DEVELOPMENT OF AN INNOVATIVE THIN-FILM COMPOSITE MEMBRANE FOR EFFICIENT ARSENIC REMOVAL

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TÓM TẮT

NGHIÊN CỨU PHÁT TRIỂN MÀNG MỎNG TỔNG HỢP ĐỂ NÂNG CAO HIỆU QUẢ LOẠI BỎ ASEN

Trong nghiên cứu này, quy trình thẩm thấu thuận (FO) mới phát triển để loại bỏ các ion Arsenic (As) ra khỏi dung dịch nước đã được nghiên cứu. Ảnh hưởng của nồng độ As, pH và nồng độ muối trong dung dịch đến khả năng loại bỏ As đã được kiểm tra. Các phát hiện đã chứng minh rằng khả năng loại bỏ As bị ảnh hưởng đáng kể bởi độ pH của dung dịch. Dạng As ion có thể được thay đổi từ trung tính sang monoanion và dianionic khi tăng độ pH. Điều này có thể cải thiện lực đẩy điện giữa bề mặt màng và các ion, do đó, khả năng loại bỏ As tăng lên. Ngoài ra, do áp suất thẩm thấu tăng nên dòng nước tăng lên khi tăng nồng độ dung dịch hòa. Tỷ lệ loại bỏ As đạt 96,6%, cao hơn so với hiệu suất của màng mỏng tổng hợp thương mại TFC. Do đó, màng mỏng tổng hợp TFC mới có chất phụ gia ưa nước trong lớp hỗ trợ được cho là có tiềm năng loại bỏ As trong hệ thống xử lý tích hợp.

Keywords*: Màng TFC, thẩm thấu thuận, Arsenic.*

1. INTRODUCTION

Millions of people have been poisoned worldwide during the last ten years due to groundwater pollution with arsenic (As) [1]. Natural sources of arsenical contamination include minerals and sediments. While organo-As species are often found in industrially contaminated water, the main species of As (V) found in groundwater are the oxyanions [H_3AsO_4, $H_2AsO_4^{1-}$, $HAsO_4^{2-}$]. The pH and redox conditions of the groundwater determine the As species' prevalence [2]. The WHO and other national and international organizations have decreased the maximum contamination limit (MCL) of As in drinking water to 10 µg/L (formerly 50 µg/L) since consuming As-contaminated water is thought to be the main cause of As poisoning [3].

Membrane technology has been a viable choice for treating wastewater in recent decades because of its low manufacturing cost and high rejection rate of pollutants including organic compounds and dye molecules [4]. Using size exclusion and Donnan exclusion, nanofiltration (NF) is a potent heavy metal removal and wastewater treatment technique [5], [6]. NF membranes, however, have a significant fouling tendency, which has led to decreased productivity and increased operating costs. Furthermore, inadequate rejection of heavy metal ions in NF procedures during the water treatment process results in additional expenses for further purification [7].

An innovative technique for treating water, forward osmosis (FO), has attracted more attention recently. According to Cath et al. (2006), water flow over a semi-permeable membrane from a lower osmotic pressure feed solution to a higher osmotic pressure draw solution is known as FO [4]. FO has a reduced fouling potential, is easy to use, and has a greater recovery rate. However, if draw solution regeneration is necessary, FO may demand a significant amount of energy. FO has been proposed for use in liquid food processing (Petrotos et al., 1999), wastewater reclamation, saltwater desalination (McCutcheon et al., 2006), and power production using a derivative pressure delayed osmosis method [8, 9]. Despite having such distinctive qualities, the existing FO technology is far from ideal. For instance, there is a limited selection of FO membranes [8], and more energy may be needed to replenish the draw solute by methods such as reverse osmosis (RO), nanofiltration, ultrafiltration (UF), and others [9]. However, compared to pressure-driven operations, FO offers the benefits of no or low operation pressure, reduced fouling propensity, and easy cleaning. In addition, it is expected that the FO thin film composite membrane (TFC) will effectively remove trace pollutants such As due to its very small pore size (0.47 nm) and negatively charged surface [10]. Nevertheless, the absence of optimal membrane characteristics, such as high water permeability and low support layer resistance of water transport, has impeded the commercial application of FO. In a prior study, we created a novel manufactured TFC membrane that may address this problem by adding hydrophilic poly-L-lysine as an addition to the polysulfone substrate layer [11].

To remove arsenic ions, a new TFC membrane was designed by casting a polyamide layer via a hydrophilic support layer from our previous work due to high flux and salt rejection performance [11]. We thus want to investigate the effect of the suggested new FO system at varied operating temperatures and concentrations of the feed and draw solutions. The promising study findings indicate that the innovative FO system may have tremendous promise for removing As ions in wastewater treatment.

2. EXPERIMENT

2.1. Materials

The feed solution included sodium hydrogen arsenate heptahydrate (Na_2HAsO_4) as a source of As(V). Using NaCl, draw solutions with different salt concentrations were made. The polymer for the support layers was polysulfone (average molecular weight: 35000 g.mol-1, pelleted, Sigma-Aldrich), and the solvent to dissolve the polymer was 1-methyl-2-pyrrolidone (NMP, Sigma). Precursors for the polyamide layer that was created on the support by interfacial polymerization (IP) included 1,2-phenylenediamine (MPD, 98% Sigma) and trimesoyl chloride (TMC, 98% Sigma). The TMC was dissolved in n-hexane (98 %, As One) solvent, and the draw solution for the FO operation and salt permeability test was made with sodium chloride (NaCl, As One). > 98% of the Poly-L-Lysine was acquired from Sigma-Aldrich. Utilizing deionized water as a feed solution.

2.2. FO membrane and experimental module of FO

The novel TFC membrane also known as the lysine membrane used in the studies was created from our earlier research [11]. The FO membrane cell was made with natural acetal copolymer (CF042 FO, Sterlitech Corporation, WA, USA). The FO membrane module consisted of a crossflow membrane cell with two channels for the draw and feed solutions. The dimensions of the channel were 9.2 cm long, 4.6 cm wide, and 0.2 cm high, resulting in an effective membrane area of 42 cm^3. A peristaltic pump was used to recycle the feed and draw solutions. The feed and draw solutions in the system were maintained between the two closed loops at a steady crossflow rate of 0.25 L/min. By digitally weighing the reservoirs, we were able to monitor weight changes over time. Conductivity and pH meters were used to record changes in the solutions every 60 minutes (Horiba F-74, Japan). The pH was measured using a pH electrode and adjusted as needed using HCl and NaOH solutions.

2.3. Preparation of support layer

The support layer was made by a phase inversion process. The dope solution of Polysulfone/N-methyl-2-pyrrolidinone (NMP) at the weight ratio of 10/90 with Poly-L-Lysine as an additive of 5% ratio weight was cast on a clean glass plate after immersing in a water bath. A detailed description of the fabrication process for flat sheet membranes has been documented elsewhere [11].

2.4. Interfacial polymerization of thin-film-composite (TFC) membranes

An interfacial polymerization reaction between MPD in the aqueous phase and TMC in the organic phase produced a thin polyamide layer on top of lysine substrates. [11].

2.5.Experimental procedures of FO

The necessary quantities of Na_2HAsO_4 were dissolved to create feed solutions containing As(V). pH changes from 4 to 8. There were 0.5 L of feed solution in total. Draw solutions with salt concentrations of difference (from 0.5 to 2 mol/L) were made; the volume of the draw solution was 0.5 L overall. NaCl was selected for the production of draw solutions because of its low molecular weight, low viscosity, high solubility, and high osmotic pressure. It is also non-toxic, easily and reasonably separated, and recyclable.

The water flux of FO (J_w) was determined by calculating the change of weight of the draw solution Eq. (1):

$$J_{\mathrm{w}} = \frac{\Delta V}{A_{\mathrm{m}} \cdot \Delta t} = \frac{\frac{\Delta m}{\rho}}{A_{\mathrm{m}} \cdot \Delta t} \tag{1}$$

where ρ is the feed solution's density, Am is the effective membrane area, and ΔV and Δm are the volume and weight changes, respectively, of the draw solution during the operating time interval Δt.

The percentage of feed solutes retained by the membrane, or the rejection of As, R(%), was determined using Equation (2).

$$R(\%) = 1 - \frac{C_{\mathrm{d}} \times V_{\mathrm{d}} / V_{\mathrm{p}}}{C_{\mathrm{f}}} \tag{2}$$

where V_d (L) is the draw solution's final volume, V_{p} (L) is the permeate water's volume, and C_f (mg/L) is the As concentration in the feed solution. At the end of each FO test, C_d (mg/L) is the As concentration in the draw solution. Inductively coupled plasma atomic emission spectrometry (ICP-AES, Shimadzu ICPS-9000) was used to measure C_d (mg/L). Based on the data obtained throughout time, an experimental procedure was used to determine the average and standard deviation of As removal and water flow. Each experiment's error bars showed the standard deviation across three runs.

3. RESULTS AND DISCUSSION

3.1. Effect of As concentration on water flux and As rejection

To assess the efficacy of the FO system for As rejection, we initially conducted FO tests at pH 6.0 with As doses ranging from 5 to 50 mg/L. The relationship between the initial concentration of As in the feed solution ([As]) and J_{w} and R(%) are displayed in Fig. 1.

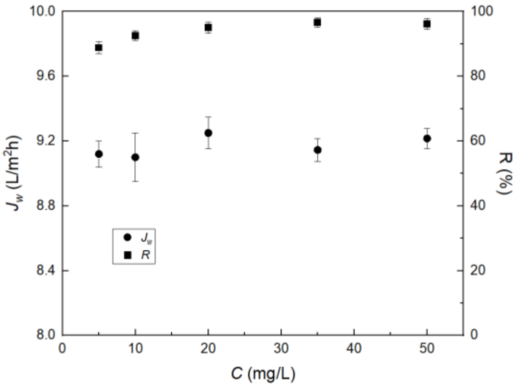

Fig 1. The associations between the initial concentration of As in the feed solution ([As]) and water flux and rejection rate

For As(V), the average J_{w} was 8.6 L/m^{2}h in the [As] range of 5 to 50 mg/L. There was a rise in As(V) R(%) from 88.8% to 96.2%. As(V)'s hydrated radii were probably the cause of its higher R(%) [12]. Furthermore, because the draw solution's Na^+ concentration was significantly higher than that of the feed solution, it may be concluded that Na^+ would less diffuse from the feed solution to the draw solution and impede the diffusion of $HAsO_4^{2-}$, which further delayed the transport of anionic $HAsO_4^{2-}$ [14]. Consequently, the high rejection rates of As by the FO process might also be attributed to the Donnan equilibrium. The same observation by research of

Pham et al., with an increase of As initial concentrations, a significant rise of As rejection was obtained [13]. However, water flux and As rejection were lower than these in this study. Pham et al. reported that 92% rejection of As(V) was obtained in the case of the Aquaporin-TFC system supported by Sterlitech Corp. In other work, Mondal et al. showed that the rejection of As(V) ranged from 94% to 95.8% for $MgSO_4$ and from 93% to 94.9% for glucose as a draw solution in commercial TFC membrane system provided by Hydration Technology Innovation [12]. Thus, it can be seen that fabricated TFC membranes in this study may have a higher performance than commercial TFC flat sheets.

3.2. Effect of draw solution concentration on water flux and As rejection

This investigation used concentrated draw solutions to speed up the FO treatment. The correlations between water flux and rejection rate and the concentration of salt in the draw solution ([NaCl]) are displayed in Fig. 2.

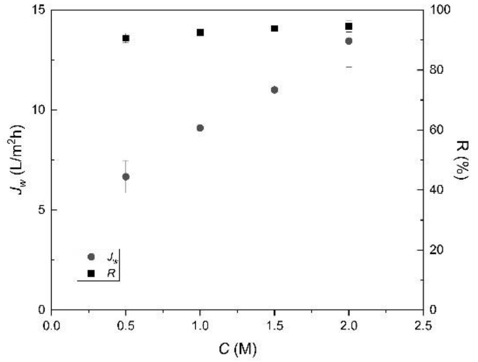

Fig 2. The correlations between water flux and rejection rate and the concentration of salt in the draw solution ([NaCl])

Because of the increased osmotic pressure, water flux rose as [NaCl] increased. J_w was around 6.7 L/m^{2}h at a concentration of 0.5 mol/L NaCl in the draw solution. A more than twofold increase in water flux was noted at a draw solution concentration of 2 mol/L for NaCl.

Fig 2 shows the increase of As rejection from 90.6% to 94.5% by an increase of draw solution concentration. There are several reasons for the high rejection of As(V). Since there was no pressure exerted during the FO process, convective flux had no impact on ion transport. The solution-diffusion process is the predominant mechanism for solute transport across TFC FO membranes, in contrast to the NF membrane [5]. Diffusion becomes less effective as the hydrated radius increases, making it easier to reject metal ions with higher radii of hydration. Additionally, the Donnan equilibrium effect may slow ionic penetration rates across the active layer because of the extremely concentrated bulky ions present in the draw solution. For instance, HAsO42 dominated the As(V) situation, with $H_2AsO_4^-$ making up a minor portion. Electrostatic repulsion between the negatively charged FO membrane and ion increases as a result. The rejection of solutes is dependent on the characteristics and properties of the membranes used for separation, this results are similar to some previous studies in which commercial TFC membranes were investigated [12]–[14].

3.3. Effect of feed solution pH on water flux and As rejection

The connections between feed solution pH and water flux and rejection rate are displayed in Fig. 3. When the pH was between 4 and 8, the water flux of As(V) remained steady at 9 L/m^{2}h. The rejection of arsenic jumped from 86.2% to 92.9% with the rise of pH. The significant variations in the dissociation constants of H_3AsO_4 (As(V)) may cause this. The following are dissociation reactions and dissociation constants [15]:

$$H_3AsO_4 + H_2O \rightleftharpoons H_2AsO_4^- + H_3O^+ \ (pK1 = 2.3) \quad (3)$$

$$H_2AsO_4^- + H_2O \rightleftharpoons HAsO_4^{2-} + H_3O^+ \ (pK2 = 7.08) \quad (4)$$

$$HAsO_4^{2-} + H_2O \rightleftharpoons AsO_4^{3-} + H_3O^+ \ (pK3 = 11.5) \quad (5)$$

The p*K*ai values may be used to compute As(V) species concentrations at various pHs. As(V), for instance, is almost entirely in the neutral form at pH 1.0. Arsenic species change from the neutral H_3AsO_4 form to the monoanionic $H_2AsO_4^-$ form between pH 2.2 and 7.0. The dianionic $HAsO_4^{2-}$ species is formed when the monoanionic $H_2AsO_4^-$ dissociates at pH 7.0. The greater hydrated radii of $HAsO_4^{2-}$ and its enhanced electric repulsion compared to $H_2AsO_4^-$ are the reasons for the rise in arsenate rejection rate at higher pH values. At higher pH values, as the zeta potential charge density decreases, the membrane surface becomes more negatively charged and increases the charge exclusion. This is in line with the usual Donnan exclusion behavior and charge interaction, which improve the negative species separation that was previously discussed [15].

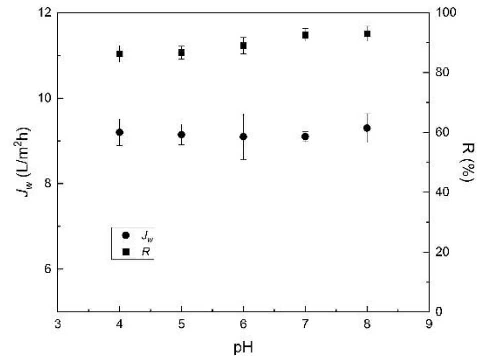

Fig 3. The connections between feed solution pH and J_w and R(%)

4. CONCLUSION

In this work, we have successfully shown that a new forward osmosis procedure may remove arsenic ions from wastewater. We employed a high-performance TFC FO membrane as the separating barrier in the suggested FO process, together with NaCl as the draw solution. Water flux and As rejection were investigated with varied As concentrations in the feed solution at different pHs and changing salt concentrations in the draw solution. The rejection of As(V) increased with increasing feed solution pH, indicating that more than 92% As rejection was conceivable. This resulted from increased electrostatic repulsion between the As(V) oxyanionic species and the negatively charged membranes.

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Declaration: The authors declare that this is the work of Le Xuan Thanh Thao, Do Van Manh, Dang Thi Thom, Duong Tuan Manh, Vo Anh Thu, Nguyen Quynh Nga, Pham Minh Tuan and this content has not been submitted to any journal.

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