Boron removal from aqueous solution by direct contact membrane distillation

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ABSTRACT

The removal of boron from aqueous solution by direct contact membrane distillation (DCMD) was studied with self-prepared polyvinylidene fluoride (PVDF) hollow fiber membranes in the present work. The effect of pH, boron concentration, temperature and salt concentration of the feed solution on the boron rejection was investigated. The experimental results indicated that boron rejection was less dependent on the feed pH and salt concentration. DCMD process had high boron removal efficiency (>99.8%) and the permeate boron was below the maximum permissible level even at feed concentration as high as 750 mg/L. Although the permeate flux was enhanced exponentially with the feed temperature increasing, the influence of feed temperature on the boron rejection could be neglected. Finally, the natural groundwater sample containing 12.7 mg/L of boron was treated by DCMD process. The permeate boron kept below 20 μg/L whether the feed was acidified or not, but pre-acidification was helpful to maintain the permeate flux stability. All the experimental results indicated that DCMD could be efficiently used for boron removal from aqueous solution.

1. Introduction

Boron element is generally found in natural water as boric acid and borate salts depending on the pH of the water [1]. The concentration of boron in groundwater depends on the surrounding geological characteristics [2], its presence in surface water occurs frequently as a consequence of the discharge of treated sewage effluents and it is also commonly present in the oceans.

Boron is one of the most important micro-nutrients for plants, and is essential for plant growth. However, boron is beneficial to plants only in small quantities, as excessive amounts are injurious and even lethal. Irrigating water with more than 1.0 mg/L of boron is harmful to most plants [3]. Long-term exposure to water with increased boron content can result in malfunctioning of cardiovascular, nervous, alimentary, and sexual systems of humans and animals. Blood composition changes, physical and intellectual progress of children decelerates and risk of the pathological births increases [4–7]. A standard for boron in drinking water at 0.5 mg/L was adopted in China recently, which was in accordance with the guidance value of boron in drinking water recommended by WHO [8]. In European Union (EU), the standard for boron in drinking water was 1.0 mg/L.

The existent accepted methods for the boron removal from water are mainly adsorption, ion exchange, and membrane process.

Adsorption was considered as a more useful and economical technique for boron removal [9]. Activated carbon [10], oxides [11–13], and other low-cost materials such as fly ash [14], red mud [15] and clays [16] have been used as boron adsorbents. Adsorption process can remove boron to the safe concentration and the treatment is cost-effective. However, the removal of boron is greatly affected by temperature, pH and mass of adsorbent. Besides, this method requires a regeneration process after the adsorbents being exhausted, which may decrease the capacity of adsorbents and produce secondary pollution.

Ion-exchange process in which N-methyl glucamine type resins such as Amberlite XE 243, Amberlite JRN-78, Amberlite IRA743, Diaion CRB01, Diaion CRB02, Wofatit MK51 and Purolite S108 have been used is the most extensively studied and reported in the literature [17–25]. As the most efficient method, ion-exchange process can even remove boron to levels of <50 μg/L, far below the required limits [26]. Although the resin performance is not affected by temperature or pH value variations of the water to be treated, the process is usually not feasible under high background salinity [27]. Besides, the high cost of resins regeneration also limits the application fields of this method.

Reverse osmosis (RO) and electrodialysis (ED) are two common membrane processes used for boron removal [28–34]. Due to the chemistry of boron, the boron is in the form of boric acid at natural pH and ED is only capable of removing about 42–75% of boron, in the case of RO treatment, this is 30–40% [31]. The low rejection of boric acid can be mainly attributed to its ability to diffuse through the membranes in a non-ionic form in the way similar to carboxylic acids or water [34]. Some investigation results showed that boric

acid might be efficiently rejected only in its ionic form at a relatively high feed water pH [32,33].

Membrane distillation (MD) is a thermally driven process that involves transport of water vapor through a porous hydrophobic membrane [35]. 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, reverse osmosis, and distillation [36]. Compared with those processes, the advantages of MD are as follows: (1) lower operating temperature and 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 [37,38]. Up to the present, MD has been applied for water desalination [39], wastewater reuse [40], juice concentration processing [41] and other industrial areas [42–44]. However, as far as we know, removal of boron from aqueous solution by MD has not been rigorously investigated.

Direct contact membrane distillation (DCMD) is the best known configuration of MD, 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.

2. Materials and methods

2.1. Reagents

All the chemicals used in the experiments were of analytical reagent grade. H_3BO_3 was obtained from E. Merck (Darmstadt, Germany). NaCl, $CaCl_2$, Na_2SO_4, NaOH and hydrochloric acid were supplied by Beijing Chemical works (China). Boron solution was prepared by dissolving H_3BO_3 with deionized water. And the other solutions were also prepared with deionized water.

2.2. Membrane and membrane module

The self-made membrane was spun from PVDF/*N,N*-dimethylacetamide (DMAc)/LiCl/ethylene glycol (EG) (12/80/5/3 wt%) dope by phase inversion process. The mixture of LiCl and EG was used as non-solvent additive and DMAc was solvent. The characteristics of the PVDF hollow fiber membrane are given in Table 1. The dry PVDF hollow fibers in the number of 50 pieces were assembled into a polyester tube (diameter (mm) $d_{in}/d_{out} = 15/20$) with two UPVC T-tubes and two ends of the bundle of fibers were sealed with solidified epoxy resin to form a membrane module. The total membrane length and the effective membrane length were 240 and 100 mm, respectively. The total efficient area of the module was about 140 cm² calculated based on the internal diameter of hollow fiber membrane.

Table 1
Characteristics of the membrane module.

Membrane material	Polyvinylidene fluoride
Housing material	Polyester
Inner diameter of the shell (mm)	15
Inner diameter of the hollow fibers (mm)	0.90
Thickness of the membrane wall (mm)	0.15
Mean pore diameter (μm)	0.25
Porosity (%)	79.50
Liquid entry pressure of water (kPa)	180
Number of hollow fibers	50
Module packing density (%)	32
Effective membrane length (mm)	100
Effective permeate area (cm²)	140

2.3. Apparatus

Experiments were carried out with the apparatus shown in Fig. 1. The feed solution, 2.0 L in volume, was heated and maintained at the required temperature flowing through the lumen side of the fibers. The permeate flowed through the shell side and its temperature was held constant by a cooling coil. The feed and the permeate flowed concurrently from the bottom to the upper part of the module with the help of two magnetic pumps. The temperature of both fluids was monitored at the inlet and outlet of the membrane module using four thermometers. The permeate flux was calculated by the following equation:

$$J = \frac{\Delta W}{A \, \Delta t} \tag{1}$$

where J is the permeate flux (kg/m² h), ΔW is the quantity of permeate (kg), A is the effective permeate area of the hollow fiber module (m²) and Δt is the sampling time (h).

2.4. Boron removal experiments

Boron removal experiments were carried out with hot boron acid aqueous solutions as the feed. The feed flow rate (V_f) and the permeate flow rate (V_p) were fixed at 60 L/h and 65 L/h, respectively. During the DCMD process, the experiment with different feed was conducted for 10 h and the obtained permeate was reflowed to the feed reservoir every one hour to keep the feed concentration constant. Feed was replaced with fresh solution every 10 h and then the permeate sample was taken from the permeate reservoir for further analysis. The boron rejection efficiency R was calculated according to the following equation:

$$R \, (\%) = \frac{C_f - C_p}{C_f} \times 100\% \tag{2}$$

where C_f is the feed boron concentration and C_p is the permeate boron concentration. The parameters chosen in DCMD experiments carried out with cold permeate temperature (T_p) at constant 20 °C
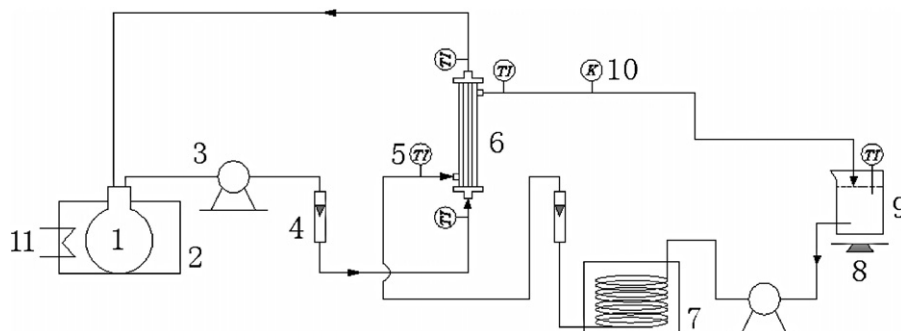
Fig. 1. Schematic diagram of the DCMD experimental setup. (1) feed reservoir, (2) water bath, (3) circulating pump, (4) flow meter, (5) thermometer, (6) membrane module, (7) cooling coil, (8) balance, (9) permeate reservoir, (10) conductivity monitor, and (11) heater.

Table 2
Experimental parameters.

Parameters	Range
pH	3.0, 5.0, 7.0, 9.0 and 11.0
Feed temperature (°C)	30, 40, 50, 60, 70 and 80
Boron concentration (mg/L)	5, 10, 15, 50, 100, 150, 250, 500, 750, 1000, 1250 and 1500
Feed salt concentration (mg/L)	0, 500, 1000, 2000, 3000, 4000 and 5000

were feed boron concentration, feed temperature (T_f), pH and feed salt concentration, whose ranges are given in Table 2. It must be noted that the liquid entry pressure of water (LEPw) of the membrane was 180 kPa and much higher than water vapor pressure at temperature range of 30–80 °C, which ensured that the feed could not penetrate through the membrane directly and kept the DCMD system operating well.

2.5. Natural groundwater application

The application of DCMD on the natural groundwater was performed with the inlet temperatures of hot feed and cold permeate at constant 50 °C and 20 °C, respectively. The feed flow rate was 60 L/h, while the permeate side being 65 L/h. The natural groundwater was taken from the northeastern region of Dandong (Liaoning Province, China). The chemical composition of the untreated natural groundwater was determined by three times analyses and the results are shown in Table 3.

2.6. Analysis methods and instruments

The concentration of boron in the permeate sample was determined by three times analyses using ICP-MS (7500a, Agilent, USA). The detection limit for boron was about 0.02 μg/L and the precision was about <2.7% RSD with comparable levels of accuracy. Linearity for boron was observed in the concentration range of 1–100 μg/L and the coefficient of regression (R^2) was 0.9996. The permeate conductivity was measured using an electric conductivity monitor (CM-230A, Shijiazhuang Create Instrumentation Technologies, China).

The concentration of boron and cations in the natural groundwater were determined by ICP-AES (Optima 2000DV, PerkinElmer, USA). The wavelength utilized for boron determination was 249.772 nm. Linearity for boron was observed in the concentration range of 1–100 mg/L and the coefficient of regression (R^2) was 0.9998. The detection limit for boron was about 0.05 mg/L and the precision was about <3.0% RSD. Anions such as F^-, Cl^- and SO_4^{2-} in the natural groundwater were determined by the ion chromatography (861, Metrohm, Switzerland). Alkalinity, carbonate and bicarbonate were measured using an alkalinity titration, the conductivity of the feed was determined by using the conductivity meter (CO150, HACH, USA).

Both the fresh and the used membrane samples were frozen in liquid nitrogen, fractured to obtain fragments, sputtered with gold and then examined with a Hithche S-3000 scanning electron microscope (SEM) (Hitachi Ltd., Japan). Elemental analysis of the

Table 3
Chemical composition of the untreated natural groundwater sample (pH = 7.7).

Ionic species	Value (mg/L)	Ionic species	Value (mg/L)
K	65.1 ± 1.5	B	12.7 ± 0.3
Ca	214.3 ± 3.8	F^-	2.1 ± 0.4
Na	1035.9 ± 15.7	Cl^-	2120.1 ± 50.4
Mg	208.1 ± 2.1	SO_4^{2-}	511.7 ± 10.8
Fe	Not detected	HCO_3^-	259.8 ± 4.0
Al	Not detected	CO_3^{2-}	Not detected
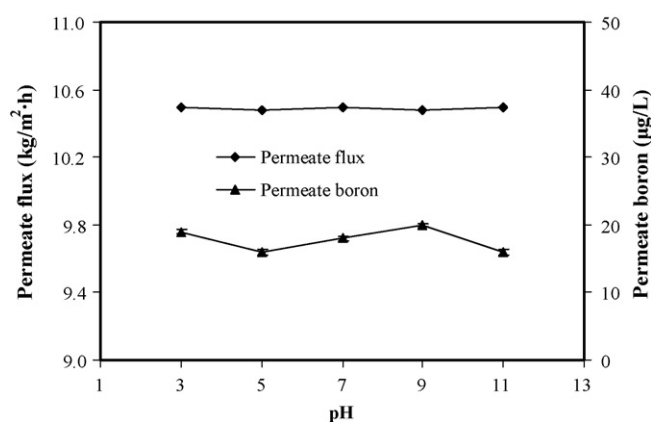
Fig. 2. Variation of permeate flux and permeate boron concentration as a function of the feed solution pH (V_f = 60 L/h, V_p = 65 L/h, T_f = 50 °C, T_p = 20 °C, C_f = 15 mg/L).

scaled membranes was accomplished using energy dispersive X-ray spectroscopy (EDS) analysis system.

3. Results and discussions

3.1. Effect of pH

To evaluate the effect of feed pH on the performance of DCMD process, a series of experiments were carried out with the hot feed at 50 °C, using aqueous solution containing boron of 15 mg/L as feed.

The dependence of the permeate flux and boron rejection on the feed pH is presented in Fig. 2. It can be found that the feed pH had no significant influence on the permeate flux and boron rejection. The permeate flux stabilized at about 10.5 kg/m² h during the whole process. In the feed pH range of 3.0–11.0, the permeate boron concentration was less than 20 ± 0.25 μg/L and all the boron rejection could be over 99.8%. Besides, the permeate conductivity kept below 2.0 μS/cm, which was not illustrated in the figure.

As far as we know, it is impossible to get so high boron removal efficiency by RO membrane process, especially at natural pH (6.5–8.5) or under acid conditions. For RO membrane process, the high boron rejection is only obtained at pH > 11.0 because of the dissociation of boric acid. Being different from RO membrane process, MD uses the temperature gradient created on membrane surfaces as its driving force, which is less dependent on the feed pH. For these reasons, the higher boron rejection can be obtained through the DCMD process whether the feed is alkali or acid.

3.2. Effect of feed concentration

The effect of feed concentration on the performance of DCMD process was investigated at natural pH without acid or alkali addition. The feed temperature was fixed at 50 °C and the feed boron concentration was in the range of 5–1500 mg/L.

The permeate boron as a function of increasing feed boron concentration is shown in Fig. 3. It can be found that all the boron rejection efficiency could be over 99.8%. The permeate boron concentration kept below the maximum permissible level even at feed boron concentration as high as 750 mg/L. When the concentration of feed boron became 1250 mg/L and 1500 mg/L, although the boron rejection efficiency could reach as high as 99.95%, the permeate boron concentration increased to 0.63 ± 0.01 mg/L and 0.71 ± 0.02 mg/L, respectively. This result can be attributed to partial wetting phenomenon because of a small amount large pores existed on the membrane surface. With the feed concentration increasing, both the feed viscosity and the boundary layer thick-
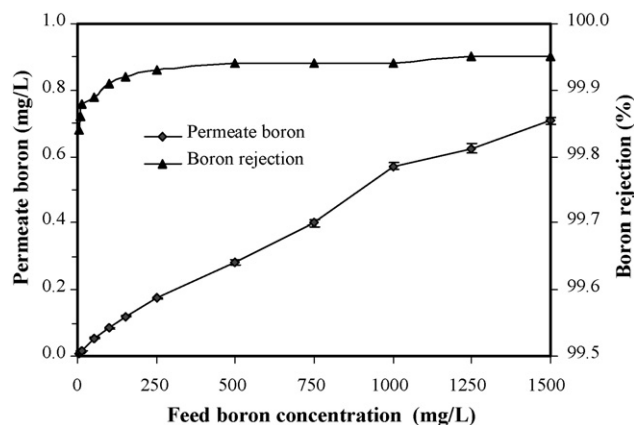
Fig. 3. Variation of permeate boron as a function of the feed boron concentration (V_f = 60 L/h, V_p = 65 L/h, T_f = 50 °C, T_p = 20 °C, at natural pH 6.5–8.5).

Fig. 5. Variation of permeate boron as a function of the feed temperature (V_f = 60 L/h, V_p = 65 L/h, T_p = 20 °C, C_f = 15 mg/L, at natural pH 6.5–8.5).

ness increased, which would aggravate the membrane wetting. Therefore, the permeate boron concentration increased. It is an efficient method to optimize the hydrophobic membrane structure to ensure the permeate quality can meet the WHO recommendation limit. Besides, the RO/MD integrated membrane process could also be a recommendable method. The feed with high concentration boron was primarily treated by RO and then the RO permeate was treated by MD.

During the whole process, with the feed concentration increasing, the permeate flux stabilized at about 10.5 kg/m² h, which meant that the feed concentration had no significant influence on permeate flux.

3.3. Effect of feed temperature

The influence of the feed temperature on permeate flux is shown in Fig. 4. It can be found that the feed temperature had a remarkable influence on permeate flux. With the feed temperature increasing, the permeate flux was enhanced exponentially. This trend could be explained by the Antoine equation [45] which predicted an exponential relationship between the vapor pressure difference and temperature. Besides, both the feed viscosity and the boundary layer thickness declined with the temperature increasing, which was favorable to enhance mass transfer coefficient.

From Fig. 5, it can be found that the effect of feed temperature on boron rejection could be neglected. The permeate boron concen-
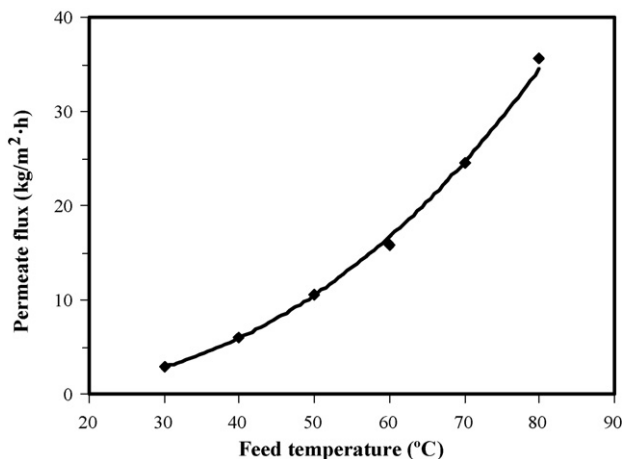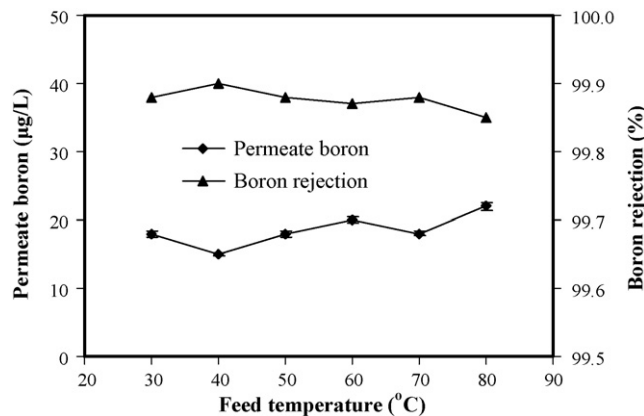
tration was less than 22 ± 0.55 μg/L at all feed temperatures and all the boron rejection efficiency could be over 99.8%. All the experiment results indicated that the PVDF membrane possessed good property of heat-resistance and it could retain hydrophobic under different feed temperature conditions.

3.4. Effect of feed salt concentration

To investigate the effect of feed salt concentration on boron rejection, a series of boron removal experiments were carried out in the presence of NaCl, CaCl₂ and Na₂SO₄, respectively. The feed temperature was fixed at 50 °C and the boron concentration of feed was 15 mg/L.

It can be noted from Fig. 6 that feed salt concentration had no marked influence on boron rejection. For these three kinds of salts, the permeate boron concentration was below 26 ± 0.50 μg/L and all the boron rejection efficiency could be over 99.8%. Besides, the permeate conductivity kept less than 3.0 μS/cm during the whole process, which was not illustrated in the figure. All of these results demonstrated that the membrane had no selective rejection of non-volatile solute. The permeate flux kept stable at about 10.5 kg/m² h and was hardly affected by feed salt concentration in the studied range. This finding is in agreement with the result previously reported by Alklaibi and Lior [46]. According to the Raoult's law, the saturated vapor partial pressure difference (ΔP) between pure water and dilute salt solution at same temperature can be calcu-
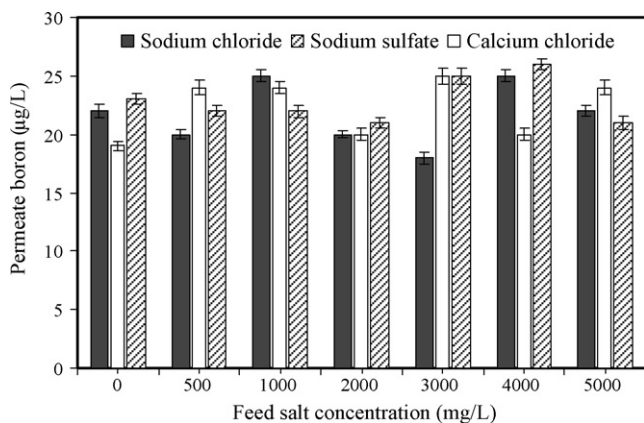

Fig. 4. Variation of permeate flux as a function of the feed temperature (V_f = 60 L/h, V_p = 65 L/h, T_p = 20 °C, C_f = 15 mg/L, at natural pH 6.5–8.5).

Fig. 6. The influence of feed salt concentration on the boron rejection (V_f = 60 L/h, V_p = 65 L/h, T_f = 50 °C, T_p = 20 °C, feed boron concentration = 15 mg/L, at natural pH 6.5–8.5).
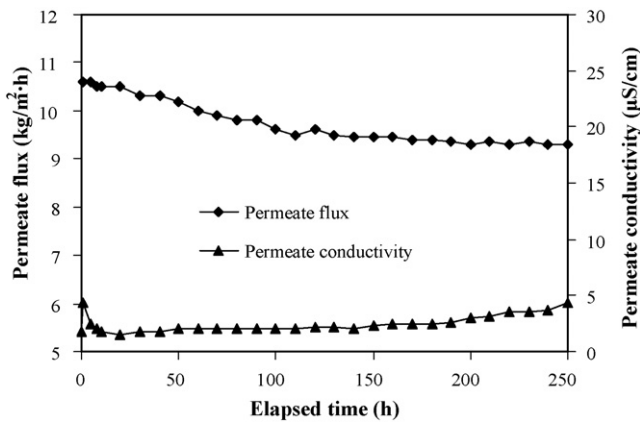
Fig. 7. Variation of permeate flux and permeate conductivity during continuous 250 h DCMD process for boron removal from natural groundwater sample (V_f = 60 L/h, V_p = 65 L/h, T_f = 50 °C, T_p = 20 °C, initial pH of feed water 7.7, without any acid addition).

lated as follows:

$$\Delta P = P_o \frac{m}{55.5} \tag{3}$$

where P_o is the saturated vapor pressure of pure water (Pa), m is the molar concentration of solute in dilute salt solution (mol/L). From Eq. (3), it can be seen that the salt concentration has no significant influence on the saturated vapor partial pressure in the given concentration range, this explaining the permeate flux had no remarkable change with the concentration increasing.

3.5. Natural groundwater application

The natural groundwater sample containing 12.7 mg/L of boron was treated by DCMD process with the feed temperature at 50 °C. The experiment results shown in Fig. 7 demonstrate that the direct application of the natural groundwater as feed for DCMD process resulted in a rapid decline of the permeate flux.

All of these results were mainly due to the formation of deposits. Heating the feed caused a shift from bicarbonate ion to the carbonate ion and scale deposits were formed from those salts whose solubility was generally limited. These scale deposits scattered on the membrane surface would cause pores clogging and pollute the membrane. Therefore, the permeate flux was decreased with the prolongation of operating time. Although the scale deposits polluted the membrane, the quality of obtained permeate was maintained. During the whole process, the permeate conductivity kept below 5.0 μS/cm and the permeate boron concentration was less than 20 ± 0.52 μg/L (Fig. 8). The SEM image of the deposits scattered on the membrane surface is shown in Fig. 9. The SEM–EDS analysis revealed that the deposit consisted chiefly of Ca (45.8 wt%), O (40.3 wt%), C (11.6 wt%) and Cl (1.7 wt%), which meant that the deposit was mainly composed of $CaCO_3$.

In order to eliminate the negative influence of scale deposits formation during the DCMD process, further studies of the DCMD process were carried out at the initial feed pH 4.0 adjusted by addition of 0.1 mol/L HCl to the feed. The experimental result is shown in Figs. 10 and 11. As can be seen, the acidification of the feed enhances the stability of the process in a significant degree. There was no obvious decline of permeate flux during the 250 h continuous operation process. The permeate conductivity stabilized at about 2.5 μS/cm and the permeate boron concentration was in the range of 15 ± 0.36 to 18 ± 0.40 μg/L. Besides, the pH of permeate remained between 7.2 and 7.6 during the whole process, which indicated that pre-acidification had no significant influence on the permeate pH. All of the results demonstrated that pre-acidification
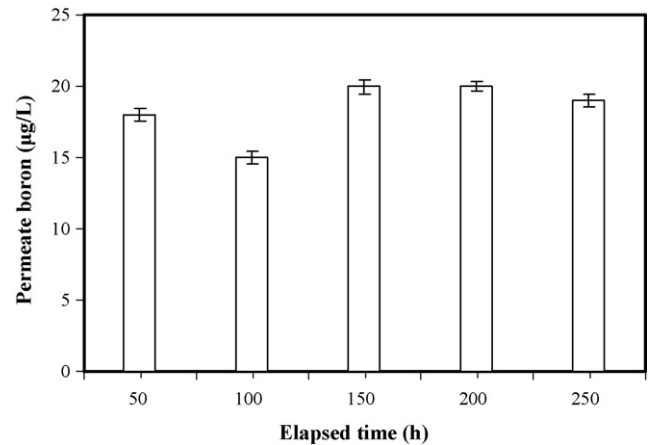

Fig. 8. Variation of permeate boron during continuous 250 h DCMD process for boron removal from natural groundwater sample (V_f = 60 L/h, V_p = 65 L/h, T_f = 50 °C, T_p = 20 °C, initial pH of feed water 7.7, without any acid addition).
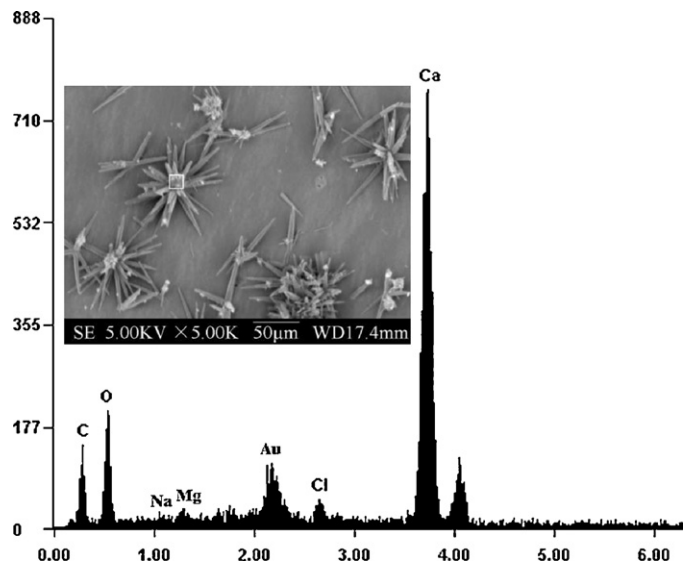

Fig. 9. SEM image and microanalysis report of the deposits scattered on the membrane surface.
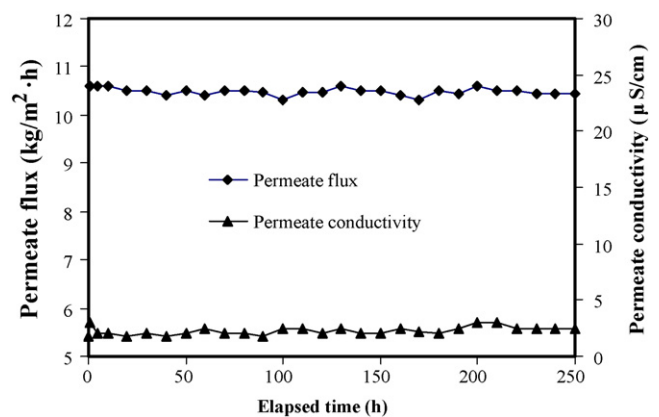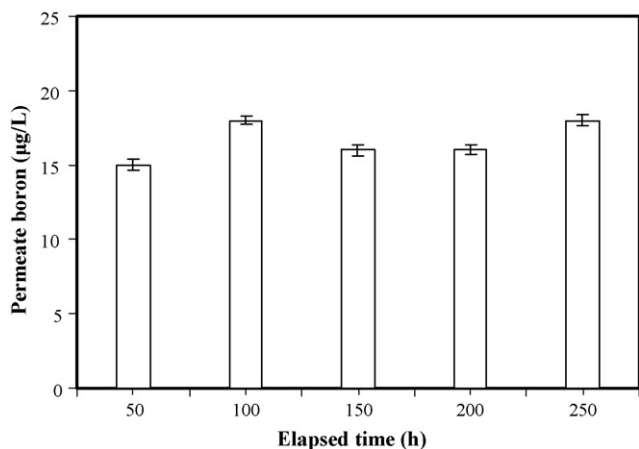

Fig. 10. Variation of permeate flux and permeate conductivity during continuous 250 h DCMD process for boron removal from natural groundwater sample (V_f = 60 L/h, V_p = 65 L/h, T_f = 50 °C, T_p = 20 °C, initial pH of feed water 4.0, with 0.1 mol/L HCl addition).

Fig. 11. Variation of permeate boron during continuous 250 h DCMD process for boron removal from natural groundwater sample ($V_f = 60$ L/h, $V_p = 65$ L/h, $T_f = 50\,°C$, $T_p = 20\,°C$, initial pH of feed water 4.0, with 0.1 mol/L HCl addition).

was an efficient method to eliminate the negative effects of scale deposits and the PVDF membrane had stable permeability and hydrophobicity.

The SEM images of the hydrophobic PVDF membranes taken before and after 250 h continuous boron removal from pre-acidified groundwater are shown in Fig. 12. It can be seen from these micrographs that there were no marked changes in the inner surface and cross-section including the finger-like cavity and sponge-like sublayer. This finding is different from the result previously reported by Barbe et al. [47], who found that the surface of polypropylene (PP) membrane changed after 72 h water contact experiment. An increase in the values of various morphology parameters such as pore area, pore length, pore breadth, and pore diameter was observed. The different results may be attributed to the difference of materials used for membrane preparation. It was well known that PVDF possessed better properties such as chemical-resistance, heat-resistance and hydrophobicity compared with PP.
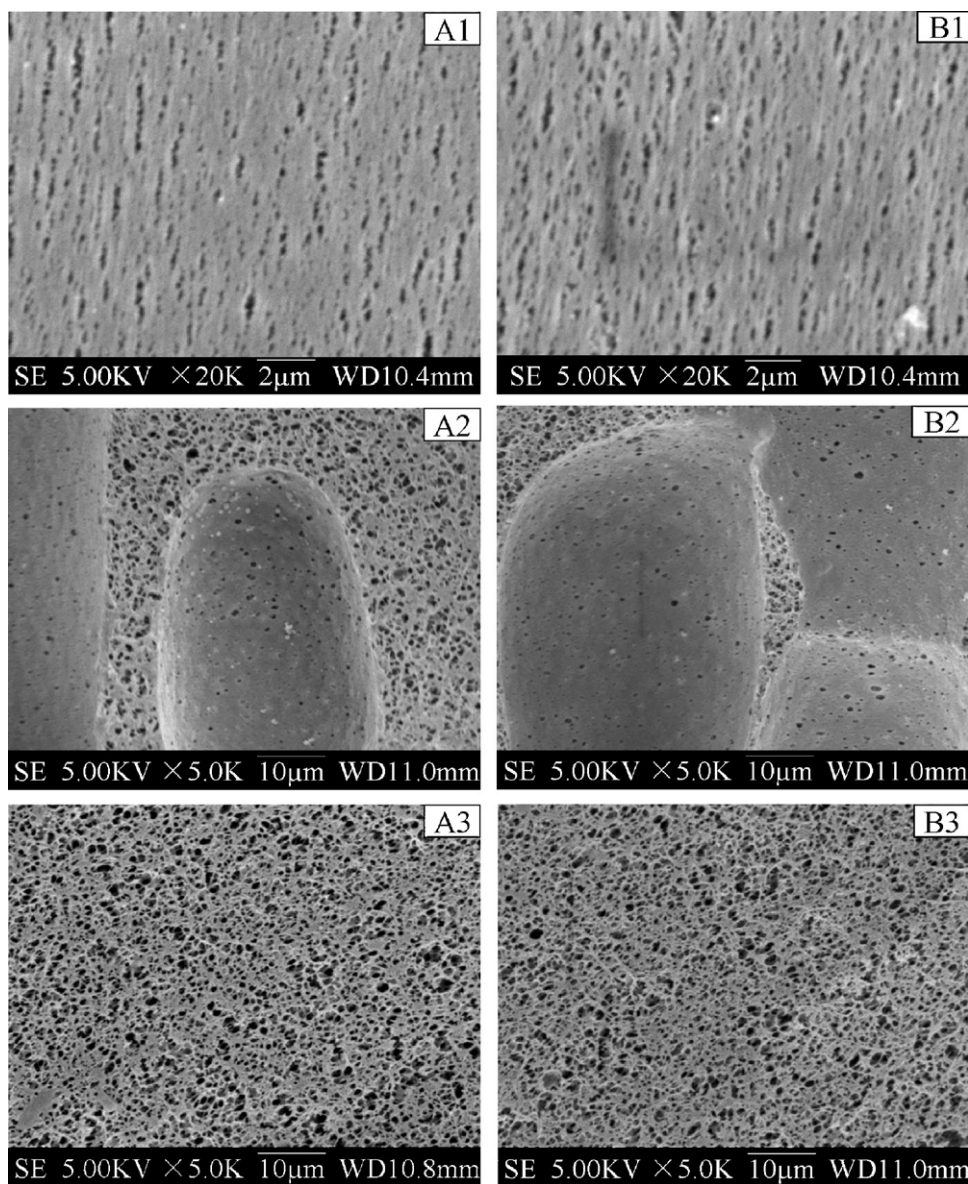
Fig. 12. SEM micrographs of the PVDF membranes: (A1) inner surface of the fresh membrane, (A2) finger-like cavity of the fresh membrane, (A3) sponge-like sublayer of the fresh membrane, (B1) inner surface of the membrane after boron removal, (B2) finger-like cavity of the membrane after boron removal and (B3) sponge-like sublayer of the membrane after boron removal.

4. Conclusions

In the present work, the application of DCMD for boron removal from aqueous solution was investigated systematically and the following conclusions were obtained:

(1) All the boron rejections were above 99.8% in the feed pH range of 3.0–11.0 and the boron rejection was less dependent on the feed pH, which was greatly different from RO process.
(2) The feed boron concentration had no significant effect on the boron rejection and the permeate boron kept below the maximum permissible level even when the feed boron concentration increased to 750 mg/L.
(3) The permeate flux was enhanced exponentially without sacrificing the boron rejection efficiency with the feed temperature increasing and boron removal was greater than 99.8% at all the temperatures tested.
(4) The feed salt concentration had no marked influence on the boron rejection and the permeate flux kept stable with the feed salt concentration increasing to some extent.
(5) The natural groundwater sample containing 12.7 mg/L of boron was treated by DCMD process. The permeate boron kept below 20 μg/L whether the feed was acidified or not, but pre-acidification was helpful to maintain the permeate flux stability.

Acknowledgments

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