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Boron removal and desalination from seawater by PVDF flat-sheet membrane through direct contact membrane distillation

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HIGHLIGHTS

- PVDF flat-sheet membrane was prepared for boron removal and desalination.
- The membrane had a narrow pore size distribution and exhibited good hydrophobicity.
- Simultaneous boron removal and desalination from real seawater was carried out.
- The influence of antiscalant on boron removal and desalination was investigated.
- The prepared membrane was efficient for boron removal and desalination by DCMD.

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ABSTRACT

Boron removal and desalination from seawater by direct contact membrane distillation (DCMD) was studied with self-prepared polyvinylidene fluoride (PVDF) flat-sheet membrane. The membrane had an ultra-thin top skin and a porous network sponge-like layer and its effective pores showed a narrow distribution with a mean pore size of 0.22 μm. The membrane exhibited good hydrophobicity and its contact angle was about 82.6 ± 0.7°. During DCMD test of 35 g/L sodium chloride solution, the maximum permeate flux can achieve 47.6 kg/m^2 h. The natural seawater containing 4.65 mg/L boron was treated by DCMD for simultaneous boron removal and desalination. Although the permeate flux decreased with concentration factor (CF) value increase, the permeate boron kept below 20 μg/L and salt rejection was over 99.9%. When the CF value exceeded 4.0, there would be scale deposits formed, and the permeate quality and flux declined rapidly. The antiscalant polyacrylic acid could delay the deposit formation and the advisable dosage was 10 mg/L. The membrane showed satisfying performance stability in a 300 h continuous DCMD experiment even with the CF value as high as 7.0, indicating that the self-prepared membrane and DCMD process could be efficiently used for boron removal and desalination from seawater.

1. Introduction

Boron is widely distributed in both the hydrosphere and lithosphere of the earth. Generally, boron in aqueous environment is found in the form of boric acid and partial borate salts [1]. Boron acts as one of the most important micronutrients for plants, and is essential for normal growth of most crops. However, there is a narrow range between its deficiency and toxicity; boron is beneficial to plants only in small quantities and excessive amounts are injurious and even lethal [2]. Long-term exposure to water with increased boron content can result in malfunctioning of cardiovascular, nervous, alimentary, and sexual systems of humans and animals [3–6].

The World Health Organization (WHO) once set a guideline limit of 0.5 mg/L for boron in drinking water and the value is revised to 2.4 mg/L recently [7]. Although this new change seems more relaxed for drinking water, the requirement of 0.5 mg/L is still kept for irrigation water since boron demonstrates herbicidal effect [8]. In the European Union, a standard for boron in drinking water was 1.0 mg/L; the standard for boron in drinking water at 0.5 mg/L was adopted in China. Due to increasing demand for water, both for potable use and for irrigation, coupled with a decrease in suitable water sources, seawater desalination has become more and more attractive. Boron exists in seawater at around 4–6 mg/L [9]; it is therefore important to control the boron level in the treated effluent for different applications.

Nowadays, reverse osmosis (RO) desalination has become more dominant as traditional thermal desalination technologies such as multiple effect distillation (MED), multi-stage flash distillation (MSF) and vapor compression (VC) lose favor on energy grounds. The RO

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technology showed excellent salt rejection but insufficient boron removal. This can be attributed to the chemistry of boron, at normal pH of operation of RO desalination plants; boron is mainly in the form of boric acid, which is uncharged and can diffuse through the RO membrane easily [10]. For most RO desalination plants, boron removal from seawater is becoming a challenging problem.

The existent accepted methods for boron removal from water are mainly adsorption, ion exchange, and membrane process. These technologies generally have certain limitations, especially for boron removal from saline water. Adsorption process can remove boron to a safe concentration and the treatment is cost-effective [11]. However, the boron removal efficiency is greatly affected by temperature, pH and properties of adsorbent [12]. Besides, this method requires a regeneration process after the adsorbents being exhausted, which may decrease the capacity of adsorbents and produce secondary pollution. As the most efficient method, ion-exchange process can even remove boron to levels of <50 μg/L, far below the required limits [13]. Although the performance of boron specific ion exchange resin cannot be affected by temperature or pH value variations of the water to be treated [14], the process is usually not feasible under high background salinity [15]. RO membrane process is the simplest method for reducing boron concentration from seawater associated with the reduction of salinity and it is also expected to have great potential [16]. The main drawback of this method is the need of multi-pass RO systems to reduce boron concentration to the current recommended level, which causes the increase in costs. In addition, elevated pH for boron removal would lead to scaling, corrosion and higher cost [17].

Membrane distillation (MD) is an emerging thermally driven membrane separation technology that involves transport of water vapor through a porous hydrophobic membrane [18]. During the MD process of solutions with non-volatile solutes, only water vapor can transfer through the membrane. It may be used as a substitute for conventional separation processes such as multistage vacuum evaporation, distillation and RO [19]. Compared with those processes, the advantages of MD are as follows: (1) lower operating temperature and less vapor space required than conventional distillation, (2) lower operating pressure than RO, (3) 100% (theoretical) rejection of non-volatile solute, (4) unlimited by high osmotic pressure and (5) lower energy consumption than multistage vacuum evaporation [20,21]. So far the MD technology has been applied for water desalination [22], waste water reuse [23], juice concentration processing [24] and other industrial areas [25–27]. Although many researchers have been working on seawater desalination by MD, most works focus on the MD membrane and module development [28–30], operation conditions investigation and optimization [31,32], novel MD hybrid process [33,34], and heat and mass transfer theory [35–37]. As far as we know, studies related to the simultaneous desalination and boron removal through MD process are rather limited.

Direct contact membrane distillation (DCMD) is the best known configuration of MD and is also considered to be the most simple in design and application, in which the feed and the distillate are directly separated by the hydrophobic membrane. In the present study, DCMD experiments were carried out for boron removal and desalination from seawater with self-prepared polyvinylidene fluoride (PVDF) flat-sheet membrane. The self-prepared PVDF flat-sheet membrane contained a hydrophobic PVDF porous separation function layer and a hydrophilic nonwoven fabric support layer, and its properties were characterized via scanning electron microscopy (SEM), an atomic force microscope (AFM), a capillary flow porometer (CFP) and contact angle measurement. The batch DCMD experiments were conducted for simultaneous boron removal and desalination from seawater at different concentration factor (CF) values and the effects of antiscalant polyacrylic acid (PAA) on mitigating the potential for membrane scaling were also investigated.

Table 1
Chemical composition of the untreated seawater.

Constituent	Content	Constituent	Content
pH	7.90	TOC (mg/L)	2.73
Turbidity (NTU)	5.86	Conductivity (μS/cm)	43,600
$\mathrm{K^+}$ (mg/L)	405.84	B (mg/L)	4.65
$\mathrm{Ca^{2+}}$ (mg/L)	383.33	$\mathrm{F^-}$ (mg/L)	3.30
$\mathrm{Na^+}$ (mg/L)	9048.75	$\mathrm{Cl^-}$ (mg/L)	18,669.70
$\mathrm{Mg^{2+}}$ (mg/L)	1186.97	$\mathrm{Br^-}$ (mg/L)	67.93
$\mathrm{Sr^{2+}}$ (mg/L)	7.39	$\mathrm{HCO_3^-}$ (mg/L)	179.21
Si (mg/L)	4.36	$\mathrm{SO_4^{2-}}$ (mg/L)	2105.75

2. Materials and methods

2.1. Materials

PVDF (FR-904, $\mathrm{Mw} = 1.02 \times 10^6$ g/mol) was obtained from Shanghai 3F new materials Co., Ltd. (China). *N*,*N*-Dimethylacetamide (DMAc, >99%) was employed as the solvent, purchased from Shanghai Jingwei Chemical Co., Ltd. (China). Acetone (AR grade, >99.5%) and phosphoric acid (AR grade, >85.0%) were supplied by Sinopharm Chemical Reagent Co., Ltd. (China). Ethanol (GR grade, 99.9%) and NaCl (99.5%) were from Beijing Chemical Works (China). Polyacrylic acid (PAA) was supplied by Zouping Dongfang Chemical Industry Co., Ltd. (China). The ultrapure water used in all experiments was produced by a Milli-Q BIOCEL unit (Millipore, USA) with the resistivity of 18 MΩ·cm.

2.2. Membrane preparation

First, a desired amount of dried PVDF powder was poured into a tank containing DMAc solvent and non-solvent additives, then the polymer dope mixture was subjected to continuous stirring for about 48 h at

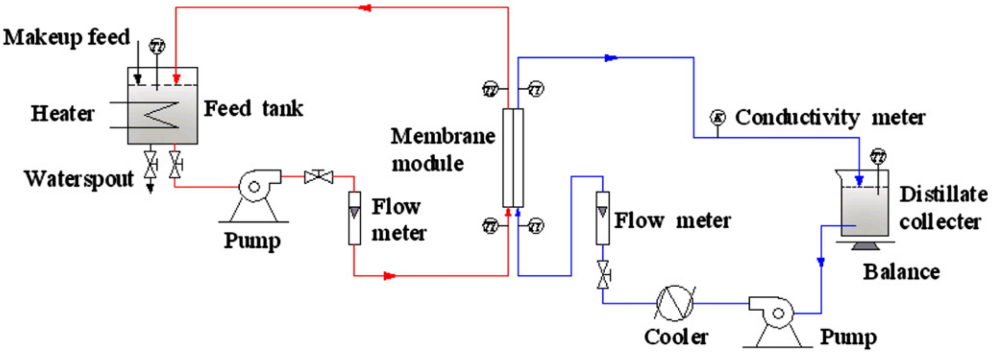

Fig. 1. Schematic diagram of the experimental DCMD set-up.