



Rejection of heavy metals in acidic wastewater by a novel thin-film inorganic forward osmosis membrane



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HIGHLIGHTS

- Rejection of heavy metals in acidic wastewater using TFI membrane was investigated.
- An average rejection efficiency of 94% was achieved for Cd²⁺, Pb²⁺, Cu²⁺ and Zn²⁺.
- TFI membrane yielded a high water flux while rejecting heavy metals in wastewater.
- The co-function of double layer overlap and membrane pore size was proposed.

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ABSTRACT

This study reports efficient rejection of four typical ionic divalent heavy metals of interest (*i.e.* Cd²⁺, Pb²⁺, Cu²⁺, Zn²⁺) using forward osmosis (FO) by our recently developed nanoporous thin-film inorganic (TFI) membrane fabricated through tetraethylorthosilicate-driven sol-gel process. Upon lab-scale FO cell with feed solution containing heavy metal electrolytes (pH 4.5 ± 0.5) and NaCl serving as draw solution, the TFI membrane yields a high water flux of 69.0 L m⁻² h⁻¹ driven by 2.0 mol L⁻¹-NaCl draw solution. Meanwhile, effective rejection of heavy metal ions was achieved, with an average efficiency of 94% at feed concentration of 200 mg L⁻¹. Since the membrane is able to reject heavy metals whose hydrated ion diameters are smaller than the membrane pore size, the charge-interaction rather than size exclusion should be responsible for heavy metal rejection. Based on classical Debye-Hückel theory and Gouy-Chapman model, we demonstrate a particular significance of double layer overlap within membrane pore induced by electrostatic interaction between heavy metal ions and silica-made pore walls. As such, the selectivity of TFI membrane depends essentially on the co-function of membrane pore size, surface potential of membrane pore wall as well as Debye length. This study not only confirms the feasibility of the TFI membrane in treating acidic heavy metal-containing wastewater without pH adjustment, but also suggests a simple theoretical scheme to better understand and design charged membrane with expected selectivity for FO applications.

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1. Introduction

Heavy metals, which constitute important composition in the crust of the Earth, can bind to proteins and some alterations in the normal functions of proteins may occur [1,2]. Therefore, heavy metals can affect the central nervous system and various human organs, when entering the food chain and accumulating in human body [3]. In order to remove heavy metals in a certain aqueous solution, it is common practice to add alkali for the formation of hydroxide precipitants, which can be separated by coagulation/

flocculation, precipitation, adsorption, and filtration methods [4]. However, such process needs further improvements due to low efficiency, high cost, and environmental incompatibility. Membrane-based technology such as reverse osmosis (RO), nanofiltration (NF) and electrodialysis (ED) has drawn growing interest in heavy metal removal due to high-rejection and less production of secondary pollutants [5,6]. However, membrane fouling and high energy cost remain limiting factors.

More recently, much attention has been devoted to forward osmosis (FO), which exhibits remarkable potential in seawater/brackish water desalination and wastewater treatment [7]. Without external pressure applied, FO produces high osmotic pressure gradient and drives water molecules from feed solution (FS, low

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osmotic pressure) to draw solution (DS, high osmotic pressure), thus realizing the removal of pollutants. The pressure-free operation gives rise to several unique advantages in terms of low energy consumption, efficient water recovery, less membrane fouling and easy fouling removal [8]. However, there are very limited studies on FO for removal of heavy metals in water or wastewater up to present. By using a novel bulky hydroacid complex as a draw solute to minimize the reverse solute flux, a thin-film composite (TFC) FO membrane has been demonstrated to effectively remove heavy metal compounds from wastewater [9]. In another study, two different FO membranes (cellulose triacetate (CTA) and polyamide-based thin-film composite (TFC) membrane) have been investigated in treating high-salinity feed waters containing heavy metal Ni^{2+} with different salinities [10]. A bench-top test showed that HTI (Hydration Technology Innovations) FO systems have superior contaminant removal performance, rejecting >88.3% Cu, Pb, As and Cr at concentrations of 10 mg L^{-1} using a sugar-electrolyte draw solution [11]. And a submerged FO system achieved almost a complete retention of trace heavy metals including Cr, Mn, Ni, Cu, Zn and Pb. Most rejection rates were higher than 99% [12]. Besides, FO has also been proposed to remove arsenic in water [13,14]. However, the handful existing studies [9–14] reported relatively low water flux ($<30 \text{ L m}^{-2} \text{ h}^{-1}$) and the organic polymeric FO membranes may be problematic for treating acidic heavy metal-containing wastewater like electroplating wastewater due to their limited pH and thermal stability. Comparatively, inorganic membranes have superior thermal and chemical stability with great potential for application to water desalination, but no studies about heavy metal removal using inorganic FO membrane have been reported.

Our most recent work developed a silica-made thin-film inorganic (TFI) membrane for FO process [15]. In the aspect of water flux, a much better performance was achieved by the TFI membrane than organic polymeric membranes and the performance remained superior in a wide range of pH (5.0–9.0) and temperature (20–70 °C) [15]. The silica interface consists of active silanols (Si–OH) that are negatively charged at pH > 2.0 with a surface density of 4.6 OH/nm^2 [16]. If the distance between two silanol surfaces is on nanoscale, the double layer overlap will raise overlapping electric potential inside nano apertures, which makes it possible to reject heavy metals using TFI membrane. In this study, we examined rejection of four typical ionic divalent heavy metals (Cd^{2+} , Pb^{2+} , Cu^{2+} , Zn^{2+} , pH 4.5 ± 0.5), which are most widely studied in industrial wastewater, by our newly developed TFI membrane based on lab-scale FO system and discussed the mechanisms for heavy metal rejection of TFI membrane.

2. Materials and methods

2.1. Materials

The sol-gel method was applied to fabricate the thin-film inorganic (TFI) membrane through micro-interfacial deposition of silica xerogels onto the stainless steel mesh (SSM, type 316L, purchased from Anping Metal Ltd. Hebei Province, China) scaffold according to the procedures in our previous study (Fig. 1) [15]. SSM weaved by superfine wires with diameter of $18 \mu\text{m}$ gave the regular network structure with individual grid size of $1.0 \mu\text{m}$. The tetraethylorthosilicate (TEOS, purchased from Sigma-Aldrich Co., St. Louis, MO) was used as precursor to produce xerogels and silica membrane. The synthetic wastewater containing divalent heavy metals was prepared by dissolving chemical stocks, i.e. $\text{Cd}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$ (purchased from Kemiou Chem. Reagent Co. Ltd. Tianjin, China) into deionized water (DI water,

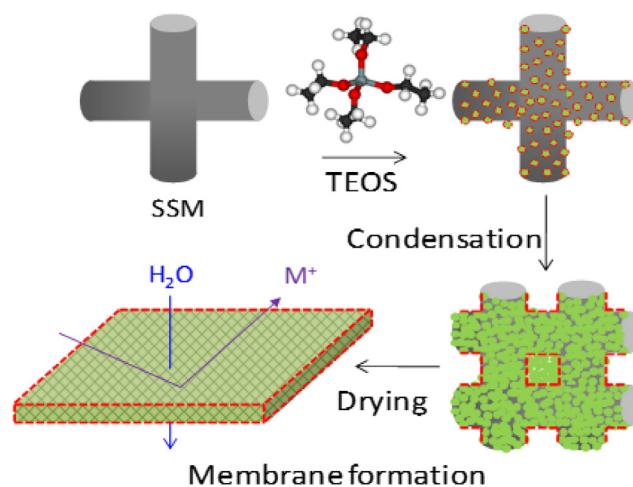


Fig. 1. Schematic diagram of TFI membrane formation.

$1.0\text{--}1.5 \mu\text{S cm}^{-1}$). The draw solution of FO was NaCl solution ($0.5\text{--}2.0 \text{ mol L}^{-1}$).

2.2. Characterizations

The porometry of the TFI membranes was performed on a Porosimetry System (ASAP 2020, Global Spec. Inc., U.S.) with a turbo molecular pump system and pressure transducer using water vapor as the condensable gas and nitrogen as the permeating gas. According to the procedures described previously, a drying temperature of 200 °C and a measurement temperature of 40 °C were used during the tests. The Kelvin diameter was calculated from the relative actual vapor pressure to saturated vapor pressure by using the Kelvin equation:

$$d_K = \frac{2\gamma V_m}{R_g T \ln(p/p_0)} \quad (1)$$

where d_K (m) is the Kelvin diameter of the pore, γ the surface tension (695.6 N m^{-1} @ 40 °C), V_m the molar volume ($1.8 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$), R_g the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T the Kelvin temperature (313 K), p_0 the saturated vapor pressure, and p the actual vapor pressure. The average pore size was defined as the pore size obtained at the 50% permeability of nitrogen gas by condensed water [17].

Zeta potential of the xerogels was measured by dispersing dried silica powders in aqueous DI water and electrolytes using zeta potential analyzer (Zetasizer nano ZS, Malvern Instruments Ltd., U.K.) at step-wise change of pH values adjusted by HCl (1.0 mol L^{-1}) and NaOH (1.0 mol L^{-1}). The concentration of heavy metals in FS was determined by ICP-OES (Perkin Elmer Optima 5300DV, U.S.) upon the measurements in triplicate.

2.3. Rejection of heavy metals based on FO experiments

The lab-scale FO cell was made of two pieces of thick Plexiglas-made plates, containing two inner cavities separated by the membrane as detailed in our previous studies (Fig. 2) [15,18].

The FS (heavy metal ions, $50\text{--}1000 \text{ mg L}^{-1}$) and DS (NaCl) were recirculated at a constant flow rate of 260 mL min^{-1} , by using two individual peristaltic pump (type BT100-1Z, Baoding, Longer Inc., China). Based on solubility product constant (K_{SP} [19]) and minimum pH to form precipitant (Table 1), unless stated otherwise, pH value of FS was adjusted at pH 4.5 ± 0.5 using nitric acid to ensure the existence of heavy metals in ionic form. The tempera-

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