

Boron removal in water using a hybrid membrane process of ion exchange resin and microfiltration without continuous resin addition



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ABSTRACT

Boron contained in seawater and some natural ground waters is harmful for plants and humans, especially water obtained by reverse osmosis desalination can contain a high level of boron. In this study, we investigated a hybrid process for boron removal from water which associates sorption on ion exchange resin in batch and microfiltration. In this approach, the ion exchange resin Amberlite IRA 743 was first ground to a mean particle size of 40–60 μm to increase its kinetics. A ceramic microfiltration membrane was used to retain the ion exchange resin in the feed tank and the circulation loop while the model solution of boron was continuously added and the permeate collected for analysis. The effect of resin dosage, boron initial concentration, transmembrane pressure and membrane pore size was studied. A concentration below 0.3 mg/L was obtained during a long time at sufficient resin dosage. The results were analyzed in terms of volume treated at breakthrough and permeate flux. In particular, it was shown that the transmembrane pressure and membrane pore size increased the permeate flux, but also decreased the volume treated at breakthrough, probably due to insufficient residence time. Moreover, the ion exchange resin and the microfiltration membrane were efficiently regenerated with HCl (0.37%) followed by NaOH (1%) and reused. Overall, it is suggested that the hybrid process of ion exchange resin in batch and microfiltration may be a possible technique for boron removal.

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1. Introduction

In seawater, boron is present mainly as boric acid $\text{B}(\text{OH})_3$ [1]. Boron is an essential micronutrient for humans, animals and plants, however, it can become toxic if the amount is slightly higher than required [2–4]. For humans, boron toxicity depends on the length, frequency, and level of exposure. A chronic exposure of boron may cause adverse effects such as cutaneous disorders, retarded growth and negative impact on reproduction [1,5]. The level set by the World Health Organization (WHO) was 0.3 mg/L until 1998, which was increased to 0.5 mg/L and then to 2.4 mg/L in 2011 [6]. For plants, the degree of damage depends upon time, concentration, crop sensitivity and crop water use, and if damage is severe enough, crop yield is reduced. It is usually admitted that boron concentration in irrigation water should not exceed 0.3–4 mg/L depending on the plant and soil characteristics [5].

Due to the growing demand of drinking and irrigation water over the world, associated to population increase, the production

of high quality water at low cost is highly needed. For that purpose, reverse osmosis (RO) seawater desalination is increasingly implemented throughout the world especially in the Middle East and North Africa regions [1]. The average boron concentration in the oceans and seas is around 5 mg/L. However, boron removal by RO is often insufficient under common RO conditions due to the small size and lack of charge of the boric acid molecule that may diffuse through the RO membrane. The membranes available at present for seawater desalination reject about 60–90% of boron [7]. Higher rejections as high as 96% have been reported for specific conditions such as a two-pass configuration and a new generation of RO membrane with higher boron rejection. However, there is still a strong need to improve the efficiency of conventional RO and to develop alternative techniques such as ion exchange and hybrid membrane systems [8].

A major technique to remove boron makes use of boron specific ion exchange resins [9]. Commercially available boron selective resins are based on a macroporous polystyrene matrix treated by chloromethylation and amination with N-methyl glucamine. The ion exchange resins exhibit good removal efficiency of boron, even at very low concentrations. They are specifically designed and used to remove boric acid and borate from water, magnesium brine or

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other solutions under a variety of conditions. Most studies on boron removal using ion exchange resins were performed in batch or fixed bed column to measure the kinetic and capacity for boron removal. Several kinetic equations have been proposed, for example the Ho pseudo-second-order kinetic model [10,11], a second-order pseudo-homogeneous reaction model [12], and a combination of film and particle diffusion [13].

In recent years, hybrid membrane processes have been increasingly reported for water treatment [14]. These processes associate membrane filtration (microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) or (RO)) to other techniques such as precipitation, ion exchange, sorption, etc, with the purpose to increase the size of the species retained by the membrane. For boron removal, hybrid membrane processes include polymer flocculation associated to UF or MF, activated carbon associated to UF or MF, and specific ion exchange resin combined to UF or MF [15]. In this last process, fine ion exchange resins are used to increase the binding area, leading to a higher sorption capacity and improved kinetics. The advantages of the hybrid membrane technique are then related to its high efficiency and low pressure drop [16–18].

Several configurations of specific ion exchange resins associated to MF have been investigated [19]. In a first configuration, a fresh relatively diluted suspension of ion exchange resin was fed into the feed tank to which the solution to be treated was continuously added; simultaneously partly saturated resin was withdrawn for regeneration by UF or MF to keep the feed volume constant [18,20–22]. UF or MF were operated in a submerged configuration [20,21] or in a circulation loop [18,22]. Different parameters have been investigated such as resin concentration in the feed suspension, flowrates of fresh and saturated resin and permeate flowrate [20,21]. At optimum conditions, boron concentration was found below the required level (0.3 mg/L or 1 mg/L) during a long period of operation. From results obtained with model solutions and sea waters, the process was applied to the removal of boron from geothermal waters. For example, the boron concentration was reduced from 11.0 mg/L to ≤ 1 mg/L in 20 min by using 2 g resin/L geothermal water with the ion exchange resin Dowex-XUS 43594.00 ground to an average particle size of 20 μm [22].

Two other configurations have been tested with less attention. In the first configuration, the feed was mixed with a concentrated suspension of ion exchange resin and flew through a MF loop [23]. The permeate obtained by MF was recovered and the ion exchange suspension entered the regeneration cycle with desorption and removal of boron. Regenerated adsorbent was then returned back to the sorption process. In another approach, the feed solution flew through a well-mixed tank containing the ion exchange resin and the permeate obtained by MF was recovered [24,25]. However, the boron concentration was found much higher than required because large ion exchange resin (diameter 190 and 530 μm) was used.

In our study, boron removal is evaluated using this last approach with fine ion exchange resin. The effects of several parameters (boron concentration, transmembrane pressure, resin dosage, and membrane pore size) are investigated on the variation of boron concentration in the permeate and permeate flux versus time. In a second part, the simultaneous regeneration of resin and membrane is performed and evaluated in terms of boron concentration in the permeate and permeate flux. The main purpose of this study is to evaluate the hybrid process using microfiltration and ion exchange resin, without continuous addition of resin. With no resin addition, the process is simple to perform and the resin can be used until a high saturation is reached. Another advantage is that the resin and the membrane can be regenerated simultaneously in the same experimental set-up.

2. Materials and methods

2.1. Chemicals

The chemicals used in this work were boric acid (99.97%) and Amberlite IRA 743 boron selective ion exchange resin supplied by Sigma-Aldrich (France). Boric acid solutions were prepared by dissolving the appropriate amount of boric acid (0.751 g) in 1 L of demineralized water, the concentration of this solution being 100 mg/L. Appropriate concentrations were obtained from this stock solution. For the regeneration of resin and membrane, hydrochloric acid (HCl 37%) and sodium hydroxide (NaOH) were supplied by Sigma-Aldrich (France). For the analysis of boron concentration, azomethine-H and other reactants were supplied by Sigma-Aldrich (France).

2.2. Preparation of fine ion exchange resins

The Amberlite IRA743 resin has a size between 300 and 720 μm . From this resin, a fine ground resin with an average particle size between 40 and 60 μm was obtained using a planetary ball mill (PM 100, Retsch, France), followed by sieving on a vibratory sieve shaker (AS 200, Retsch, France).

The size distribution of the resin was obtained using a Mastersizer 2000 (Malvern, France) which measures the intensity of scattered light as a laser beam passes through a sample of dispersed particles.

2.3. Sorption/MF set-up

The experimental set-up included a Micro Kerasep[®] membrane device (Novasep, France) as shown in Fig. 1. The boron solution was continuously added to the 3 L reactor using a Quattroflow 150S pump (Pall, France). The resin suspension was recirculated in a

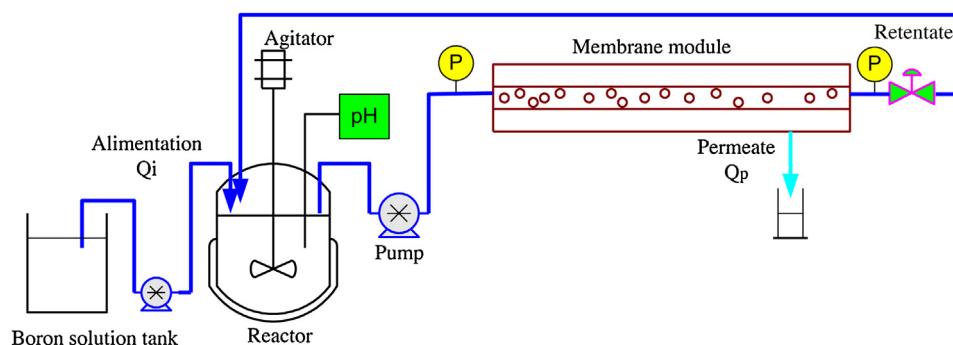


Fig. 1. Experimental set-up of the ion exchange/MF hybrid system, P: pressure gauge, Q_p : permeate flowrate, Q_i : inlet flowrate of the boron solution.

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