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Combinatorial approach for removal of boron from water by membrane surface modification and boron complex formation

Hiren Raval*, Mohit Samnani, Maulik Gauswami, Prashant Makwana

CSIR-Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI), Council of Scientific & Industrial Research (CSIR), Gijubhai Badheka Marg, Bhavnagar, 364 002, Gujarat, India

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ABSTRACT

The present paper demonstrates the novel combinatorial approach to decrease the Boron concentration in RO permeate by making surface modification of polyamide layer and making a boron complex in feed water to achieve higher removal efficiency. Thin Film Composite Reverse Osmosis membrane was subjected to treatment with sodium hypochlorite of 2000 mg/L for duration of 1 h, 2 h, 3 h, and 4 h respectively. The treatments resulted in increase in significant increase in water-flux with minor increase in boron rejection. Feed solution with 10 mg/L boron was mixed with mannitol and methyl salicylate to form the complex with boron. It was observed that boron rejection increased 97.56% at 125 psig (pounds per square inch gauge) and 97.81% at 400 psig pressure when mannitol was added in feed at pH 10. The highest boron rejection with methyl salicylate was 92.84%, although the water flux with methyl salicylate addition in feed water were higher as compared to the feed water with mannitol or plain feed water. The formation of boron complex responsible for increased boron rejection was confirmed by FTIR and NMR spectra. The membrane samples were characterized to understand the change in chemical structure and morphology of the membrane by ATR-FTIR, SEM, AFM and XRD.

1. Introduction

Although more than 70% of earth surface is occupied by water, the fresh water is quite less and is depleting on account of rapid growth in human population and industrialization. About 1.2 billion people lack the access to safe drinking water and about 2.6 billion people lack the basic sanitation facility in the world [1]. The membrane based desalination methods have gained much popularity worldwide because of lower capital cost, modular and scalable nature and lower energy consumption as compared to thermal desalination. The reverse osmosis technology has been proven very effective with useful in mitigating growing water demand [2].

One of the major stumbling blocks of the conventional RO membrane is its lower efficiency to remove boron from water. Boron removal efficiency of RO membrane is not at par with salt removal efficiency; therefore the alternate strategy i.e. two-pass RO system or boron removal resin etc. have to be implemented to match the Boron level in permeate within the stipulated limit. Thus, high removal efficiency of Boron is very important in desalination.

Boron is one of the seven important micronutrients. In small quantities it is found to help in bone development, brain function, improved metabolism and helps in immune functions [3,4]. However, boron beyond a certain limit is toxic and harmful. According to WHO report the acceptable quantity of boron in drinking water is set at 2.4 mg/L [5].

Boron is present in sea water in the form of uncharged boric acid up to about 6 mg/L [6]. The rejection of boron by TFC RO membrane depends upon the type of feed, pH, and operating pressure [7]. At pH lower than 9, boric acid is able to form non-dissociated molecular species at lower concentrations. The size of such molecules is very small that is why it passes through the RO membrane thereby increasing the concentration of boron in RO permeate and thus rejection of boron decreases [7,8].

The rejection of boron has gained much importance over the years. The uncharged boric acid at pH lower than 9 can form hydrogen bridges with active groups in the membrane and it can easily pass through membrane like water molecules and therefore increasing its concentration in RO permeate [9]. At pH > 9 the uncharged boric acid ions dissociate into borate ions as follows [8,9]:

$$H_3BO_3 + H_2O \leftrightarrow B(OH)_4^- + H^+, \; pKa = 9.24$$

On increasing the pH, the boric acid ions turns fully into borate ions between pH 10–11 [10].

The borate ions can be rejected more efficiently than the boric acid

* Corresponding author.
E-mail addresses: hirenraval@csmcri.res.in, raval.hiren@rediffmail.com (H. Raval).

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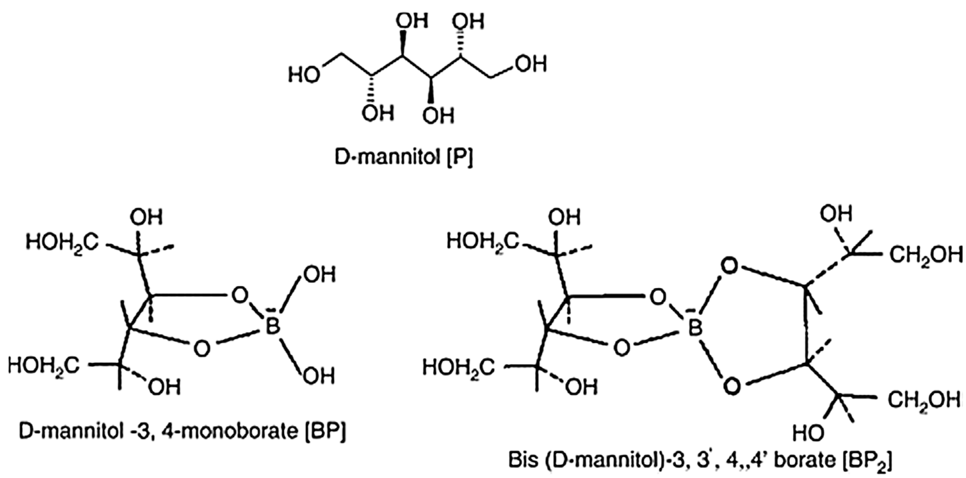

Fig. 1. Mannitol and negatively charged borate complexes.

ions by RO membrane. Thus, it can be stated that the rejection of boron by RO membranes increases by increasing the pH up to 11 [10,11]. As the pH of feed water increases, the deposition of various salts like calcium carbonate and magnesium hydroxide increases [11,12]. Anti-scalants are required to reduce the scaling because of alteration of pH of feed water [13]. It is evident that the boron rejection efficiency of commercial RO membranes is comparatively less than other ions. Thus, it is difficult to achieve the required boron concentration in a single pass RO system, so a multi-pass system may be required to achieve higher boron rejection [14]. Boron removal from water has been attempted by many different technologies e.g. bipolar membrane Electrodialysis, ion exchange – membrane Hybrid process, hybrid membrane inters-stage design etc. [15–17].

Boric acid and borate compounds are reactive with compounds containing multiple hydroxyl groups (polyols) to form complexes. One of such polyols is mannitol which can be added to the feed containing boron to form complexes. The mannitol in feed water containing boric acid can form borates with ester as a functional group which is shown in Fig. 1 below [18].

The acidity of the borate and boric acid solutions increases due to the complexes formed. These acids can be stronger than boric acid and are used as a property for titrations including boron compounds and alkali hydroxides [19]. Researchers found that the increase of acidity is due to the making of cyclic borate esters [20].

Studies have also shown that due to the treatment of sodium hypochlorite on TFC RO membrane, boron rejection is found to improve [21]. Moreover, by controlling the amount of exposure of sodium hypochlorite on TFC RO membrane, water-flux can be enhanced quite remarkably [22]. The membranes show greater resistance to fouling when exposed to sodium hypochlorite [23]. The membranes which are discarded due to low water-flux could be rejuvenated by successive treatments of sodium hypochlorite [24]. Thus, sodium hypochlorite has proven capability to modify the polyamide membrane surface.

To improve boron rejection glycidyl methacrylate has also been tested and it had showed promising result with loss in flux [25]. The boron removal rate also increases with increasing polyol concentrations and having large number of hydroxyl group in a compound [26]. The operating conditions for removal of boron also play a major part in its performance [27]. Testing of boron concentration is also very important in developing solution for boron removal [28,29]

Because of low boron rejection of commercial membrane, process design modifications such as two-pass system, diverting a part of first pass permeate with increased pH to second pass or boron selective resin etc. have to be incorporated, which results in increased cost of the overall process. Thus, there is a need to address this problem by alternate approach. No literature shows the interdisciplinary or combinatorial approach to address this problem. This paper shows the combinatorial approach to modify the surface of RO membrane and also to form a complex in feed water to increase the boron rejection significantly.

2. Experimental

2.1. Materials

Thin Film Composite RO membrane of CPA2 grade from Hydranautics USA. Sodium hypochlorite (laboratory reagent grade with available chlorine of 4%–6% w/v from RFCL limited, India), Sodium thiosulphate (Thermo Fisher Scientific India Pvt. Ltd. India), Sodium m-bisulfite (RFCL limited, India) Potassium iodide (Analytical reagent from RFCL limited, India). Acetic acid glacial (Thermo Fisher Scientific India Pvt Ltd. India) Starch soluble (High Purity Laboratory Chemicals, India), boric acid (Thermo Fisher scientific India Pvt Ltd. India), sodium hydroxide (Thermo Fisher scientific India Pvt Ltd. India), mannitol (Thermo Fisher scientific India Pvt Ltd. India), methyl salicylate (Tokyo chemical industry co. Ltd, Tokyo Japan)

2.2. Method

Polyamide TFC RO membrane was cut into a strip of 10 cm × 20 cm. The surface of the membrane was thoroughly cleaned with Deionized water. The membrane strip was then carefully stuck on a glass plate to ensure that only the top layer was subjected to treatment. The membrane was then brought into contact with sodium hypochlorite solution of 2000 mg/L for 1 h, 2 h, 3 h, and 4 h respectively. After that the membrane was dipped into solution of sodium Meta bisulphite for neutralization of free chlorine. The membrane was washed with deionized water and taken for testing the boron rejection. The membrane samples were retained for characterization.

2.3. Membrane performance

The membrane coupons were tested for boron rejection in the standard kit at 125 psig and 400 psig pressure in feed water containing 10 mg/L boron at 10 pH. The membranes were also tested after adding 2 g/L mannitol in feed water containing 10 mg/L boron at pH 10. They were also tested after addition of 0.3 g/L methyl salicylate in feed water containing 10 mg/L boron at pH 10. The membrane coupons used in the test kit were of circular shape of area 19.25 cm^2.

The permeate flux and boron content were monitored after pressurizing the membrane samples for 20 min. The boron content in feed and permeate was measured by inductively coupled plasma- optical emission spectrometry.