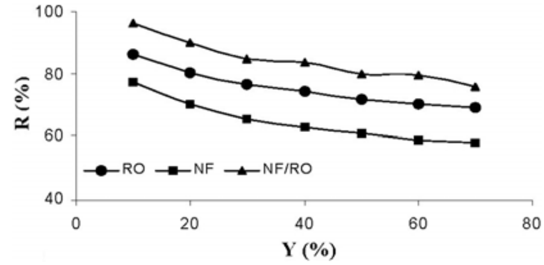

Fig. 5. Rejection rate vs. recovery factor for RO/NF parallel coupling with recirculation.

5. Conclusions

The removal of boron from aqueous solution was investigated by using RO and NF Osmonics membranes. It was confirmed that the boron element might be efficiently removed separately on RO and NF membranes at a pH close to 11. This may be lowered to pH = 9 when using a parallel RO/NF coupling with recirculation. With this coupling and this lower pH, boron concentration in the permeate will be within the limits fixed by the guidelines of the WHO and EU for drinking water quality. Moreover, the recirculation of NF permeate reduces the osmotic pressure of the feed water and increase the RO permeate flow and conversion rate.

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