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Effect of operating parameters on boron removal from seawater using membrane distillation process

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HIGHLIGHTS

- DCMD is a suitable process for boron removal from synthetic water and seawater.
- Knudsen-molecular model dominates the transfer of water vapor through pores.
- Evaluation of flux and boron rejection under different operating conditions
- Feed pH solution had no marked influence on permeate and boron rejection.
- DCMD application of seawater showed promising performance.

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ABSTRACT

Theoretical and experimental studies of direct contact membrane distillation (DCMD) using commercially flat sheet hydrophobic polyvinylidene fluoride (PVDF) membrane were investigated to remove boron from simulated and natural seawater. Mass transfer mechanism and theoretical flux were determined using the dusty-gas model (DGM). Mass transfer analysis showed that the combined Knudsen-molecular model is considered to be the dominant mechanism which describes the transport of water vapor through the membrane pores. Then, the effect of various operating parameters such as feed temperature, boron concentration, salt concentration and feed solution pH on DCMD performance was investigated. Experimental runs showed that the permeate flux was enhanced exponentially with feed temperature, and maximum permeate flux of 27.5 kg/m^2·h was obtained at 74 °C. The permeate flux decreases slightly with feed boron and salt concentration. Feed solution pH had no significant effect on DCMD performance. DCMD process can produce water with high boron rejection of more than 90% even at feed concentration as high as 200 mg/L. Natural seawater, containing 5.37 mg/L of boron, was treated by DCMD process. During 18 h of working period, the permeate flux had showed a reduction of about 15.75%, and permeate boron was kept below 0.47 mg/L. The decreasing of contact angle value can explain the performance decline of DCMD process.

1. Introduction

Boron is an essential micronutrient for plants and animals as well as a useful component for various industries such as glass and ceramic, cleaning products, semiconductors, cancer treatment, cosmetics products, etc. [1]. Moreover, boron plays an important role in the normal growth of vegetables and fruits. However, it becomes toxic to plants and human when the amount of boron is higher than required. Long-term consumption of water with high boron content can led to many healthy problems, including cardiovascular, nervous, and reproductive systems of humans and animals [2]. Even, it causes changes in blood composition, neurological effects, physical disorders and intellectual development of children [3]. The World Health Organization (WHO) had recommended, for many years, the limit of 0.3 mg/L for boron in drinking water, but this value was revised as 2.4 mg/L in 2011 due to the positive effects of boron on human health [4]. On the other hand, the EU still suggests the maximum limit of boron in drinking water at 1 mg/L [5].

In seawater, boron is naturally occurring at an average concentration of 4–6 mg/L [6]. In this range, dissolved boron is mainly found as boron acid ($B(OH)_3$) or borate ion ($B(OH)_4^-$) [7]. Boric acid presents a very weak Lewis acid according to the dissociation reaction as follows:

$$B(OH)_3 + H_2O \rightleftarrows B(OH)_4^- + H^+. \quad (1)$$

The equilibrium reaction takes place with a pKa value around 9.3 [8], and leads to a pH dependent distribution of boric acid/borate ion containing species.

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Nowadays, the methods developed for boron removal from seawater can be grouped into three wide categories: sorption on solids [9], thermal processes [10] and membrane separation techniques [11]. However, each one of the above methods presents some drawbacks. For example, the negative environmental impact due to the use of chemical products for the regeneration steps and the loss of adsorbent capacity with time are the some issues of concern related to the adsorption on selective resins technique [12]. Thermal process has effectively remove boron with high efficiency, but in the last decades, this technology has lost favor because of its high-energy demand. Reverse osmosis (RO) process can produce water with very low content of borate ions, whereas is not able to well reject boron in its boric acid form, as in seawater. For this reason, it was recommended to design multi-pass RO to reduce boron seawater concentration at allowable value, which causes the increase of the plant cost.

Membrane distillation (MD) is an innovative membrane process, which has been investigated as a possible alternative for the removal of various contaminants. The principle of MD is based on a thermal gradient that involves transport of water vapor through the microporous hydrophobic membrane [13]. MD offers several benefits as its low operating pressure and temperature, which reduce the capital cost due to use of usual materials. These were the more important advantages compared to the classical membrane technologies, such as reverse osmosis or nanofiltration. MD can also able to produce permeate with very high rejection of ions, macromolecules, colloids, cells and other non-volatiles compounds. Although, MD is considered as a thermal separation process and which operates at moderate temperature, it is inherently more energy efficient than thermal distillation and RO [14].

Membrane distillation systems may be classified into four configurations with respect to the cold side arrangement, including direct contact membrane distillation (DCMD), vacuum membrane distillation (VMD), sweeping gas membrane distillation (SGMD) and air gap membrane distillation (AGMD). DCMD is considered the best configuration, in which the feed and permeate are separated by membrane. Moreover, DCMD requires the least cost of equipment and is the simplest to design and operate. Up to now, researches on the removal of contaminants from water using DCMD process have been investigated only in very few studies. Boubakri et al. [15] conducted experiments in DCMD laboratory scale for the removal fluoride from synthetic water. It was found that the used PVDF membrane presents high retention of fluoride, which can reach 99.9% with maximum permeate flux around 22.4 kg/m^2·h at feed temperature of 71 °C, in which the water vapor diffuse through the membrane according to the combined Knudsen molecular model. Boubakri et al. [16] have investigated the removal of nitrate contaminant by DCMD using PVDF and PP membranes. The study had shown an almost complete nitrate rejection (higher than 99.9%). In addition, under the same operating conditions, PVDF membrane showed higher permeate flux of 37.21 L/m^2·h than PP membrane with 4.12 L/m^2·h. Pal and Manna [17] have studied the efficiency of solar driven membrane distillation to remove arsenic from contaminated groundwater. An almost 100% arsenic separation was achieved after 120 h of working period. The permeate flux has reached 49.80 kg/m^2·h with a PTFE membrane, which is the best one compared to other tested membranes. Hou et al. [18] applied DCMD using self-prepared PVDF membrane to remove boron contaminant from aqueous solution. They obtained a high boron removal of about 99.8% and the permeate boron content was below the maximum permissible level even at high feed concentration of 750 mg/L.

It is known that MD is a thermally driven process that involves transport of vapor through porous hydrophobic membrane, while all non-volatile compounds (like boron contaminant) are retained at the feed compartment. The transport mechanism of water vapor in the MD process can take place following Knudsen model, Poiseuille model or molecular diffusion model. Many researchers have focused on modeling of membrane distillation using the dusty-gas model in order to expand the application of membrane distillation process to eliminate various contaminants such as chromium [19] and fluoride [15]. These studies have considered that the combined Knudsen-molecular model is the dominant transfer mechanism.

This study was realized with the aim of measuring the capability of the DCMD, using PVDF membrane, to remove boron from seawater. We have proceeded as follows:

- Modeling of mass transfer mechanisms with the aim of selecting the most accurate one for water-vapor transport through the membrane in the case of boron rejection by DCMD,
- studying the effect of operating parameters on DCMD performance to remove boron from synthetic solution and identifying the optimized ones, and
- applying optimized parameters to remove boron from Mediterranean seawater, and evaluating the DCMD performances.

2. DCMD mass transfer

The mass flux (J) of water vapor diffusing through the dry porous membrane is proportional to the vapor pressure difference across the membrane, and can be expressed by Darcy's law for laminar flow in packed beds [17]:

$$J = B_m(P_{mf} - P_{mp}) \tag{2}$$

where B_m is the membrane coefficient, P_{mf} and P_{mp} are the vapor pressures at the feed and permeate vapor/liquid interface, respectively. P_{mf} and P_{mp} are the vapor pressures at temperatures T_{mf} and T_{mp}, respectively, and are related to the activity of the solution by the following:

$$P_{mi} = a_{wi}P^0_{mi} \quad i = f, p \tag{3}$$

where a_{wi} is the water activity and P^0_{mi} is pure water vapor and can be evaluated by using Antoine equation [20]:

$$P^0_{mi} = \exp\left(23.238 - \frac{3841}{T_{mi} - 45}\right). \tag{4}$$

P^0_{mi} is in Pascal and T_{mi} in Kelvin.

The vapor pressure composition can be estimated using the Raoult's law, which can be written in case of dilute solutions as follows:

$$P_{mi} = (1 - x_{mi})P^0_{mi} \tag{5}$$

where x_{mi} is the mole fraction of the solute at the membrane interface.

According to the dusty gas model, the diffusive mass transfer through microporous membrane can be divided into three mechanisms, including Knudsen diffusion, viscous flow and molecular or transition mechanism [21]. These models relate the transport with collisions between molecules, and/or molecules with walls of porous. To judge the dominating mechanism of the mass transfer in the pores, the K_n number is used:

$$K_n = \frac{\lambda}{d_p} \tag{6}$$

where d_p is the membrane pore diameter and λ is the mean free path of transported molecules which can be calculated as follows [22]:

$$\lambda = \frac{k_B T_m}{\pi\left(\frac{\sigma_w - \sigma_a}{2}\right)^2 * P * \sqrt{1 + \left(\frac{M_w}{M_a}\right)}} \tag{7}$$

where k_B is the Boltzmann constant, P is the total pressure inside the pore, T_m is the average membrane temperature, σ_w and σ_a are the