Chemical Engineering Journal 160 (2010) 170–175

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Modeling of the Donnan dialysis process for arsenate removal

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ARTICLE INFO

Article history:
Received 12 December 2009
Received in revised form 15 March 2010
Accepted 16 March 2010

Keywords:
Arsenate
Anion exchange membrane
Diffusion coefficient
Donnan dialysis
Nernst–Planck equation

ABSTRACT

Donnan dialysis is an ion exchange membrane process driven by an electrochemical potential gradient that is capable of removing ionic contaminants from water. To better understand and simulate arsenate (As(V)) removal by Donnan dialysis, a simple model focusing on intermembrane ionic diffusion at steady state was developed based on the Nernst–Planck equation in this study. Using experimental data from independent ion exchange reaction experiments and dialysis experiments, the self-diffusion coefficient of As(V) in the anion exchange membrane was calculated. This value was on the order of 10^{-8} m^2 h^{-1} and related to the system pH and membrane type. The As(V) removal by Donnan dialysis (feed solution: 1 L, 1.3×10^{-2} mol As m^{-3} (1000 μg As L^{-1}) with 10 mol m^{-3} NaCl; stripping solution: 1 L, 100 mol m^{-3} NaCl) was conducted with different types of membrane at different system pH. At the end of the 12-h dialysis, the removal efficiency was lowest (35%) for the heterogeneous membrane at pH 4.5 and highest (95%) for the homogeneous membrane at pH 9.2. Higher ion-membrane affinity, higher intermembrane ionic mobility, and thinner membrane thickness facilitated the As(V) transfer according to the model results. Using the calculated membrane phase self-diffusion coefficients and the corresponding distribution coefficients of As(V) between the membrane and the solution, the present model successfully predicted the As(V) removal profiles of different dialytic conditions.

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1. Introduction

Contaminated groundwater with geogenic arsenic poses a potential cancer threat to the health of millions of people worldwide [1]. Even though many technologies have been developed for arsenic removal [2–4], the problem has not been well addressed in rural areas. Due to poor economic conditions and inadequate technical expertise, rural residents cannot afford either the routine maintenance of reverse-osmosis systems [3] or the regular replacement of the exhausted adsorbents [4]. As a consequence, sustained use of these conventional technologies has been difficult to achieve, and therefore their effectiveness has been seriously undermined.

Donnan dialysis is a semipermeable membrane process driven by an electrochemical potential gradient [5]. In a previous study, it was proven to be able to successfully remove arsenate ions (As(V)) from drinking water supplies [6]. Because no electrical field is applied and the membrane is not susceptible to fouling, the Donnan dialysis system is simple and cost effective. These traits make it a promising point-of-use technology for arsenic removal in rural areas.

Modeling of the Donnan dialysis process can facilitate an understanding of the theoretical transfer behavior of the target ions and the accurate prediction of its performance under different conditions. The intermembrane diffusion is generally considered to be the rate-limiting step of the Donnan dialysis process as long as the bulk solution is adequately agitated. Therefore, the Nernst–Planck equation is usually used to model the ionic transfer [7–10]. In this equation, the membrane phase self-diffusion coefficient is an important parameter for characterizing the ionic intermembrane mobility. Its value is closely related to the nature of the counter ions and the properties of the membranes [7,9,11–15].

To our knowledge, modeling of the Donnan dialysis process for As(V) removal and the calculation of the As(V) self-diffusion coefficient in the anion exchange membrane have not yet been studied. In contrast to previous studies on NO_3^- removal [16] and Al^{3+} recovery [9], the diffusion of As(V) in Donnan dialysis is assumed to be principally related to the system pH. This is because arsenate is a weak electrolyte and the pH value determines its fractionation into different species, namely, H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-}. Different As(V) species exhibit different intermembrane mobilities due to their differences in ionic valence and hydration enthalpies. In addition, the arsenic is a trace component in groundwater for its concentration is generally within the range of ppb (μg L^{-1}) to ppm (mg L^{-1}). Therefore, its transfer in the membrane approxi-

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doi:10.1016/j.cej.2010.03.033

Table 1
Properties of the anion exchange membranes.

	Type[a]	Water content[b] (%)	Exchange capacity[a] (eq kg^{-1} (dry))	Thickness (wet)[b] (10^{-3} m)	Density (wet)[b] (10^3 kg m^{-3})
JAM	Homogeneous	18.8	1.4	0.11 ± 0.01	1.09
YAM	Heterogeneous	56.2	1.8	0.60 ± 0.06	1.02

[a] Information obtained from the manufacturer.
[b] Information obtained in the laboratory.

mately follows Fick's first law of diffusion, and its ion exchange interaction with the membrane resembles an adsorption process. As a result, compared to other studies on the macro-components [7,9] the development and application of the dialytic model in the case of As(V) can be substantially simplified.

In this study, a simple model based on the Nernst–Planck equation was developed in order to predict As(V) removal during the Donnan dialysis process. Using the results from the batch dialysis experiments and the independent ion exchange experiments, the membrane phase self-diffusion coefficients of As(V) ($\bar{D}_{\mathrm{As}}$) was calculated from this model for both homogeneous membrane (JAM) and the heterogeneous membrane (YAM) and for solution pH values of 4.5, 7.0, and 9.2. This simple model was finally used to predict As(V) removal by Donnan dialysis under different experimental conditions.

2. Theoretical

In the present study, NaCl was used to prepare the stripping solution. According to the Nernst–Planck equation for the Donnan dialysis process [9,17], the coupled transfer of arsenate and chloride ions in the anion exchange membrane can be written as

$$J_{m,\mathrm{As}} = -\bar{D}_{\mathrm{As}}\left(\frac{dq_{\mathrm{As}}}{dx} + z_{\mathrm{As}}q_{\mathrm{As}}\frac{F}{RT}\frac{d\phi}{dx}\right) \tag{1}$$

$$J_{m,\mathrm{Cl}} = -\bar{D}_{\mathrm{Cl}}\left(\frac{dq_{\mathrm{Cl}}}{dx} + z_{\mathrm{Cl}}q_{\mathrm{Cl}}\frac{F}{RT}\frac{d\phi}{dx}\right) \tag{2}$$

where J_m, $\bar{D}$, q, and z are the flux (mol m^{-2} h^{-1}), self-diffusion coefficient (m^2 h^{-1}), concentration (mol m^{-3}), and valence of ions in the membrane, respectively; x refers to the thickness of the membrane (m), and F, R, T, and ϕ are respectively Faraday's constant (9.6485×10^4 c mol^{-1}), the gas constant (8.314 J mol^{-1} K^{-1}), the temperature in Kelvin (K), and the electrical potential (V). Integrating the principle of electroneutrality (Eq. (3)) and the condition of no electric current (Eq. (4)) into Eqs. (1) and (2), the flux of As(V) through the membrane is rewritten as Eq. (5)

$$z_{\mathrm{As}}q_{\mathrm{As}} + z_{\mathrm{Cl}}q_{\mathrm{Cl}} = Q \tag{3}$$

$$z_{\mathrm{As}}J_{m,\mathrm{As}} + z_{\mathrm{Cl}}J_{m,\mathrm{Cl}} = 0 \tag{4}$$

$$J_{m,\mathrm{As}} = -\bar{D}_{\mathrm{As-Cl}}\frac{dq_{\mathrm{As}}}{dx} \tag{5}$$

where Q is the exchange capacity of the membrane (mol m^{-3}) and $\bar{D}_{\mathrm{As-Cl}}$ is the membrane phase interdiffusion coefficient (m^2 h^{-1}), which is defined as

$$\bar{D}_{\mathrm{As-Cl}} = \bar{D}_{\mathrm{As}}\bar{D}_{\mathrm{Cl}}\left(\frac{z_{\mathrm{As}}^2 q_{\mathrm{As}} + z_{\mathrm{Cl}}^2 q_{\mathrm{Cl}}}{z_{\mathrm{As}}^2 q_{\mathrm{As}}\bar{D}_{\mathrm{As}} + z_{\mathrm{Cl}}^2 q_{\mathrm{Cl}}\bar{D}_{\mathrm{Cl}}}\right) \tag{6}$$

As the concentration of As(V) in the system is much lower than that of the chloride ions, the value of $q_{\mathrm{As}}/q_{\mathrm{Cl}}$ is approximately zero. Thus, Eq. (6) can be simplified to

$$\bar{D}_{\mathrm{As-Cl}} = \bar{D}_{\mathrm{As}} \tag{7}$$

which means that $\bar{D}_{\mathrm{As}}$ can be substituted for $\bar{D}_{\mathrm{As-Cl}}$ in such a case.

3. Materials and methods

3.1. Membranes

Two commercial anion exchange membranes, namely JAM from Huanyld (China) and YAM from Qianqiu (China), were used in this study. JAM is a homogeneous membrane, which is produced by quaternizing the base membrane of glycidyl methacrylate and divinylbenzene copolymer. YAM is a heterogeneous membrane, which is produced by melting and pressing styrene type strong basic anion exchange resins with polyethylene polymers. The membrane properties are listed in Table 1. The water content was obtained in the laboratory following a previously published method [18]. The thickness of the wet membrane was measured with a vernier caliper. The wet density was calculated by the wet mass of the membrane divided by its corresponding volume. Before use, the membrane was cleaned by successive immersions in a 1 mol L^{-1} HCl solution and in a 1 mol L^{-1} NaOH solution. Finally, it was equilibrated in Cl$^-$ form in a 1 mol L^{-1} NaCl solution. A new membrane was used for each test. All these chemicals are reagent grade, purchased from Sinopharm Chemical Reagent Beijing Co. Ltd.

3.2. Donnan dialysis experiments

A batchwise dialyzer made of Plexiglas was used to conduct the dialysis experiments at room temperature. The anion exchange membrane, with an effective area of 7.0×10^{-3} m^2, was tightly fastened between the two chambers, namely, the feed chamber and the stripping chamber; the effective volume of each chamber was 1 L. The feed solutions were prepared by adding a predetermined amount of $Na_2HAsO_4 \cdot 7H_2O$ (reagent grade, Sinopharm Chemical Reagent Beijing Co. Ltd.) into 10 mol m^{-3} NaCl solutions. The stripping solutions were solutions of 10 or 100 mol m^{-3} NaCl. Before each experiment, both the feed and stripping solutions were adjusted to the same pH value with a solution of 0.1 mol L^{-1} HCl or NaOH, and it was not further adjusted during the process; pH values of 4.5 ± 0.2, 7.0 ± 0.2, and 9.2 ± 0.2 were investigated. A mechanical stirring of 400 rpm was applied in each chamber with a 4 cm × 5 cm rectangular propeller. The feed solution was sampled at regular intervals. The total loss of the solutions due to sampling was less than 3% in volume. The arsenic concentration in the sample was determined using inductively coupled plasma mass spectrometry (ICP-MS) (XSeries II, Thermo). Several correction equations in EPA method 200.8 were employed to eliminate the possible interference of chloride [19].

3.3. The ion exchange reaction experiments

The ion exchange reaction experiments were performed in a series of 250-mL conical flasks to which 100 mL of test solutions and 10-cm^2 pieces of anion exchange membrane were added. The test solutions consisted of 0–2.7×10^{-2} mol m^{-3} (0–2000 μg L^{-1}) As(V) solutions in 10 or 100 mol m^{-3} NaCl solutions. Their pH values were adjusted to 4.5 ± 0.2, 7.0 ± 0.2, or 9.2 ± 0.2. All flasks were shaken for 8 h at 200 rpm at 25 °C. Based on our previous kinetics study, by this time the ion exchange reaction between the arsenate ions and the membrane had reached its equilibrium. The As(V) uptake onto the membrane (q_{As}, mol m^{-3}) was calculated as

$$q_{As} = \frac{(c_{As,initial} - c_{As,eq}) \times V}{m/\rho} \quad (8)$$

where $c_{As,initial}$ and $c_{As,eq}$ are, respectively, the initial and equilibrium concentrations of As(V) in the test solution (mol m^{-3}), V is the volume of the test solution (m^3), and m and ρ are the wet mass (kg) and the wet density of the membrane (kg m^{-3}), respectively.

4. Results and discussion

4.1. The concentration of As(V) in the membrane

To calculate the membrane phase self-diffusion coefficient, the concentration of ions in the membrane, i.e., q in the Nernst–Planck equation, is required. However, this variable is not directly measurable in the Donnan dialysis process. As the ion exchange reaction at the membrane surface is assumed to be fast enough to reach equilibrium at any time, the membrane selectivity coefficient has often been used to relate the ion concentrations in the membrane and in the solution in previous studies [7,9]. In the present study, the amount of As(V) is rather small relative to the aqueous chloride ion concentration and the exchange capacity of the membrane; therefore, the ion exchange process was considered to be an adsorption process. As shown in Fig. 1, a Henry model, i.e., a linear model, depicted the equilibrium partitioning of As(V) between the anion exchange membrane and the 10 mol m^{-3} NaCl solution well, with correlation coefficients (r^2) greater than 0.97. Thus, the As(V) concentration in the membrane during Donnan dialysis can be expressed using the aqueous As(V) concentration (c_{As}, mol m^{-3}), i.e.,

$$q_{As} = Kc_{As} \quad (9)$$

The values of distribution coefficient K were derived from the slopes of the fitted lines and are listed in Table 2.

In the cases of both JAM and YAM, the values of K increased as the pH increased, indicating that the aqueous arsenate ions were more prone to exchange with the membrane-bound chloride ions at higher pH. This phenomenon is related to the As(V) species in the solution. According to the dissociation constants of the arsenate acid in solution (pK_{a1} = 2.19, pK_{a2} = 6.94, pK_{a3} = 11.50) [20], for a pH between 4.5 and 9.2, the arsenate ions exist mainly in the forms of $H_2AsO_4^-$ and $HAsO_4^{2-}$, and the $HAsO_4^{2-}$ fraction increases with an increase in the pH value. The electrostatic attraction with the positively charged quaternary ammonium groups ($N(CH_3)_3^+$) in the membrane is stronger for the divalent anions than for the monovalent ones. Therefore, the membrane preferentially takes up $HAsO_4^{2-}$ to $H_2AsO_4^-$, which resulted in the higher value of K at higher pH. The higher As(V) uptake by YAM was attributed to its higher exchange capacity compared to that of JAM (Table 1).

4.2. Model development for As(V) removal by Donnan dialysis

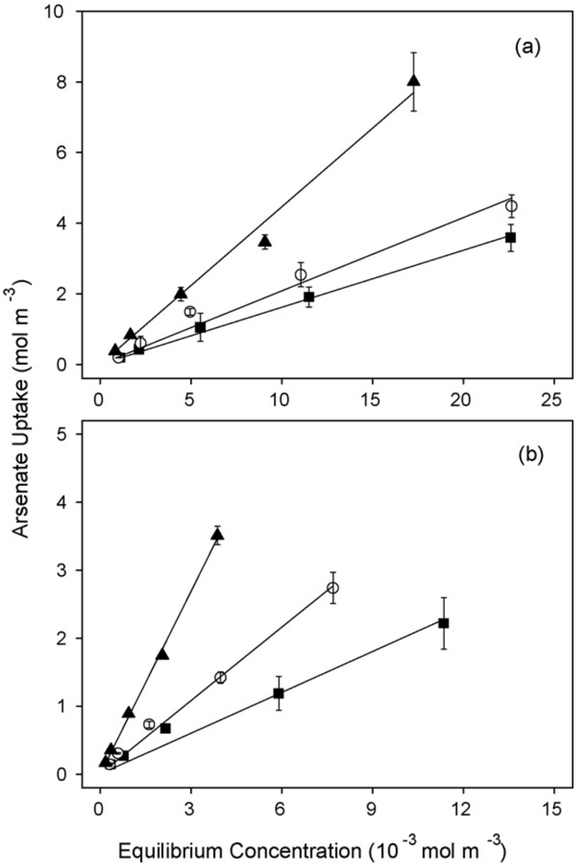

Fig. 1. As(V) uptake by JAM (a) and YAM (b) in 10 mol m^{-3} NaCl solutions at pH 4.5 ± 0.2 (■), 7.0 ± 0.2 (○), and 9.2 ± 0.2 (▲). Lines represent the results fitted according to Henry model.

Our previous investigation on the effects of the rotation speeds on As(V) transfer indicated that the ionic transfer resistance in the aqueous boundary layer was negligible compared to that in the membrane when the rotation speed of stirrers was 400 rpm; therefore, the model developed in the present study focused on the intermembrane ionic diffusion. Because arsenate ions were regarded as a trace component, $\bar{D}_{As}$ was substituted for $\bar{D}_{As-Cl}$ in Eq. (5). Then, the flux of As(V) through the anion exchange membrane can be represented in the same form as in Fick's first law of diffusion

$$J_{m,As} = -\bar{D}_{As}\frac{dq_{As}}{dx} \quad (10)$$

The concentration gradient of As(V) in the membrane is assumed to be linear along the x direction, namely the thickness direction of the membrane. With the relationship between the As(V) concentrations in the solution and in the membrane from Eq. (9), Eq. (10) can be rewritten as

$$J_{m,As} = -\bar{D}_{As}\frac{K_s c_{As,s} - K_f c_{As,f}}{x} \quad (11)$$

Table 2
Parameter values used for the calculation of membrane phase self-diffusion coefficients of As(V) under different experimental conditions.

	pH	t_0 (h)	S (10^{-3} m^2)	V_f (10^{-3} m^{-3})	x (10^{-3} m)	c_{As,t_0} (10^{-3} mol m^{-3})	c_{As,f,t_0} (10^{-3} mol m^{-3})	K_f	K_s
JAM	4.5	0.25	7	1.0	0.11	6.7	6.7	162	162
	7.0	0.25	7	1.0	0.11	6.4	6.2	208	208
	9.2	0.25	7	1.0	0.11	6.2	6.1	446	446
YAM	4.5	3.0	7	1.0	0.60	6.1	5.9	201	201
	7.0	3.0	7	1.0	0.60	4.3	4.2	360	360
	9.2	3.0	7	1.0	0.60	4.0	3.8	896	896

Table 3
Membrane phase self-diffusion coefficients for As(V).

	Diffusion coefficient (10^{-8} m^2 h^{-1})		
	pH 4.5	pH 7.0	pH 9.2
JAM	0.59	1.78	1.01
YAM	1.02	3.39	1.45

where the subscripts *f* and *s* refer to the feed side and the stripping side of the system, respectively.

At steady state ($t \geq t_0$), the As(V) flux in the feed solution is equal to that in the membrane, i.e.,

$$-\frac{V_f}{S}\frac{dc_{\mathrm{As},f}}{dt} = -\bar{D}_{\mathrm{As}}\frac{K_s c_{\mathrm{As},s} - K_f c_{\mathrm{As},f}}{x} \tag{12}$$

and the boundary conditions are

$$c_{\mathrm{As},f} = c_{\mathrm{As},f,t_0} \quad \text{at } t = t_0 \text{ and} \qquad c_{\mathrm{As},f} = c_{\mathrm{As},f,t} \quad \text{at } t > t_0 \tag{13}$$

where V_f is the volume of the feed solution (m^3), S is the effective area of the membrane (m^2), t refers to time (h) and t_0 is the time at which steady state is reached (h). Because the initial volumes of the feed and stripping solutions are equal in the present study and their volume changes during the dialytic process are small enough to be neglect, the sum of the As(V) concentrations in the feed and stripping solutions remain unchanged after the steady state was achieved, i.e.,

$$c_{\mathrm{As},s} + c_{\mathrm{As},f} = c_{\mathrm{As},t_0} \tag{14}$$

Here, $\bar{D}_{\mathrm{As}}$ is assumed to be constant. Then, integrating Eq. (12) gives

$$\ln\left[\frac{K_s c_{\mathrm{As},t_0} - (K_f + K_s)c_{\mathrm{As},f,t}}{K_s c_{\mathrm{As},t_0} - (K_f + K_s)c_{\mathrm{As},f,t_0}}\right] = -\frac{(K_f + K_s)\bar{D}_{\mathrm{As}}S}{V_f x}(t - t_0) \tag{15}$$

After the transient As(V) concentrations in the feed solution within the dialytic process were determined, the values of $\ln[(K_s c_{\mathrm{As},t_0} - (K_f + K_s)c_{\mathrm{As},f,t})/(K_s c_{\mathrm{As},t_0} - (K_f + K_s)c_{\mathrm{As},f,t_0})]$ are calculated and plotted linearly against the values of $(t - t_0)$. Then, the value of $\bar{D}_{\mathrm{As}}$ can be derived from the slope of the line fitted using the least squares method.

Rearranging Eq. (15), the As(V) concentration in the feed solution is expressed as a function of time by

$$c_{\mathrm{As},f,t} = \frac{K_s}{(K_f + K_s)}\left\{c_{\mathrm{As},t_0} - \left[c_{\mathrm{As},t_0} - \left(\frac{K_f}{K_s} + 1\right)c_{\mathrm{As},f,t_0}\right] \exp\left[-\frac{(K_f + K_s)\bar{D}_{\mathrm{As}}S}{V_f x}(t - t_0)\right]\right\} \tag{16}$$

This equation can be used to model As(V) removal by Donnan dialysis if the parameters of K_f, K_s, and $\bar{D}_{\mathrm{As}}$ are given.

4.3. Identification of the membrane phase self-diffusion coefficients for As(V)

Six Donnan dialysis tests were carried out. The feed solutions were composed of 6.7×10^{-3} mol As m^{-3} (500 μg As L^{-1}) in 10 mol m^{-3} NaCl solutions, while the stripping solutions consisted of 10 mol m^{-3} NaCl solutions; other experimental conditions and parameter values are listed in Table 2. With the dialytic data, the linearization technique mentioned in Eq. (15) was implemented, as shown in Fig. 2. The $\bar{D}_{\mathrm{As}}$ values calculated under different experimental conditions are shown in Table 3.

The $\bar{D}_{\mathrm{As}}$ values were different at different pH values. As mentioned in Section 4.1, the pH determines the proportions among the different As(V) species, namely, H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-}. In addition, it should also be highlighted that the dominant species of As(V) in the anion exchange membrane is not the same as that in the bulk solution. According to the Donnan exclusion theory, H$^+$ are excluded by the fixed $N(CH_3)_3^+$ groups in the membrane. Therefore, the pH value in the membrane pore solution is higher than that in the bulk solution. The equilibrium between these pH values can be expressed as [12,21]

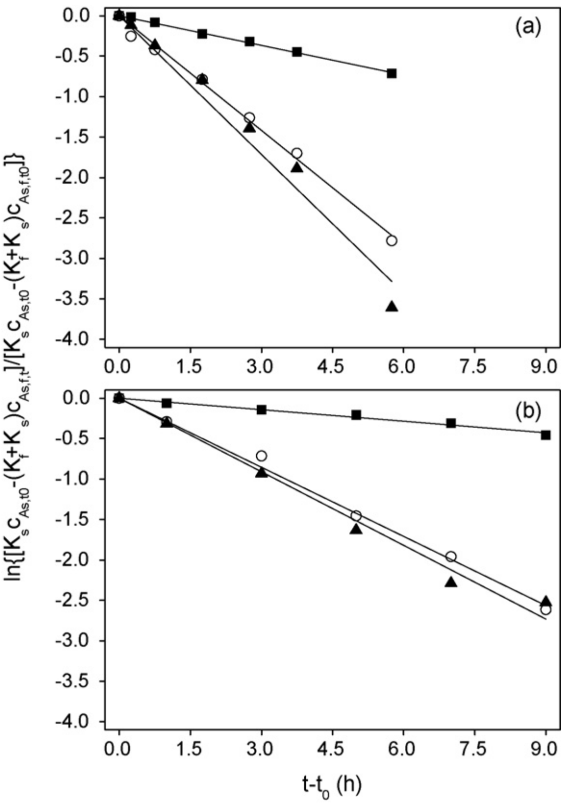

Fig. 2. Calculation of the membrane phase self-diffusion coefficients of As(V) in JAM (a) and YAM (b) at pH 4.5 ± 0.2 (■), 7.0 ± 0.2 (○), and 9.2 ± 0.2 (▲) by separation of variables.

$$\frac{\tilde{X}_{\mathrm{OH}^-}}{\tilde{X}_{\mathrm{Cl}^-}} = \tilde{K}\frac{c_{\mathrm{OH}^-}}{c_{\mathrm{Cl}^-}} \tag{17}$$

where $\tilde{X}$ and c refer to the equivalent anion concentrations (mol m^{-3}) in the membrane pore solution and in the bulk solution (mol m^{-3}), respectively, and $\tilde{K}$ is the selectivity coefficient. Disregarding trace components such as arsenate ions and OH$^-$, $\tilde{X}_{\mathrm{Cl}^-}$ was estimated based on the water content and exchange capacity of the membrane in Table 1, namely 7.45×10^3 mol m^{-3} for JAM and 3.20×10^3 mol m^{-3} for YAM. The value of $\tilde{K}$ was taken as 0.43 for the approximate estimations [12,22]. Then, the pH values in the membrane pore solution were calculated according to Eq. (17), and the corresponding dominant As(V) species in the membrane were also determined based on the calculated pH and the arsenate acid dissociation constants (Table 4).

For both membrane types, the calculated $\bar{D}_{\mathrm{As}}$ followed the following sequence: pH 7.0 > pH 9.2 > pH 4.5. Therefore, it can be inferred that the intermembrane diffusion mobility of As(V) was higher for $HAsO_4^{2-}$ ions than for AsO_4^{3-} ions, which in turn moved more easily in the membrane than did the $H_2AsO_4^-$ ions. This result is consistent with that obtained for the membrane conductivity of the AMX anion exchange membrane equilibrated with different species of phosphate [12], which shares similar properties with arsenate. The relatively low mobility of the $H_2AsO_4^-$ ions was attributed to their low hydration. Due to the low ratio of the "charge to crystal radius", the hydration shell around $H_2AsO_4^-$ ions is smaller than that present in the case of $HAsO_4^{2-}$ or AsO_4^{3-} ions.

Table 4
Calculated pH values in the membrane pore solution and the corresponding dominant As(V) species in the membrane under different experimental conditions.

	Bulk solution		Membrane pore solution	
	pH	Dominant As(V) species	pH	Dominant As(V) species
JAM	4.5	$H_2AsO_4{}^-$	7.0	$H_2AsO_4{}^-$, $HAsO_4{}^{2-}$
	7.0	$H_2AsO_4{}^-$, $HAsO_4{}^{2-}$	9.5	$HAsO_4{}^{2-}$
	9.2	$HAsO_4{}^{2-}$	11.7	$HAsO_4{}^{2-}$, $AsO_4{}^{3-}$
YAM	4.5	$H_2AsO_4{}^-$	6.6	$H_2AsO_4{}^-$, $HAsO_4{}^{2-}$
	7.0	$H_2AsO_4{}^-$, $HAsO_4{}^{2-}$	9.1	$HAsO_4{}^{2-}$
	9.2	$HAsO_4{}^{2-}$	11.3	$HAsO_4{}^{2-}$, $AsO_4{}^{3-}$

Therefore, the hydrophilicity of the $H_2AsO_4{}^-$ ions is weaker and their motion in the hydrophilic zone of the membrane is relatively difficult. Because the translocation of the trivalent $AsO_4{}^{3-}$ ions on the membrane inner surface requires three adjacent available $N(CH_3)_3{}^+$ groups, the movement of $AsO_4{}^{3-}$ ions in the membrane is more restricted compared to that of the divalent $HAsO_4{}^{2-}$ ions.

In addition, the calculated $\bar{D}_{\mathrm{As}}$ was 0.4–0.9 times higher for YAM in comparison with JAM at each pH. This result plausibly disagrees with the superior electrochemical properties of the homogeneous membrane, e.g., uniformly distributed functional groups on the membrane inner surface and small non-conducting inert fraction [17]. In order to interpret it, both the membrane structure and the ionic transfer mechanism are taken into consideration. For JAM, its water content (18.8%) is small and its structure is dense. Therefore, the counterions are transported mainly in the inner surface region of the membrane by hopping between neighboring fixed charged groups. However, for the heterogeneous membrane YAM, meso- and macropores as well as fissures and cavities exist between different ion exchange particles embedded in the membrane [23]. These interfacial regions and channels are called "intergel phase" in the microheterogeneous model [24]. The intergel phase is filled with free water; therefore, the water content of YAM (56.6%) is much higher than that of JAM. These water molecules would form hydrophilic channels for the counterion transfer, and the ionic transfer mechanism in these regions is the same as that in the aqueous solution [23,25]. Hence, the corresponding resistance is assumed to be smaller than that in the inner surface regions of the membrane. In addition, even though the non-conducting inert matrix spaces the ion exchange particles in the heterogeneous membrane, the higher ion exchange capacity of YAM indicates that some of these particles have a sufficiently good contact with each other at least in some regions within the membrane. Moreover, the presence of water channels in YAM would connect these separated ion clusters, and facilitate the ionic transfer. As a result, the membrane phase self-diffusion coefficient of As(V) is higher for YAM than for JAM.

4.4. Model predictions under different experimental conditions

Another six dialytic experiments were carried out in this part of the study. The initial As(V) concentration in the feed solutions was increased to 1.3×10^{-2} mol m^{-3} (1000 μg L^{-1}), while the stripping solutions were solutions of 100 mol m^{-3} NaCl. The distribution coefficients of As(V) between the anion exchange membranes and the stripping solutions, K_s, were calculated using the same method as described in Section 4.1. The values of K_f listed in Table 2 and $\bar{D}_{\mathrm{As}}$ listed in Table 3 were used for the model predictions.

The model results and the corresponding experimental results are shown in Fig. 3. Here, one can see that the As(V) concentration profile derived from Eq. (16) provided values slightly higher than the experimental concentrations in most cases. This deviation was attributed to the likely retention of As(V) in the membrane in the initial period of the Donnan dialysis process. From the viewpoint of predicting As(V) removal, the model calculation was conducted with the assumption that steady state of the dialysis was reached at the beginning of each experiment, i.e., $t_0 = 0$; however, this was not true. According to the total As(V) amounts in both feed and stripping solutions, steady state was not reached until 0.25 h later for the JAM system and 2 h later for the YAM system. By then, around 5% and 20% of the total arsenate ions had been retained in the JAM and YAM membranes, respectively. This fraction of the As(V) was not accounted for in the model, and therefore the calculated As(V) concentrations were higher. In addition, it is worth mentioning that the use of the $\bar{D}_{\mathrm{As}}$ values in Table 3 was approximate, as they represented only the initial situations on the feed side surface of the membrane. The true value of $\bar{D}_{\mathrm{As}}$ was actually not a constant. Due to the different NaCl concentrations in the feed and stripping solutions, the As(V) species were different on each membrane surface. Therefore, $\bar{D}_{\mathrm{As}}$ was a variable across the membrane. In addition, the value of $\bar{D}_{\mathrm{As}}$ also changed with time as OH^- was transported to the stripping side during the Donnan dialysis process and the pH of the feed solution gradually decreased. Overall, the model results matched the experimental results reasonably well. This model can therefore be used to predict As(V) removal using either membrane.

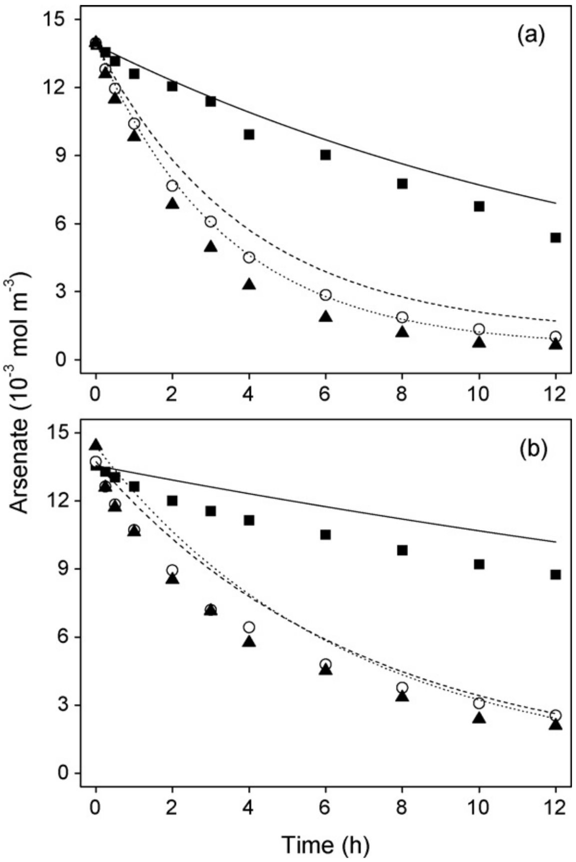

Fig. 3. Experimental (symbols) and modeled (lines) results of As(V) concentration profiles in the feed solution with JAM (a) and YAM (b) at pH 4.5 ± 0.2 (■, —), 7.0 ± 0.2 (○, --), and 9.2 ± 0.2 (▲, ····).

It has been reported that the kinetics of ion transfer in Donnan dialysis is affected by several factors associated with the feed solution, the membrane, and the stripping solution [16]. In the present study, these factors were represented by the model parameters, namely K_f, $\bar{D}_{\mathrm{As}}$, x, and K_s. Regardless of the type of membrane, a low pH was unfavorable for As(V) removal as a result of the low values of K_f and $\bar{D}_{\mathrm{As}}$. This result is in agreement with the conclusion that higher ion-membrane selectivity and higher intermembrane ionic mobility accelerate the target ion transfer [16]. The better performance with JAM was mainly attributed to its lower membrane thickness, which was only one sixth that of YAM. Therefore, much less membrane-associated resistance was present for As(V) transfer in the case of JAM. When a 100 mol m^{-3} NaCl solution was used as the stripping solution in these trials, the value of K_s was much smaller compared to that of K_f. As a consequence, an intermembrane diffusion against the aqueous As(V) concentration gradient between the feed and stripping solutions was possible. At the end of the 12-h dialysis, over 90% of the arsenate ions were transported to the stripping solution in the JAM system at neutral or alkaline pH, whereas the As(V) removal was around 80% in the YAM system.

5. Conclusions

As(V) removal by Donnan dialysis was investigated at different pH values using two types of anion exchange membranes, namely, the homogeneous membrane JAM and the heterogeneous membrane YAM. A simple model representing the As(V) removal with time was derived based on the Nernst–Planck equation and the trace arsenate assumption. The membrane phase self-diffusion coefficient of As(V) was calculated from the model using the results of independent ion exchange reaction experiments and dialysis experiments. This value was closely related to the system pH, following the sequence pH 7.0 > pH 9.2 > pH 4.5. $HAsO_4{}^{2-}$ was believed to be the most mobile As(V) species in both membranes. Because of the differences in the membrane structure and ionic transfer mechanism, the self-diffusion coefficient of As(V) was higher in YAM than that in JAM. The ion-membrane affinity, intermembrane ionic mobility, and membrane thickness played important roles in determining the As(V) removal kinetics. The thinner JAM was more effective, and over 90% of the arsenate ions were removed from the feed solution at pH 7.0 and 9.2 after 12 h. Using the calculated parameters, the model developed in the present study was able to predict the levels of As(V) removal by Donnan dialysis under different experimental conditions.

Acknowledgements

The authors are very grateful to the National Nature Science Foundation (Grant No. 20607001), the National Basic Research Program (Grant No. 2006BAD01B02) of China, 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] Z.G. 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.
[3] 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.
[4] M. Walker, R.L. Seiler, M. Meinert, Effectiveness of household reverse-osmosis systems in a Western US region with high arsenic in groundwater, Sci. Total Environ. 389 (2008) 245–252.
[5] 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.
[6] A. Oehmen, R. Viegas, S. Velizarov, M.A.M. Reis, J.G. Crespo, Removal of heavy metals from drinking water supplies through the ion exchange membrane bioreactor, Desalination 199 (2006) 405–407.
[7] H. Miyoshi, Diffusion coefficients of ions through ion-exchange membranes for Donnan dialysis using ions of the same valence, Chem. Eng. Sci. 52 (1997) 1087–1096.
[8] H. Miyoshi, Diffusion coefficients of ions through ion exchange membrane in Donnan dialysis using ions of different valence, J. Membr. Sci. 141 (1998) 101–110.
[9] P. Prakash, D. Hoskins, A.K. SenGupta, Application of homogeneous and heterogeneous cation-exchange membranes in coagulant recovery from water treatment plant residuals using Donnan membrane process, J. Membr. Sci. 237 (2004) 131–144.
[10] D.N. Amang, S. Alexandrova, P. Schaetzel, Mass transfer characterization of Donnan dialysis in a bi-ionic chloride-nitrate system, Chem. Eng. J. 99 (2004) 69–76.
[11] T. Sata, Studies on anion exchange membranes having permselectivity for specific anions in electrodialysis - effect of hydrophilicity of anion exchange membranes on permselectivity of anions, J. Membr. Sci. 167 (2000) 1–31.
[12] 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.
[13] C.T. Matos, R. Fortunato, S. Velizarov, M.A.M. Reis, J.G. Crespo, Removal of mono-valent oxyanions from water in an ion exchange membrane bioreactor: Influence of membrance permselectivity, Water Res. 42 (2008) 1785–1795.
[14] A. Tor, Removal of fluoride from water using anion-exchange membrane under Donnan dialysis condition, J. Hazard. Mater. 141 (2007) 814–818.
[15] J.K. Wang, C.S. Hsieh, Preferential transport behaviors of ternary system cupric-nickel-zinc ions through cation-exchange membrane with a complexing agent by dialysis, Chem. Eng. J. 138 (2008) 103–110.
[16] 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.
[17] P. Prakash, A.K. SenGupta, Modeling Al^{3+}/H^+ ion transport in Donnan Membrane Process for coagulant recovery, AIChE J. 51 (2005) 333–344.
[18] 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.
[19] EPA Method 200.8, Determination of Trace Elements in Water and Wastes by Inductively Coupled Plasma-Mass Spectrometry, Revision 5.4, Methods for the Determination of Metals in Environmental Samples—Supplement I, EPA/600/R-94-111, May (1994).
[20] A. Ringbom, Complexation in Analytical Chemistry, Interscience Publishers, New York/London, 1963.
[21] F. Helfferich, Ion Exchange, McGraw-Hill, New York, 1962.
[22] F. de, Dardel, Techniques de l'Ingénieur, in: Génie des Procédés, Paris, 1996.
[23] E. Volodina, N. Pismenskaya, V. Nikonenko, C. Larchet, G. Pourcelly, Ion transfer across ion-exchange membranes with homogeneous and heterogeneous surfaces, J. Colloid Interf. Sci. 285 (2005) 247–258.
[24] V.I. Zabolotsky, V.V. Nikonenko, Effect of structural membrane inhomogeneity on transport-properties, J. Membr. Sci. 79 (1993) 181–198.
[25] N.P. Berezina, N.A. Kononenko, O.A. Dyomina, N.P. Gnusin, Characterization of ion-exchange membrane materials: Properties vs structure, Adv. Colloid Interf. Sci. 139 (2008) 3–28.