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Experimental study of arsenic removal by direct contact membrane distillation

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ABSTRACT

Arsenite (As(III)) and arsenate (As(V)) removal by direct contact membrane distillation (DCMD) were investigated with self-made polyvinylidene fluoride (PVDF) membranes in the present work. Permeability and ion rejection efficiency of the membrane were tested before the arsenic removal experiments. A maximum permeate flux 20.90 kg/m^2 h was obtained, and due to the hydrophobic property, the PVDF membrane had high rejection of inorganic anions and cations which was independent of the solution pH and the temperature. The experimental results indicated that DCMD process had higher removal efficiency of arsenic than pressure-driven membrane processes, especially for high-concentration arsenic and arsenite removal. The experimental results indicated that the permeate As(III) and As(V) were under the maximum contaminant limit (10 μg/L) until the feed As(III) and As(V) achieved 40 and 2000 mg/L, respectively. The 250 h simultaneous DCMD performance of 0.5 mg/L As(III) and As(V) solution was carried out, respectively. The permeate arsenic was not detected during the process which showed the PVDF membrane had stable arsenic removal efficiency. Membrane morphology changed slightly after the experiments, however, the permeability and the ion rejection of the membrane did not change.

1. Introduction

Arsenic is present in water as a result of both natural and anthropogenic activities. Inorganic arsenic occurs in the environment in several forms. In natural waters, As(III) and As(V) are generally considered to be the dominant species. Arsenic contamination of groundwater has become one of the most serious problems in water environment, and it is particularly problematic when the groundwater is utilized as drinking water [1].

Exposure to arsenic contaminated water can lead to a number of health problems. Usually arsenic is built up in the body through drinking water, food contaminated with arsenic, and causes increased risks of cancer in the skin, lungs, liver, kidneys, and bladder. Consumption of arsenic also leads to disturbances of the cardiovascular and nervous system functions which eventually lead to death [2]. A new standard for arsenic in drinking water at 10 μg/L was adopted in China recently, which was in accordance with the maximum contaminant level of arsenic in drinking water recommended by WHO [3].

The methods developed for arsenic removal are mainly precipitation [4], ion-exchange [5], adsorption [6], and membrane processes [7]. To effectively decrease arsenic by precipitation requires a large amount of chemicals. This process also creates volumetric sludge, which needs further treatments before disposing it into the environment. Ion-exchange process has a disadvantage of releasing noxious chemical reagents used in the resin regeneration into the environment. Adsorption was considered to be an efficient way to remove arsenic from natural waters and wastewaters [6]. Activated carbon [8], oxides [9,10], biosorbents [11] and other low-cost adsorbents [12–14] were used for arsenic removal. However, the adsorption method requires a regeneration process after the adsorbents being exhausted, which may decrease the capacity of adsorbents.

Reverse osmosis and nanofiltration are two common pressure-driven membrane processes used for arsenic removal. The experimental results showed high removal efficiency of As(V) but very low removal efficiency of As(III) for both the two membrane processes, especially for the nanofiltration. Furthermore, the removal efficiency of arsenic by reverse osmosis and nanofiltration are strongly influenced by the solution pH and the kinds of membranes [15–19]. Here, a hydrophobic membrane process-membrane distillation was presented for arsenic removal.

Membrane distillation (MD) is a thermally driven process that involves transport of water vapor through a porous hydrophobic membrane. During the MD process of solutions with non-volatile solutes, only water vapor can transfer through the membrane. Thus, theoretically speaking, the MD process enables the production of pure water from natural water. Compared with the pressure-driven membrane processes, membrane distillation is less dependent on the initial salinity of the feed as well as a higher salt rejection ratio

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[20]. Thus, membrane distillation has been used in seawater desalination [21], juice concentration [22], and other industrial areas [23–25]. However, membrane distillation has little been used for arsenic removal.

Direct contact membrane distillation (DCMD) is one of the four basic configurations of MD, in which the feed and the permeate are directly separated by the membrane. And DCMD is considered to be the most simple, economical and efficient configuration [26]. Thus, in the presented work, DCMD was used for arsenic removal. Both the removal of As(III) and As(V) were investigated.

2. Materials and methods

2.1. Reagents and analysis methods

All chemicals used in the experiments were of analytical reagent grade. As_2O_3 and $Na_2HAsO_3\cdot 7H_2O$ were obtained from E. Merck (Darmstadt, Germany). As(III) and As(V) solutions were prepared with tap water (Beijing, no. 9 plant), respectively. And the other solutions were prepared with deionized water.

The conductivity of the feed was measured using a conductivitymeter (CO150, HACH, USA). Analysis of Cl^- and $SO_4{}^{2-}$ were made by ion chromatograph (861, Metrohm, Switzerland), respectively. Ca^{2+} was analyzed using EDTA titration method. Arsenic analysis was performed by hydrid-generation atomic fluorescence spectrometry (HG-AFS) (AF-610, Rayleigh, China), following the reduction of As(V) to As(III). And the reducing agents were thiourea and ascorbic acid.

2.2. Membranes and DCMD unit

The hydrophobic polyvinylidene fluoride (PVDF) capillary membranes used in the experiments were self-made and the characteristics are shown in Table 1.

The DCMD experimental installation is shown in Fig. 1. It consisted of two thermostatic cycles, the feed one, and the permeate one, which were connected to the membrane module. The membrane module with the diameter of 0.015 m and the effective length of 0.10 m was assembled in a vertical position. The module was equipped with 50 hydrophobic PVDF membranes, and the total effective area of the module was calculated for the internal capillary diameter and amounted to $12.56 \times 10^{-4}\,m^2$. Both the feed and the permeate were pumped from the bottom to the upper part of the module. The feed flowed inside the capillaries, whereas the permeate flowed through the intertubular space. There were four thermometers equipped on the inlets and the outlets of the feed side and the permeate side, respectively. The permeate flux was measured by the overflow volume of the permeate reservoir.

Table 1
Membrane characteristics

d_{out}/d_{in}[a] (μm)	1/0.8
ε[b] (%)	80
Average pore radius (μm)	0.15
δ[c] (mm)	0.20
LEPw[d] (kPa)	250

[a] Outside/inside diameter of the capillary membrane.
[b] Porosity.
[c] Membrane thickness.
[d] Liquid entry pressure of water.

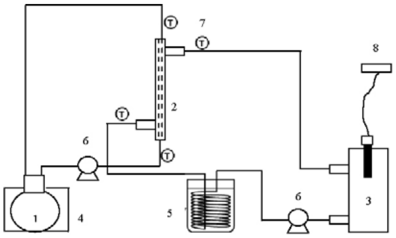

Fig. 1. DCMD setup: (1) feed reservoir; (2) membrane module, (3) permeate reservoir, (4) water bath, (5) cooling coil, (6) pump, (7) thermometer and (8) conductivity monitor.

2.3. Permeability and ion rejection tests

To investigate the water vapor permeability of the membrane, a set of experiments were carried out using pure water as feed. The mean feed temperature varied from 40 to 70 °C while the permeate temperature was kept at 20 °C. Besides, at each feed temperature, the permeate fluxes were also measured in a range of feed flow rate (V_f) from 0.23 to 0.96 m/s. The permeate flow rate (V_p) was kept at 0.10 m/s.

To investigate the ion rejection efficiency of the membrane, 0.10 mol/L NaCl, Na_2SO_4 and $CaCl_2$ solutions were prepared for DCMD experiments. The feed and the permeate temperature were kept at 50 and 20 °C, respectively. The feed and permeate flow were kept at 0.80 and 0.10 m/s, respectively. The ion rejection efficiency was calculated both according to the conductivity and the ion concentration.

2.4. Arsenic removal experiments

Arsenic removal experiments were carried out with aqueous As(III) and As(V) solutions, respectively. The solution pH was adjusted to 5.0, and the operating parameters of the DCMD process were in accordance with the ion rejection tests. Then batch concentrating experiments were carried out with initial feed arsenic 0.20 mg/L. The permeate arsenic was measured during the whole concentrating process, and the experiments were shut down when the permeate arsenic concentration exceeded the maximum contaminant limit (10 μg/L). The arsenic rejection efficiency R was calculated according to the following equation:

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

where C_f is the feed arsenic concentration and C_p is the permeate arsenic concentration.

In order to investigate the stability of arsenic removal efficiency, 250 h DCMD performance of 0.5 mg/L As(III) solution and As(V) solution was carried out, respectively. The solution pH was adjusted to 5.0, and the operating parameters of the DCMD process were in accordance with the above concentrating experiments. In addition, the permeate flux, conductivity and the permeate arsenic were measured during the whole process.

2.5. SEM analysis

Both the fresh membrane and the used membrane samples were made by liquid nitrogen and dried in the oven at 50 °C. Then the membrane samples were sputter coated with gold and examined by using a Hithche S-3000 scanning electron microscope (Japan). The accelerating voltage used was 5 kV, and all samples were imaged at 5000×.