



## Arsenate removal from simulated groundwater with a Donnan dialyzer

Bin Zhao<sup>a,b,c,d</sup>, Huazhang Zhao<sup>c,d,\*</sup>, Seok Dockko<sup>e</sup>, Jinren Ni<sup>c,d</sup>

<sup>a</sup> School of Environmental and Chemical Engineering, Tianjin Polytechnic University, Tianjin 300160, China

<sup>b</sup> State Key Laboratory of Hollow Fiber Membrane Materials and Processes, Tianjin 300160, China

<sup>c</sup> Department of Environmental Engineering, Peking University, Beijing 100871, China

<sup>d</sup> Key Laboratory of Water and Sediment Sciences, Ministry of Education, Beijing 100871, China

<sup>e</sup> Department of Civil and Environmental Engineering, Dankook University, Chungnam 330714, Republic of Korea

### ARTICLE INFO

#### Article history:

Received 29 June 2011

Received in revised form 16 February 2012

Accepted 18 February 2012

Available online 24 February 2012

#### Keywords:

Arsenate

Anion exchange membrane

Donnan dialysis

Point of use

Rural areas

### ABSTRACT

A simple point of use (POU) device based on the theory of Donnan dialysis was developed for the removal of arsenate (As(V)) in the present study. A commercial anion exchange membrane was used as a semipermeable barrier between the feed and stripping solution (As(V)-spiked groundwater and a 12 g L<sup>-1</sup> table salt solution, respectively). The proposed POU device could be operated 26 times before replacing the stripping solution. In each batch, approximately 80% of the arsenate anions were transported across the membrane within 24 h, and the arsenic concentration of the stripping solution was finally more than 180 times greater than that of the treated water. Cations were well preserved in treated water; however, a slight increase in the sodium ion concentration was observed due to electrolyte leakage. Alternatively, the chloride ion concentration significantly increased at the expense of a loss of sulfate and bicarbonate. The quality of treated water was in compliance with drinking water standards. Membrane fouling was investigated, and a reduction in the As(V) removal rates was not observed when the membrane was used repeatedly. Our results showed that the proposed Donnan dialysis POU device could effectively remove arsenic from drinking water in rural areas in a sustainable manner.

© 2012 Elsevier B.V. All rights reserved.

### 1. Introduction

Naturally occurring arsenic is one of the most serious contaminants in drinking water. Millions of people worldwide suffer from arsenism due to long-term arsenic exposure via drinking water [1], especially in rural areas of developing countries such as China, India, Bangladesh, etc. [2–4].

Many technologies are available to reduce the arsenic concentration of drinking water, including coagulation, adsorption, and reverse osmosis [5–7]. However, in rural areas, where centralized water supply facilities are generally lacking, these methods are rarely successfully used due to economic and technical obstacles. Technologies designed exclusively for rural and poor settings are more pertinent and effective for the removal of arsenic in these areas.

Point of use (POU) technology improves water quality by treating water in the home and has great potential for providing safe drinking water to rural areas of developing countries in an effective

and affordable manner [8]. The ability to provide continued protection is essential for a successful POU technology. Therefore, specific properties regarding the sustained use of a technology are often assessed during the evaluation of a POU device. Sobsey [9] reviewed several POU technologies for water disinfection and concluded that POU technologies for rural families should provide a sufficient safe water supply, stable performance for different water sources, low labor and time burdens, low cost, reliable and accessible supply chains, and straightforward operation and maintenance.

Donnan dialysis is an electrochemical potential driven membrane process dealing solely with completely ionized electrolytes. It obeys the Donnan membrane equilibrium and could be depicted by the second law of thermodynamics [10,11]. The specific Donnan membrane equilibrium arises from the membrane impermeability to at least one kind of ions in system. In a typical Donnan dialysis process, an ion exchange membrane is used to separate two solutions. The ion exchange membrane excludes co-ions (ions with the same electrical charge as the ion exchange membrane) from permeating the membrane. Therefore, the flux of a counter-ion (ions with the opposite electrical charge to the ion exchange membrane) through the membrane caused by a concentration difference is always coupled with the transport of identical numbers of counterions in the opposite direction to maintain the electroneutrality in either solution [12]. The apparent flux of each counter-ion becomes zero when the Donnan membrane equilibrium is achieved.

\* Corresponding author at: Department of Environmental Engineering, Peking University, Beijing 100871, China. Tel.: +86 10 6275 4292 815; fax: +86 10 6275 6526.

E-mail addresses: [zhaobin@tjpu.edu.cn](mailto:zhaobin@tjpu.edu.cn) (B. Zhao), [zhaohuazhang@pku.edu.cn](mailto:zhaohuazhang@pku.edu.cn) (H. Zhao).

**Table 1**  
Properties of the JAM-I membrane.<sup>a</sup>

Property	JAM-I
Type	Homogeneous strong base anion exchange membrane
Ionic form as shipped	Cl <sup>-</sup>
Base membrane	Glycidyl methacrylate and divinylbenzene copolymer
Ion exchange group	-N <sup>+</sup> (CH <sub>3</sub> ) <sub>3</sub>
Exchange capacity	≥ 1.4 mequiv. g <sup>-1</sup> (dry)
Water content	≥ 20%
Membrane thickness	0.10–0.12 mm

<sup>a</sup> Information obtained from the manufacturer.

Donnan dialysis has already provided many environmental application opportunities for the recovery of valuable metal ions from wastewater and suspensions [13,14] and for the removal of ionic pollutants from drinking water [15–17]. Electronic fields or high pressures are not required, and the membrane is not susceptible to fouling; thus, Donnan dialysis is straightforward to operate, easy to maintain, and affordable to implement. Moreover, our previous results showed that the performance of Donnan dialyzers was reliable for the removal of arsenate (As(V)) from different water sources [18]. Therefore, Donnan dialysis can be used to develop novel POU water treatment technologies.

In the present study, a POU device based on Donnan dialysis was designed for the removal of As(V) in rural environments. An anion exchange membrane was used as a selective barrier between the contaminated solution and working solution (the feed and the stripping solution, respectively). Using the optimal stripping solution, the performance of the proposed POU device was comprehensively investigated with respect to As(V) removal, treated water composition, and membrane fouling. Its capacity for sustained use was highlighted throughout the present study.

## 2. Experimental

### 2.1. Materials

The anion exchange membrane (JAM-I) used in the current study was supplied by Huanyld (China), and its properties are listed in Table 1. Reagent grade Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O, NaCl, Na<sub>2</sub>SO<sub>4</sub>, and CaCl<sub>2</sub> were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. (China), and commercial table salt was obtained from Beijing Salt Industry Corporation (China). As(V) stock solutions (100 mg-As L<sup>-1</sup>) were prepared by dissolving Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O in deionized water, and stored at 4 °C in the refrigerator. The As(V) stock solution was prepared once a week.

### 2.2. Experimental Donnan dialyzer

A two-chamber experimental Donnan dialyzer was used to investigate the effects of the stripping solution on As(V) removal. The structure of the dialyzer has been described in detail in our previous paper [18]. The dialyzer was operated in batch mode at a retention time of 24 h, and the speed of the mechanical stirrers was set to 400 rpm. Various solutions such as 0.1 mol L<sup>-1</sup> NaCl, 1.0 mol L<sup>-1</sup> NaCl, 0.5 mol L<sup>-1</sup> CaCl<sub>2</sub>, and 0.5 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> were tested as the stripping solution. A 0.01 mol L<sup>-1</sup> NaCl solution spiked with 500 μg L<sup>-1</sup> As(V) was used as the feed solution, and the pH of the feed and stripping solutions was adjusted to 7.0 ± 0.2 prior to use. The feed solution was sampled at regular time intervals for chemical analysis.

### 2.3. Household Donnan dialyzer

The household Donnan dialyzer was designed as a POU device with a treatment capacity of 35 L per batch (Fig. 1). An anion

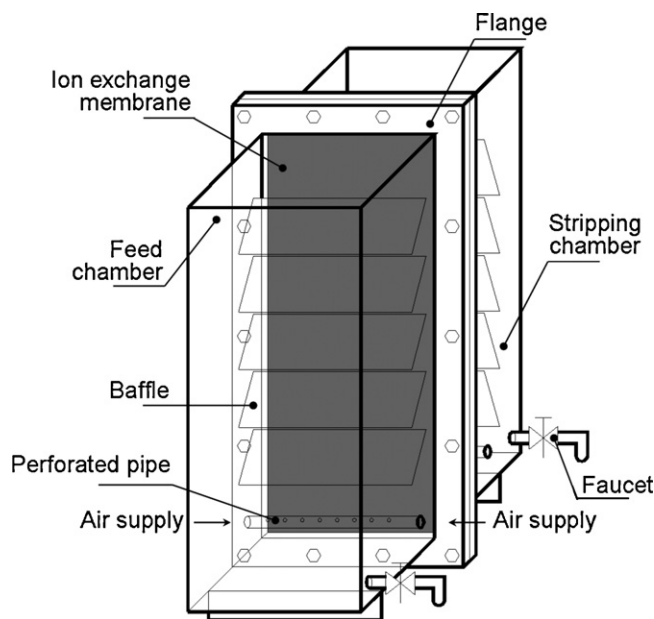


Fig. 1. Diagram of the household Donnan dialyzer.

exchange membrane with an effective area of 0.21 m<sup>2</sup> was tightly fastened between the two chambers. An air pump was used as a power supply to stir the solution and reduce the thickness of the solution-membrane boundary layer. The output of the air pump was equal to 4.7 L min<sup>-1</sup>. The feed and stripping solutions were prepared with arsenic-free groundwater from Peking University. The feed solution was spiked with a specific amount of As(V), while the stripping solution contained 12 g L<sup>-1</sup> of commercial table salt. The transient arsenic concentrations of the feed solution during the first 2 h of operation were analyzed, and the initial As(V) flux was calculated according to Eq. (1):

$$J_{As} = -\frac{V_f}{S} \times \frac{dc_{As,f}}{dt} \quad (1)$$

where  $V_f$  is the volume of the feed solution,  $S$  is the effective area of the membrane, and  $dc_{As,f}/dt$  was obtained by conducting least square fitting analysis on the arsenic concentration of feed solution ( $c_{As,f}$ ) and the treatment time ( $t$ ). The composition of the treated feed solution and the corresponding arsenic concentration of the stripping solution were also analyzed.

### 2.4. Analytical

The arsenic concentration was determined using inductively coupled plasma mass spectrometry (ICP-MS) (XSeries II, Thermo). Potential interference by Cl<sup>-</sup> was eliminated by applying the equations recommended in EPA method 200.8 [19]. The arsenic species in both feed and stripping solutions were determined using an atomic fluorescence spectroscopy (AFS-9130, Beijing Jitian Instruments Co., Ltd., China) coupled with a liquid chromatography system. The liquid chromatography system consisted of a Shimadzu LC-10AT vp plus pump and a Hamilton PRP-X100 anion exchange column. The species analysis indicated that As(V) did not reduce to arsenite (As(III)) under the experimental conditions. An ion chromatograph (ICS 2500, Dionex) was used to determine the concentration of cations (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup>) and anions (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and PO<sub>4</sub><sup>3-</sup>), and a CS12A column and an AS11-HC column were employed, respectively. The bicarbonate concentration was calculated based on the aqueous inorganic carbon concentration, which was determined using a TOC analyzer (Fusion, Teledyne Tekmar). The pH was determined with a pH meter (pH-201, Hanna).

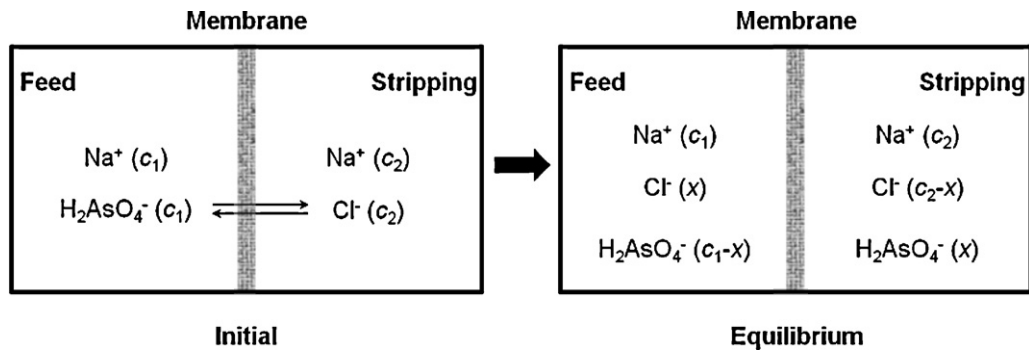


Fig. 2. Schematic diagram of the Donnan dialysis process for the extraction of  $\text{H}_2\text{AsO}_4^-$  with  $\text{Cl}^-$ .

The membrane surface morphology was investigated using a scanning electron microscope (SEM) (Nova NanoSEM 430, FEI). Prior to SEM analysis, the membrane was covered with a thin layer of Au to increase its conductivity. Energy dispersive X-ray spectroscopy (EDS) (SUTW-Sapphire, EDAX) was used to determine the element content of the membrane surface.

### 3. Results and discussion

#### 3.1. Fundamentals of Donnan membrane equilibrium

Assuming that  $\text{H}_2\text{AsO}_4^-$  is the only species of arsenate anions in solution, a simple example is presented herein to explain the Donnan dialysis phenomenon and the Donnan equilibrium for the As(V) removal. Fig. 2 shows a bi-ionic system in which an anion exchange membrane separates two aqueous solutions of equal and constant volume initially containing only  $\text{NaH}_2\text{AsO}_4$  and  $\text{NaCl}$  respectively. The terms  $c_1$ ,  $c_2$ ,  $(c_1 - x)$ , and  $(c_2 - x)$  denote the initial and equilibrium molar concentrations of the respective ions. The concentrations of  $\text{H}^+$  and  $\text{OH}^-$  in solutions are neglected for simplification, and the ions are assumed to act like ideal solutes. Since the available work (decrease of free energy) is zero at equilibrium, we have

$$\delta n \cdot RT \ln \frac{[\text{H}_2\text{AsO}_4^-]_{(F)}}{[\text{H}_2\text{AsO}_4^-]_{(S)}} + \delta n \cdot RT \ln \frac{[\text{Cl}^-]_{(S)}}{[\text{Cl}^-]_{(F)}} = 0 \quad (2)$$

where  $\delta n$  denotes the molar quantities of the transported ions when the equilibrium is achieved, the square brackets denote the molar concentrations of the respective ions,  $R$  and  $T$  are respectively the gas constant and the temperature in Kelvin, and the subscripts of F and S respectively denote the feed and the stripping solutions. So that

$$\frac{[\text{H}_2\text{AsO}_4^-]_{(F)}}{[\text{H}_2\text{AsO}_4^-]_{(S)}} = \frac{[\text{Cl}^-]_{(F)}}{[\text{Cl}^-]_{(S)}} \quad (3)$$

Thus,

$$\frac{c_1 - x}{x} = \frac{x}{c_2 - x} \quad (4)$$

$$x = \frac{c_1 c_2}{c_1 + c_2} \quad (5)$$

The equilibrium state of the system can therefore be expressed as

$$\frac{[\text{H}_2\text{AsO}_4^-]_{(F)}}{[\text{H}_2\text{AsO}_4^-]_{(S)}} = \frac{[\text{Cl}^-]_{(F)}}{[\text{Cl}^-]_{(S)}} = \frac{c_1}{c_2} \quad (6)$$

According to Eq. (6), it can be inferred that the  $\text{H}_2\text{AsO}_4^-$  ions can be effectively extracted to the stripping solution from the feed solution as long as the initial  $\text{NaCl}$  concentration of the stripping

solution is high enough compared to the initial  $\text{NaH}_2\text{AsO}_4$  concentration of the feed solution.

#### 3.2. Stripping solution

The dynamic performance of Donnan dialysis is dependent on the stripping solution. The properties of the driving ion in the stripping solution, including its charge, hydraulic radius, and affinity towards the membrane, affect the intramembrane diffusion of the target ion [15,20,21]. Compared to a stripping solution based on  $\text{Cl}^-$ , when  $\text{SO}_4^{2-}$  was used as the driving ion, arsenate anion transport was dramatically reduced, and the As(V) removal rate was only 46% after 24 h, as shown in Fig. 3a. This result is in agreement with the hypothesis that monovalent driving ions are superior for obtaining high ionic flux [21].

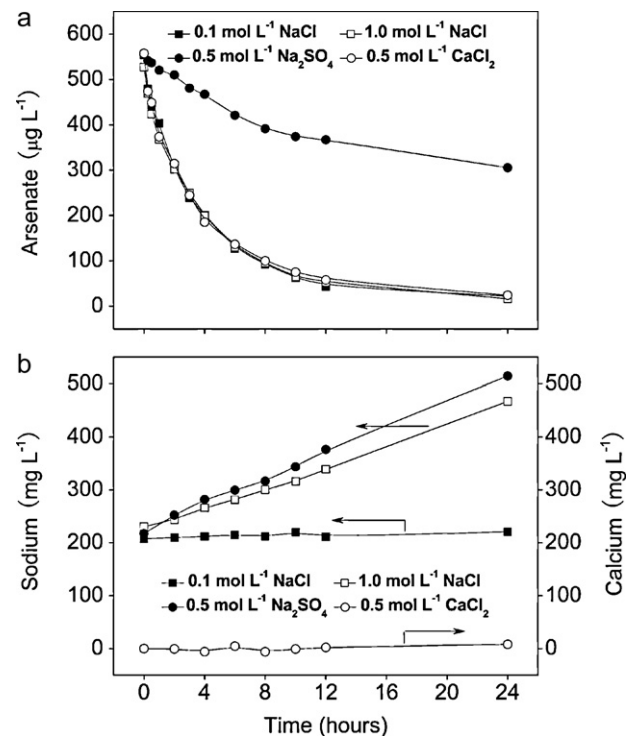
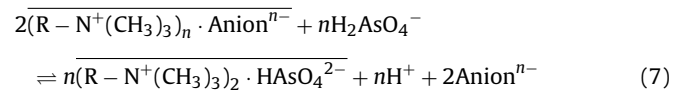
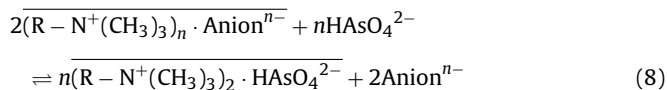


Fig. 3. Transient arsenic concentration (a) and cation concentration (b) of the feed solution during Donnan dialysis process using different stripping solutions.



The ion exchange reactions (Eqs. (7) and (8)) between the aqueous arsenate anions ( $H_2AsO_4^-$  and  $HAsO_4^{2-}$ , which are the dominant species of As(V) at neutral pH) and the quaternary ammonium groups on the inner surface of the membrane result in arsenate anion transport through the membrane [22]. However, the uptake of As(V) by the membrane is strongly inhibited by  $SO_4^{2-}$  because the strong base anion exchanger preferentially binds  $SO_4^{2-}$  over arsenate anions [23]. A higher stripping solution concentration promotes ion transport dynamically and thermodynamically due to an increase in the electrochemical potential gradient across the membrane [24]. However, in the present study, an enhancement in As(V) removal was not observed when the  $Cl^-$  concentration of the stripping solution was increased from 0.1 to 1.0 mol L<sup>-1</sup>. A higher stripping solution concentration also increases the risk of electrolyte leakage due to a reduction in the selectivity of the ion exchange membrane. This phenomenon should be avoided because electrolyte leakage increases the conductivity (i.e., the total dissolved solid concentration) of treated water. When a 1.0 mol L<sup>-1</sup> NaCl solution was used as the stripping solution, strong electrostatic shielding decreased the Donnan exclusion between the anion exchange membrane and  $Na^+$ . As a consequence,  $Na^+$  leakage from the stripping to the feed solution was enhanced, and the  $Na^+$  concentration of the feed solution doubled at the end of the dialytic process (Fig. 3b). Significant amounts of  $Ca^{2+}$  were not transported to the feed solution, even though the  $Ca^{2+}$  concentration of the stripping solution was as high as 0.5 mol L<sup>-1</sup> (Fig. 3b).  $Ca^{2+}$  transport to the feed solution was inhibited because the anion exchange membrane more effectively excludes divalent cations than monovalent cations. Decreasing the NaCl concentration of the stripping solution also protects the system from electrolyte leakage. Although a reduction in the NaCl concentration decreases the capacity for arsenic accumulation, a stripping solution with a lower NaCl concentration is preferred for household use because it can be easily prepared from table salt and has a reliable, accessible, and affordable supply.

### 3.3. The performance of the household Donnan dialyzer

The household Donnan dialyzer was operated in batch mode, and a retention time of 1 day was applied. Treated water was transferred into a sanitary storage container for drinking and cooking, and the feed chamber was filled with raw water for another batch treatment. Fig. 4a shows the long-term performance (26 days) of the household Donnan dialyzer without changing the anion exchange membrane and the stripping solution. The feed groundwater was initially spiked with approximately 500  $\mu\text{g L}^{-1}$  As(V) (Phase I). During the first 13 days, over 90% of the arsenate anions in the feed solution were transported to the 12 g L<sup>-1</sup> table salt stripping solution. As arsenic accumulated in the stripping solution (Fig. 4b), the electrochemical potential gradient across the membrane gradually decreased. Therefore, the initial As(V) flux decreased from  $1.78 \times 10^{-4} \text{ mol m}^{-2} \text{ h}^{-1}$  (1st day) to  $1.15 \times 10^{-4} \text{ mol m}^{-2} \text{ h}^{-1}$  (13th day), and the As(V) removal rate decreased from 97% to 92%. On the 14th day, the arsenic concentration of the treated water exceeded 50  $\mu\text{g L}^{-1}$ , which is the maximum contaminant level (MCL) for drinking water in small communities in rural China [25]. At this time, the arsenic concentration of the stripping solution was more than 120 times greater than that of the treated feed solution. To further investigate the arsenic accumulation capacity of the 12 g L<sup>-1</sup> table salt stripping

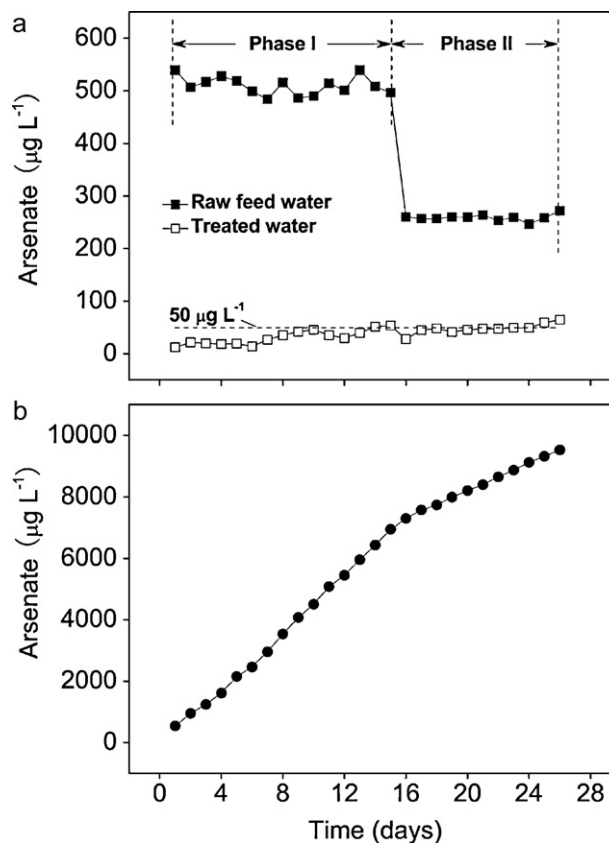


Fig. 4. Performance of the household Donnan dialyzer for repeated use of the 12 g L<sup>-1</sup> table salt stripping solution: (a) As(V) removal in the feed solution and (b) As(V) accumulation in the stripping solution.

solution in the Donnan dialysis process, the household Donnan dialyzer continued to treat groundwater spiked with 250  $\mu\text{g L}^{-1}$  of As(V) on the 16th day of operation (Phase II). After another nine batches (24th day), the As(V) removal rate decreased to less than 80%, and 9135  $\mu\text{g L}^{-1}$  of arsenic in the stripping solution was in quasi-equilibrium with 49  $\mu\text{g L}^{-1}$  of arsenic in the feed solution. Thus, to guarantee the arsenic level of the treated water, the stripping solution had to be replaced. According to these results, the proposed household Donnan dialyzer is able to remove over 80% arsenate ions from groundwater initially containing 250–500  $\mu\text{g L}^{-1}$  of As(V). This is comparable to the POU filters based on aluminum oxide and iron oxide for arsenic removal [26]. The dynamics of the Donnan dialysis process is generally slow, and the diffusion coefficient of arsenate ions in the anion exchange membrane ( $\sim 10^{-8} \text{ m}^2 \text{ h}^{-1}$ ) is even much smaller than those of nitrate ions ( $\sim 10^{-7} \text{ m}^2 \text{ h}^{-1}$ ) and fluoride ions ( $10^{-7}$  to  $10^{-6} \text{ m}^2 \text{ h}^{-1}$ ) due to the presence of the divalent and trivalent arsenate species ( $HAsO_4^{2-}$  and  $AsO_4^{3-}$ ) [15,22,27]. As a result, a batch treatment time of 24 h is proposed for the household Donnan dialyzer in order to guarantee the effective arsenic removal. It is much longer compared to other POU devices or techniques such as adsorption with activated alumina or coagulation with ferric salts [28,29]. However, the common use of household water storage containers in rural areas would help solving this problem. The replacement frequency of the stripping solution is mainly determined by the arsenic concentration of the groundwater. In the case of groundwater containing arsenic higher than 500  $\mu\text{g L}^{-1}$ , this POU device is not recommended because it would require over frequent replacement of the stripping solution, e.g., every several days. However, if groundwater initially contains 100  $\mu\text{g L}^{-1}$  of As(V), the proposed household Donnan dialyzer can be continuously operated

for approximately 6 months before replacing the stripping solution. In this case, the operation of the household Donnan dialyzer is simple and will not significantly contribute to the users' labor and time burdens. A recent published paper investigated the Donnan dialysis–coagulation combined process for the As(V) removal [30]. The treatment of the arsenic-accumulating stripping solution generated through Donnan dialysis was considered in the combined process, and its parameters are listed in Table 2 together with ours for comparison. Most of the parameters are comparable between these two studies; however, the proposed device in our study is closer to the actual POU device and can be used directly in rural areas.

Table 3 lists the composition of the feed water before and after Donnan dialysis treatment. Cations such as  $K^+$ ,  $Ca^{2+}$ , and  $Mg^{2+}$  were well preserved due to exclusion by the anion exchange membrane. Nevertheless, the  $Na^+$  concentration increased slightly due to electrolyte leakage. Unlike cations, the concentration of anions in the treated water drastically changed. The  $Cl^-$  concentration dramatically increased at the expense of a loss of  $SO_4^{2-}$ ,  $NO_3^-$ , and  $HCO_3^-$ . Other than the transport of arsenate anions, the electrochemical potential also drove the transport of other anions through the anion exchange membrane [18]. Therefore, the concentrations of  $SO_4^{2-}$ ,  $NO_3^-$ , and  $HCO_3^-$  of the treated water decreased compared to their initial concentrations of raw groundwater. The loss of these anions was compensated by the transport of  $Cl^-$  from the stripping solution by an ion exchange mechanism. The transport of another part of  $Cl^-$  ions to the treated water was accompanied by the transport of  $Na^+$  by a non-exchange mechanism, i.e., electrolyte leakage. Overall, the treated water quality was in compliance with the national standards for drinking water in small communities in rural China [25]. The proposed household Donnan dialyzer is also effective for the treatment of contaminated groundwater with excess arsenic and nitrate (Table 3). Since only an anion exchange membrane is used, the proposed Donnan dialyzer is not effective for the removal of heavy metal cations possibly coexisting with arsenic in the case of real groundwater. If both cation and anion exchange membranes are used in a three-chamber Donnan dialyzer, which consists of two stripping chambers and one feed chamber in between, heavy metal ions could be simultaneously removed with the arsenate anions. This new Donnan dialyzer is being investigated in our research group.

Cost is an important criterion for the adoption and sustained use of a POU technology. In the present study, the household Donnan dialyzer produced 770 L of purified water. The operating cost of the dialyzer, which consists of the cost of power and table salt, was only 0.087 cents per liter water. This is less than the cost for annual replacement of the commercial activated alumina cartridge for arsenic removal (approximately 0.1 cents per liter water) [28]. Thus, the Donnan dialyzer is affordable for rural families in developing countries. In addition, the operating cost strongly depends on the arsenic concentration of raw groundwater and will decrease if the groundwater contains less arsenic.

#### 3.4. Membrane fouling

Membrane fouling restricts the application of pressure-driven membrane processes such as ultrafiltration and nanofiltration [31,32]. Donnan dialysis is driven by an electrochemical potential; thus, the membrane is not susceptible to fouling [13]. Fig. 5 shows the surface morphology of the anion exchange membrane before and after its use in the above household Donnan dialyzer. JAM-I is a homogeneous membrane produced by quaternizing the polymer composites of glycidyl methacrylate and divinylbenzene, and a polyvinyl chloride cloth is used as the skeleton. The fibrous texture of the raw membrane surface was barely visible, and meso- and macropores, fissures, and cavities were not observed (Fig. 5a). The

**Table 2**  
Comparison table for the As(V) removal by Donnan dialysis.

Membrane	Feed solution	Stripping solution	Agitation method	Operation mode	Retention time (h)	Water produced per day (L)	Ref.
AR204-UZRA	Tap water spiked with $100 \mu\text{g L}^{-1}$ As(V)	$10 \text{ g L}^{-1}$ NaCl solution <sup>a</sup>	Stir at 700 rpm	Continuous-flow	50	0.064	[30]
JAM-I	Groundwater spiked with $250\text{--}500 \mu\text{g L}^{-1}$ As(V)	$12 \text{ g L}^{-1}$ table salt solution	Aeration at $4.7 \text{ L min}^{-1}$	Batch	24	35	This work

<sup>a</sup>  $AlCl_3$  coagulant was daily added into the stripping solution during the first 20 days of the long-term run.

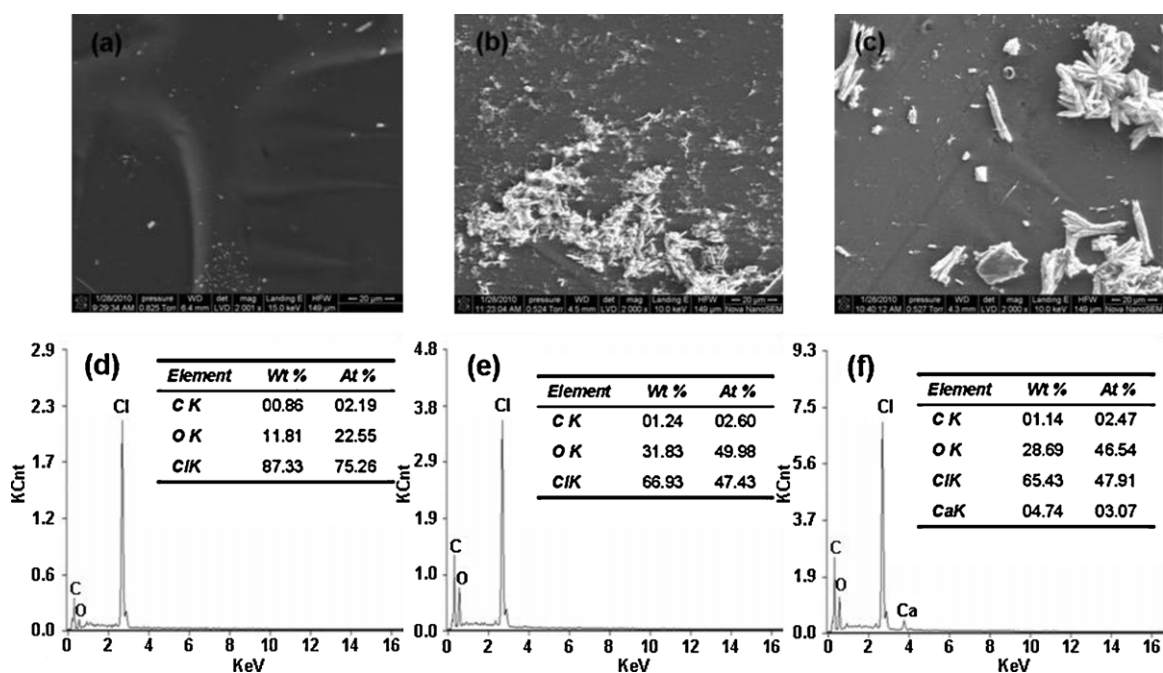


Fig. 5. SEM images and EDS results of a new JAM-I membrane (a, d), the feed side of a used JAM-I membrane (b, e), and the stripping side of a used JAM-I membrane (c, f).

elements of C and O in Fig. 5d are derived from the base membrane material, while the presence of Cl is due to the shipped ions ( $\text{Cl}^-$ ) in the new ion exchange membrane. After use in the household Donnan dialyzer for nearly one month, depositions were detected on both sides of the membrane; however, unlike pressure driven membrane processes, a dense cake layer did not form. Depositions located on the feed side of the membrane (Fig. 5b) were smaller and less crystallized compared to those on the stripping side (Fig. 5c). Metallic elements were not detected by EDS (Fig. 5e) because the depositions on the feed side of the membrane were covered by negatively charged natural organic matters (NOM) in the groundwater via electrostatic attraction. Alternatively, depositions on the stripping side of the membrane contained calcium (Fig. 5f). Based on its morphology (Fig. 5c), aragonite was likely formed on the stripping side of the membrane. The formation of aragonite was attributed to high  $\text{HCO}_3^-$  concentrations accumulated in the stripping solution and the dissociation of  $\text{HCO}_3^-$  to  $\text{CO}_3^{2-}$  in and on the anion exchange membrane [33]. Overall, the membrane matrix was still visible after one month of use; therefore, channels for intramembrane ion transport were not seriously blocked.

In order to investigate the effect of the depositions on the As(V) removal from As(V)-spiked groundwater, specific experiments were conducted in the experimental Donnan dialyzer using the new membrane and the membrane cut from that had been used in the above household Donnan dialyzer for 26 batches (Section 3.3).

**Table 3**  
Analysis of As(V)-spiked groundwater before and after Donnan dialysis treatment.

	Raw	Treated
As ( $\mu\text{g L}^{-1}$ )	254–540	13–65
pH	7.2–7.9	7.0–8.4
$\text{Na}^+$ ( $\text{mg L}^{-1}$ )	21.3–25.4	43.9–54.9
$\text{K}^+$ ( $\text{mg L}^{-1}$ )	0.7–1.9	0.5–1.8
$\text{Mg}^{2+}$ ( $\text{mg L}^{-1}$ )	25.8–28.8	26.4–29.0
$\text{Ca}^{2+}$ ( $\text{mg L}^{-1}$ )	50.6–59.4	54.2–61.9
$\text{Cl}^-$ ( $\text{mg L}^{-1}$ )	19.0–24.0	182.6–276.0
$\text{SO}_4^{2-}$ ( $\text{mg L}^{-1}$ )	59.0–67.1	0.6–8.5
$\text{NO}_3^-$ ( $\text{mg L}^{-1}$ )	7.3–10.7	0.5–6.0
$\text{HCO}_3^-$ ( $\text{mg L}^{-1}$ )	207.0–221.5	12.3–126.4

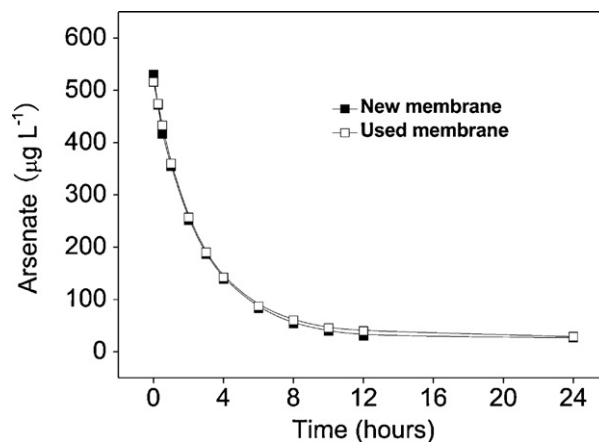


Fig. 6. As(V) removal from As(V)-spiked groundwater with the new membrane and the membrane after used for 26 batches.

The stripping solution was prepared by dissolving 12 g of table salt into 1 L of groundwater. As shown in Fig. 6, the operation of the used membrane was similar to that of the new membrane. Therefore, prolonged use of the anion exchange membrane does not significantly impair As(V) removal, and membrane fouling is not a problem in Donnan dialysis. As a result, cleaning or replacing the membrane is not necessary for the household Donnan dialyzer. Thus, the maintenance of the proposed system is straightforward enough to integrate into the daily lives of rural residents.

#### 4. Conclusions

Donnan dialysis is an electrochemical potential-driven membrane process. The proposed household Donnan dialyzer uses a table salt solution as the working solution (the stripping solution) and is able to treat As(V)-spiked groundwater with over 80% removal rates. The membrane maintenance or replacement is not necessary because no significant reduction in As(V) removal due to membrane fouling exists. Replacing the stripping solution every several months is the only required maintenance. The household

Donnan dialyzer is a one-time purchase, and its operating cost is less than 0.1 cents per liter water. Moreover, the structure of the dialyzer is simple enough for users to assemble and disassemble independently. Compared to other conventional POU devices focusing on the arsenic removal, the proposed household Donnan dialyzer is more competitive in terms of sustained usability and has the potential to become widely employed in rural areas of developing countries.

### Acknowledgements

The authors are grateful to the National Nature Science Foundation (Grant No. 21077001) and the China-Korea Joint Research Project (Grant No. 20911140275) for their financial support.

### References

- [1] D.K. Nordstrom, Public health – worldwide occurrences of arsenic in ground water, *Science* 296 (2002) 2143–2145.
- [2] G.Q. Yu, D.J. Sun, Y. Zheng, Health effects of exposure to natural arsenic in groundwater and coal in China: an overview of occurrence, *Environ. Health Perspect.* 115 (2007) 636–642.
- [3] R. Haque, D.N.G. Mazumder, S. Samanta, N. Ghosh, D. Kalman, M.M. Smith, S. Mitra, A. Santra, S. Lahiri, S. Das, B.K. De, A.H. Smith, Arsenic in drinking water and skin lesions: dose-response data from West Bengal, India, *Epidemiology* 14 (2003) 174–182.
- [4] D. Chakraborti, M.M. Rahman, B. Das, M. Murrill, S. Dey, S.C. Mukherjee, R.K. Dhar, B.K. Biswas, U.K. Chowdhury, S. Roy, S. Sorif, M. Selim, M. Rahman, Q. Quamruzzaman, Status of groundwater arsenic contamination in Bangladesh: a 14-year study report, *Water Res.* 44 (2010) 5789–5802.
- [5] D. Mohan, C.U. Pittman, Arsenic removal from water/wastewater using adsorbents – a critical review, *J. Hazard. Mater.* 142 (2007) 1–53.
- [6] P. Mondal, C.B. Majumder, B. Mohanty, Laboratory based approaches for arsenic remediation from contaminated water: recent developments, *J. Hazard. Mater.* 137 (2006) 464–479.
- [7] M.C. Shih, An overview of arsenic removal by pressure-driven membrane processes, *Desalination* 172 (2005) 85–97.
- [8] J. Wright, S. Gundry, R. Conroy, Household drinking water in developing countries: a systematic review of microbiological contamination between source and point-of-use, *Trop. Med. Int. Health* 9 (2004) 106–117.
- [9] M.D. Sobsey, C.E. Stauber, L.M. Casanova, J.M. Brown, M.A. Elliott, Point of use household drinking water filtration: a practical, effective solution for providing sustained access to safe drinking water in the developing world, *Environ. Sci. Technol.* 42 (2008) 4261–4267.
- [10] F.G. Donnan, The theory of membrane equilibria, *Chem. Rev.* 1 (1924) 73–90.
- [11] F.G. Donnan, Theory of membrane equilibria and membrane-potentials in the presence of non-dialyzing electrolytes – a contribution to physical-chemical physiology, *J. Membr. Sci.* 100 (1995) 45–55.
- [12] H. Strathmann, Ion exchange membrane separation process, in: M. Wessling, K. Sirkar (Eds.), *Membrane Science and Technology*, Elsevier, Amsterdam, 2004, pp. 215–218.
- [13] P. Prakash, A.K. Sengupta, Selective coagulant recovery from water treatment plant residuals using donnan membrane process, *Environ. Sci. Technol.* 37 (2003) 4468–4474.
- [14] J.K. Wang, Preferential transport behaviors of ternary system ferric-cupric-nickel ions through cation ion exchange membrane with a complex agent by dialysis, *Desalination* 161 (2004) 277–285.
- [15] M. Hichour, F. Persin, J. Molenat, J. Sandeaux, C. Gavach, Fluoride removal from diluted solutions by Donnan dialysis with anion-exchange membranes, *Desalination* 122 (1999) 53–62.
- [16] C.T. Matos, S. Velizarov, M.A.M. Reis, J.G. Crespo, Removal of bromate from drinking water using the ion exchange membrane bioreactor concept, *Environ. Sci. Technol.* 42 (2008) 7702–7708.
- [17] A. Tor, Removal of fluoride from water using anion-exchange membrane under Donnan dialysis condition, *J. Hazard. Mater.* 141 (2007) 814–818.
- [18] B. Zhao, H.Z. Zhao, J.R. Ni, Arsenate removal by Donnan dialysis: effects of the accompanying components, *Sep. Purif. Technol.* 72 (2010) 250–255.
- [19] U.S. Environmental Protection Agency, Methods for the determination of metals in environmental samples-supplement I, EPA/600/R-94-111, Washington, DC, 1994.
- [20] H. Ayyildiz, H. Kara, Boron removal by ion exchange membranes, *Desalination* 180 (2005) 99–108.
- [21] F. Durmaz, H. Kara, Y. Cengeloglu, M. Ersoz, Fluoride removal by Donnan dialysis with anion exchange membranes, *Desalination* 177 (2005) 51–57.
- [22] B. Zhao, H.Z. Zhao, J.R. Ni, Modeling of the Donnan dialysis process for arsenate removal, *Chem. Eng. J.* 160 (2010) 170–175.
- [23] B. An, T.R. Steinwinder, D.Y. Zhao, Selective removal of arsenate from drinking water using a polymeric ligand exchanger, *Water Res.* 39 (2005) 4993–5004.
- [24] S. Velizarov, M.A. Reis, J.G. Crespo, Removal of trace mono-valent inorganic pollutants in an ion exchange membrane bioreactor: analysis of transport rate in a denitrification process, *J. Membr. Sci.* 217 (2003) 269–284.
- [25] Ministry of Health of the People's Republic of China, Standardization Administration of the People's Republic of China, Standards for Drinking Water Quality, GB 5749-2006, Beijing, 2006.
- [26] Y. Jeong, M. Fan, S. Singh, C.L. Chuang, B. Saha, H. van Leeuwen, Evaluation of iron oxide and aluminum oxide as potential arsenic(V) adsorbents, *Chem. Eng. Process.* 46 (2007) 1030–1039.
- [27] D.N. Amang, S. Alexandrova, P. Schaezel, The determination of diffusion coefficients of counter ion in an ion exchange membrane using electrical conductivity measurement, *Electrochim. Acta* 48 (2003) 2563–2569.
- [28] B.M. Thomson, T.J. Cotter, J.D. Chwirka, Design and operation of point-of-use treatment system for arsenic removal, *J. Environ. Eng. -ASCE* 129 (2003) 561–564.
- [29] X. Meng, G.P. Korfiatis, C. Christodoulatos, S. Bang, Treatment of arsenic in Bangladesh well water using a household co-precipitation and filtration system, *Water Res.* 35 (2001) 2805–2810.
- [30] A. Oehmen, R. Valerio, J. Llanos, J. Fradinho, S. Serra, M.A.M. Reis, J.G. Crespo, S. Velizarov, Arsenic removal from drinking water through a hybrid ion exchange membrane – Coagulation process, *Sep. Purif. Technol.* 83 (2011) 137–143.
- [31] W. Gao, H. Liang, J. Ma, M. Han, Z.L. Chen, Z.S. Han, G.B. Li, Membrane fouling control in ultrafiltration technology for drinking water production: a review, *Desalination* 272 (2011) 1–8.
- [32] N. Hilal, H. Al-Zoubi, N.A. Darwish, A.W. Mohammad, M. Abu Arabi, A comprehensive review of nanofiltration membranes: treatment, pretreatment, modelling, and atomic force microscopy, *Desalination* 170 (2004) 281–308.
- [33] N. Pismenskaya, E. Laktionov, V. Nikonenko, A. El Attar, B. Auclair, G. Pourcelly, Dependence of composition of anion-exchange membranes and their electrical conductivity on concentration of sodium salts of carbonic and phosphoric acids, *J. Membr. Sci.* 181 (2001) 185–197.