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Potential of Donnan dialysis water purification processes

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ABSTRACT

Donnan dialysis is an ions separation process utilizing ion exchange membranes. In this process, a solution of target ionic species is held in a feed compartment separated by an ion exchange membrane from a receiver compartment holding a counter ion stripping solution of high concentration. Migration of counter-ions from the receiver compartment to the feed compartment induces an equivalent counter flow of target ions from the feed to the receiver compartment. The attractive features of Donnan dialysis lie in operational simplicity, low energy requirement and no chemicals requirement. Donnan dialysis holds a potential for many beneficial water purifications encompassing hardness removal and elimination of unwanted ions such as borates, nitrates and arsenates. The objective of the present paper is to describe a simple model enabling characterization of Donnan dialysis systems and to analyze developmental efforts required for enhancing practical application of Donnan dialysis water purification processes.

Keywords: Donnan dialysis; Ion exchange; Design model; Potential applications; Commercialization

1. Process principle

Donnan dialysis is an ions separation process utilizing ion exchange membranes (IEMs). In this process, a solution of target ionic species is held in a feed compartment separated by an IEM from a receiver compartment holding a counter ion stripping solution of high concentration. Migration of counter-ions from the receiver compartment to the feed compartment induces an equivalent counter flow of target ions from the feed to the receiver compartment [1–4].

The principle of the process is illustrated in Fig. 1 for the simple case of a solution of 5 mM KNO_3 held in the feed compartment (F) separated by an anion exchange membrane (AEM) from the receiver compartment (R) holding a 95 mM NaCl stripping solution. Since the receiver compartment contains a high chloride concentration, chloride ions will permeate to the feed compartment. As no cations can permeate through the AEM, electrical balance is maintained by the migration of an equivalent stream of nitrate ions from the feed compartment to the receiver.

Assuming activity coefficients near unity, the Donnan separation equations outlined below show that the equilibrium concentrations of the nitrate and chloride ions in two equal volume compartments are given by:

$$\frac{[C^*_{NO_3^-}]_F}{[C^*_{NO_3^-}]_R} = \frac{[C^*_{Cl^-}]_F}{[C^*_{Cl^-}]_R} \tag{1}$$

where the asterisk, *, represents equilibrium conditions. Denoting the maximum concentration of the nitrate (= chloride) ions migration by x^*, Eq. (1) shows that:

$$\frac{[5-x^*]_F}{[x]^*} = \frac{[x^*]}{[95-x]_R^*} \tag{2}$$

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The value x^* = 4.75 mM obtained from Eq. (1) shows that up to 95% of the nitrate can be separated from the feed solution by a very simple dialysis operation.

The separations can be modified by altering the volume ratios of the solutions in the feed and in the receiver as illustrated in Table 1.

It can be easily shown that if the receiver holds a threefold higher solution volume, the maximum nitrate removal increases to 98%, but the nitrate concentration in the receiver will be reduced from 4.75 to 1.64 mM. The maximum nitrate concentration in the receiver can be increased at the expense of a slight reduction in the nitrate transfer to the receiver by decreasing the receiver volume. For the case of a receiver holding one third of the solution in the feed, the maximum nitrate removal from the feed decreases from 95% to 86%, but the nitrate concentration in the receiver increases from 4.75% to 12.95 mM.

The separation is greatly enhanced when the ion is multivalent. For a divalent ion such as sulfate, Eq. (1) takes the form of Eq. (3):

$$\sqrt{\frac{[C_{SO_4^{2-}}]_F^*}{[C_{SO_4^{2-}}]_R^*}} = \frac{[C_{Cl^-}]_F^*}{[C_{Cl^-}]_R^*} \tag{3}$$

Taking again the case of compartments of equal volumes with 5 mM of Na_2SO_4 in the feed and using a 95 mM NaCl stripping solution, the maximum possible sulfate removal from the feed solution is 99.7%.

2. Simplified design equations

The essential features of the kinetic models characterizing Donnan separations are illustrated below by considering separation of nitrate ions from a KNO_3 feed solution with a NaCl stripping solution. The main simplifying assumptions are use of concentrations instead of activities and a selectivity coefficient (Kc) near unity.

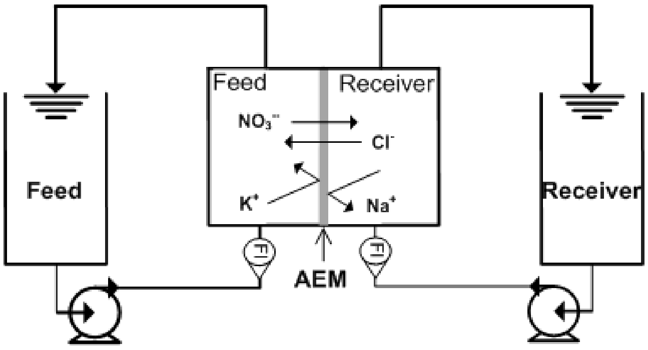

Fig. 1. Dialysis system analyzed.

The steps involved in transfer of the nitrate ions to the receiver are [5] mass transfer from the bulk solution of the feed to the solution membrane interface, migration of the nitrate ions from the solution interface into the membrane, diffusion of the nitrate ions through the AEM from to its feed side to its receiver side, migration of the ions from the membrane receiver side to the solution interface and mass transfer of the ions from membrane-solution interface to the to the bulk solution of the receiver. Fig. 2 describes the corresponding nitrate concentration profile. The index F symbolizes feed side, R – receiver side, w – solution membrane interface and m – membrane.

Similar steps are involved in the transfer of the chloride ions from the receiver compartment to the feed compartment.

The nitrate ion flux $J_{NO_3^-}$ is defined by the following equations:

$$\begin{aligned} J_{NO_3^-}\left(\frac{mol}{m^2 s}\right) &= k\left\{\left[NO_3^-\right]_F - \left[NO_3^-\right]_{wF}\right\} = \\ &\frac{D_m}{\delta}\cdot\left\{NO_{3mF}^- - \left[NO_3^-\right]_{mR}\right\} = \\ &k\left\{\left[NO_3^-\right]_{wR} - \left[NO_3^-\right]_R\right\} = -J_{Cl^-} \end{aligned} \tag{4}$$

where k is the Reynolds number dependent convective mass transfer coefficient, D_m is the ion diffusion coefficient through the membrane and δ is the membrane thickness.

The concentration difference between the ions on the solution membrane interface creates a potential difference, called the Donnan potential. The Donnan potential equations lead to expressions relating concentrations at the solution membrane interface on the feed side and receiver side, respectively [5,6]:

$$\frac{[NO_3^-]_{mF}}{[NO_3^-]_{wF}} = \frac{\left[Cl^-\right]_{mF}}{\left[Cl^-\right]_{wF}} = \frac{\left[X^+{}_m\right]}{\left[K^+\right]_o} \tag{5}$$

$$\frac{[NO_3^-]_{mR}}{[NO_3^-]_{wR}} = \frac{\left[Cl^-\right]_{mR}}{\left[Cl^-\right]_{wR}} = \frac{\left[X^+{}_m\right]}{\left[Na^+\right]_o} \tag{6}$$

where $[X^+_m]$ is the fixed ion concentration of the membrane and $[K^+]_o$ and $[Na^+]_o$ represent the initial ion concentrations in the feed and receiver solutions, respectively.

Table 1
Effects of target ion valence and of feed to receiver volume on target

Initial feed solution (5 mM)	Initial receiver solution (95 mM)	Volume ratio feed/receiver	Target ion final feed conc. (mM)	Target ion removal (%)	Target ion final receiver conc. (mM)
KNO_3	NaCl	$V_F/V_R = 1$	NO_3^- 0.25	95.0	NO_3^- 4.75
KNO_3		$V_F/V_R = 1/3$	0.09	98.3	1.64
KNO_3		$V_F/V_R = 3/1$	0.68	86.4	12.95
K_2SO_4		$V_F/V_R = 1$	SO_4^{2-} 0.02	99.7	SO_4^{2-} 4.98

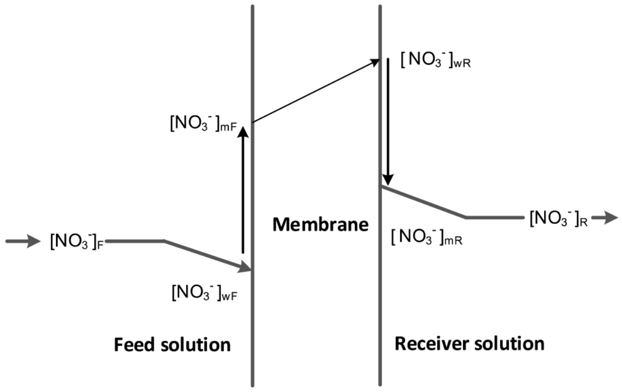

Fig. 2. Concentration profiles across the membrane.

Substituting the solution concentrations of Eqs. (5) and (6) into Eq. (4), the final flux equation describing transfer of nitrate ions from the feed to the receiver compartment is given by:

$$J_{NO_3^-}\left(\frac{mol}{m^2h}\right) = -\frac{d\left[NO_3^-\right]_F}{dt}\cdot\frac{V_F}{S} = P\cdot\left\{\frac{\left[NO_3^-\right]_F}{\left[K^+\right]_o} - \frac{\left[NO_3^-\right]_R}{\left[Na^+\right]_o}\right\} \tag{7}$$

where P represents an overall kinetic coefficient given by:

$$\frac{1}{P} = \frac{1}{P_D} + \frac{1}{P_M} \tag{8}$$

P_D is a parameter characterizing the ions diffusion across the membrane:

$$P_D\left(\frac{mol}{m^2h}\right) = \frac{D_m\cdot[X_m^+]}{\delta} \tag{9}$$

and P_M is a parameter characterizing the mass transfer of the ions through the boundary layers:

$$\frac{1}{P_M} = \frac{1}{k}\cdot\left\{\frac{1}{\left[K^+\right]_o} + \frac{1}{\left[Na^+\right]_o}\right\} \tag{10}$$

Eq. (8) shows that the overall kinetic coefficient is determine by the sum of two resistances-a membrane diffusion resistance [$1/P_D$] and a mass transfer resistance [$1/P_M$]. Two limiting cases are diffusion control and mass transfer control transfer rates. Diffusion control of the dialysis process is promoted by relatively low membrane ion diffusivities, high solutions concentrations of the diffusing ions and high mass transfer coefficients. Mass transfer control is promoted by relatively low solutions concentrations, low mass transfer coefficients, and high membrane ion diffusivities.

The change in feed vessel concentration with time in a batch system similar to that of Fig. 1 is obtained by integration of Eq. (7) which yields the following expression:

$$\frac{1}{B_1}\ln\left\{\frac{B_1\cdot\left[NO_3^-\right]_F - B_2}{B_1\cdot\left[NO_3^-\right]_0 - B_2}\right\} = -\left(P\cdot\frac{S}{V_F}\right)\cdot t \tag{11}$$

where

$$B_1 = \left\{\frac{1}{\left[K^+\right]_F} + \frac{1}{\left[Na^+\right]_R}\right\},\quad B_2 = \frac{\left[K^+\right]_F}{\left[Na^+\right]_R}$$

Determination of the overall kinetic coefficient P is obtained from the linear plot of the feed experimental $\left[NO_3^-\right]_F$ data in the form of $\frac{1}{B_1}\ln\left(B_1\cdot\left[NO_3^-\right]_F - B_2\right)$ vs. t.

3. Illustrating examples

An example illustrating mass transfer control separation of nitrate using a NaCl stripping solution is reproduced below from data measured in a batch system similar to that depicted in Fig. 1 [7]. The feed and receiver solutions of 2 L volume each were recycled through the feed and receiver rectangular channels of the dialysis system at a controlled flow rate. The area of the "Selemion AMV" AEM membrane (Asahi Glass, Japan) used to separate the feed and receiver cells was 0.02 m^2.

Table 2 shows the effect of Reynolds number on the fractional transfer of nitrate ions from feed to receiver vessel in a period of 5 h using a 100 mM NaCl stripping solution. Values of the overall kinetic coefficient P listed in Table 2 were evaluated using Eq. (11).

The enhanced removal of nitrate at increasing Reynolds number is due to the increase in the magnitude of the mass transfer coefficient k with the Re number. Evidence indicating that the transfer of the nitrate ions occurred under mass transfer control conditions was obtained by comparing the experimental decays in nitrate ion concentration with time with theoretical values. This is illustrated in Fig. 3 for a run carried out at the Reynolds number of 7475. It is seen that here is an excellent agreement between experimental measurements and values predicted from Eq. (11) assuming pure mass transfer control (i.e., $P = P_M$ and $1/P_D = 0$). The mass transfer coefficient k used in the calculation was independently determined from a mass transfer correlation fitting the experimental system.

The data in Figs. 4 and 5 relating to Donnan dialysis of sulfate ions illustrate the effect of the concentration level on the transfer mechanism. Fig. 4 shows that stripping of a dilute sulfate feed solution of initial 3.9 mM concentration with a 100 mM NaCl solution occurred under mass transfer control.

Table 2
Effect of the Re number on fractional removal of nitrate ions from the feed vessel

Re	Inlet (mM)	Outlet (mM)	Removal (%)	P (mmol/h m^2)
288	1.08	0.46	43	13
575	1.08	0.62	57	18
1,035	0.94	0.78	83	38
2,000	1.05	0.90	86	46
3,450	1.12	1.04	93	60
7,475	1.05	0.97	92	82

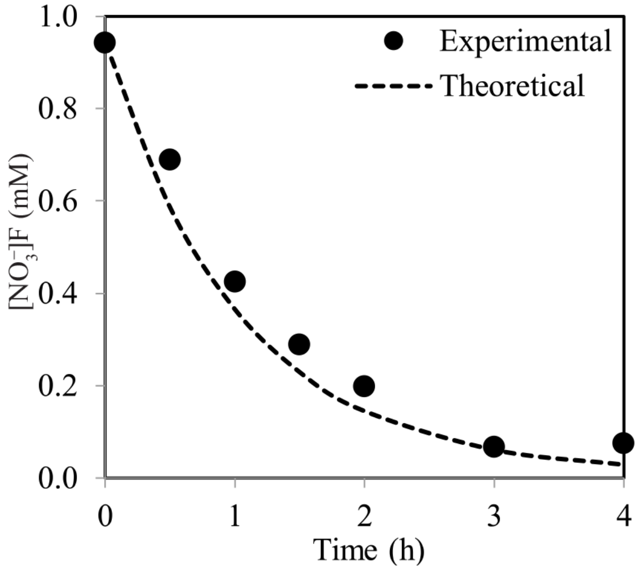

Fig. 3. Feed nitrate concentration decay with time compared with theoretical prediction.

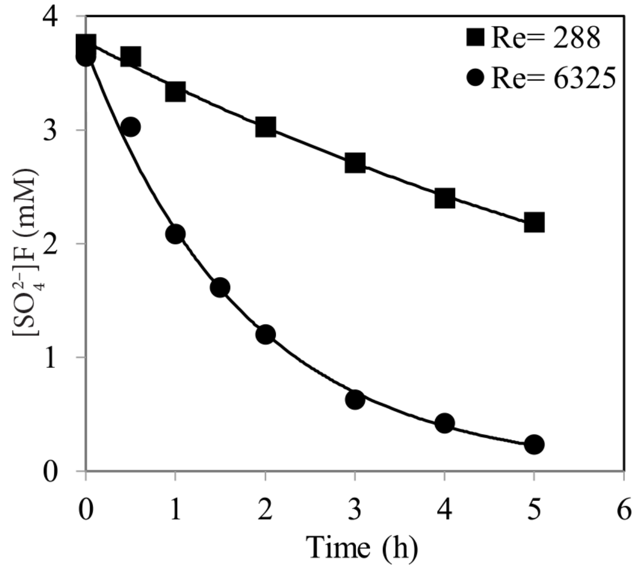

Fig. 4. Effect of Re number on sulfate ions removal at initial feed of 3.9 mM (100 mM NaCl stripping solution).

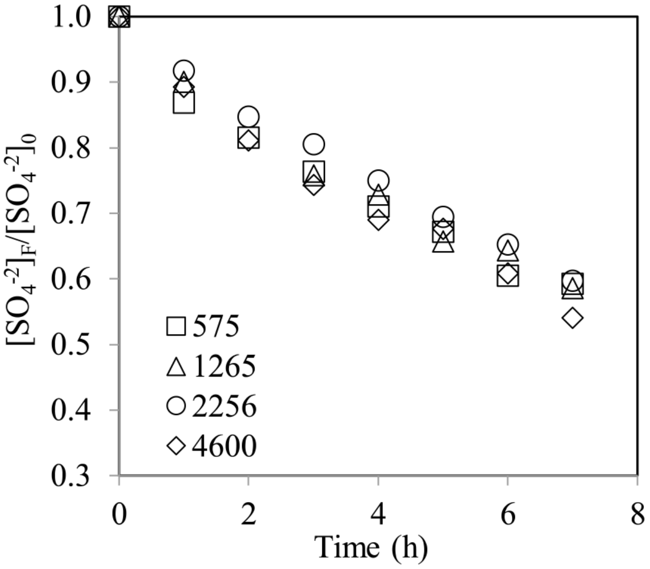

Fig. 5. Effect of Re number on sulfate ions removal at initial feed of 39 mM (1000 mM NaCl stripping solution).

This is evident from the increase in the sulfate ions removal accompanying the Re number increase (sulfate removal in a 5-h period increased from 42% to 94% when the Re number was augmented from 288 to 6325). Fig. 5 presents clear evidence showing that that the stripping of the concentrated sulfate feed solution of initial 39 mM concentration with a 1000-mM NaCl solution occurred under diffusion control. Increase of the Re number from 575 to 4600 had no effect on the sulfate removal level which remained substantially constant at about 35% in a 5-h period.

Many literature publications including the present study disclose Donnan dialysis ion fluxes in the range of 50–200 mmol/h m^2 with high percentage removal of target contaminants feed ions in the range of 1–10 mM. These figures indicate that for removal of 5 mM target ion, the required specific area of the IEM is around 25–100 m^2 per m^3/h. of feed solution. Such membrane area requirements are similar to the typical magnitudes of 20–40 m^2 per m^3/h of many RO and NF processes.

4. Promising applications

Donnan dialysis holds a potential for many beneficial water purifications encompassing hardness removal [8–12] and elimination of unwanted ions such as arsenates [13–15], borates [16,17], fluoride [18,19], bromide [20] and nitrate [21]. A few promising applications are described below.

One of the most serious contaminants occurring in some natural waters is the highly toxic arsenic. Millions of people living in rural areas of developing countries such as India and Bangladesh are exposed to the hazard of arsenates contaminated water. Promising results were obtained in a Donnan dialysis study which examined the effectiveness of various AEMs under both batch and continuous flow conditions [15]. The experiments were carried out with feed waters containing 0.1 mM arsenate (7.5 mg/L as As) and 10 mM NaCl stripping solution. The fractional arsenate removal from the feed was found to vary strongly with the anion-exchange membrane used under batch operating conditions but was substantially similar under continuous operation conditions. Under continuous flow, the fractional feed removal of the arsenate was 64% and the average of arsenate fluxes was 2.75 mmol/h m^2. Assuming operation at mixed flow conditions, the data indicate a reasonable area requirement of 23 m^2 per m^3/h flow rate of the feed solution. However, much higher recoveries are necessary for purifying water from arsenates.

A recent study describes development of an interesting point of use household device enabling arsenate removal to drinking water standards by batch Donnan dialysis [14].

A feed compartment holding 35 L of arsenate contaminated groundwater is dialyzed with a 12 g/L NaCl stripping solution. Agitation of the solutions is carried out with an air pump. As seen in Table 3, 24 h of operation are sufficient to reduce the arsenate content to drinking water standards.

The above data indicate a specific area requirement of 144 m^2 per m^3/h feed indicating that it should be possible to apply large arsenate purification installations.

Of particular interest is the use of Donnan separations for pretreating brackish water fed to desalination plants in order as to reduce the concentration of the scale forming ions (mainly calcium, magnesium, sulfate and bicarbonate). Partial removal of nitrate, sulfate and bicarbonate ions by various membranes was investigated in a Donnan dialysis unit containing 20 cell pairs having a membranes working area of 0.140 m^2 [9]. The equipment was operated batch wise with a feed solution of 10 L and a receiver solution of 2.5 L. The initial feed solution contained 3 mM each of $NaNO_3$, Na_2SO_4 and $NaHCO_3$ while the initial stripping solution contained 300 mM NaCl. The best results were obtained with the Neosepta AFN membrane. The extent of nitrate, sulfate and bicarbonate removal from the feed in a period of 2.5 h was 80%, 98% and 78%, respectively. The respective overall fluxes were 210, 154, and 90 mmol/h m^2. These results also indicate a reasonable specific membrane area requirement of about 35 m^2 per m^3/h feed solution.

An interesting concept is to use all or part of an RO concentrate stream as the stripping solution as shown in Fig. 6. This concept was investigated using two raw waters – a treated industrial wastewater and simple tap water [12]. Partial removal of the calcium and magnesium hardness of the water enabled increase of the waste water recovery from 72% to 84%. However, an economic analysis indicated that the process would be economic only if the membrane cost is reduced from its current value of 300 Euro/m^2 to 10–30 Euro/m^2.

Table 3
Groundwater composition before and after 24 h Donnan dialysis [14]

Ion	Raw water	Treated water
As (μg/L)	254–540	13–65
pH	7.2–7.9	7.0–8.4
Na^+ (mg/L)	212.3–25.4	43.9–54.9
Mg^{2+} (mg/L)	25.8–28.8	26.4–29.0
Ca^{2+} (mg/L)	50.6–59.4	54.2–61.9
Cl^- (mg/L)	19.0–24.0	182.6–276.0
SO_4^{2-} (mg/L)	59.0–67.1	0.6–8.5
NO_3^- (mg/L)	7.3–10.7	0.5–6.0
HCO_3^- (mg/L)	207.0–221.5	12.3–126.4

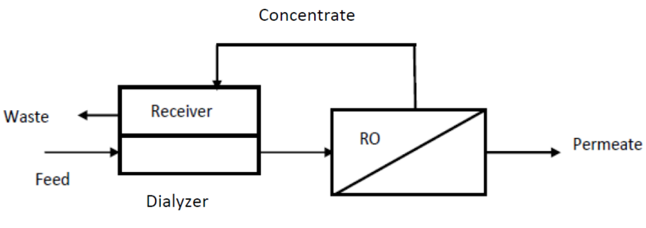

Fig. 6. Pretreatment of RO feed water using the concentrate waste stream as a hardness removal stripping solution.

5. Concluding remarks

Donnan dialysis has the advantage of simple operation and low energy requirement. Despite numerous Donnan dialysis studies demonstrating possibilities of purifying waters from ionic contaminants and for recovery of valuable metals from waste solutions, this separation technology has not been commercialized. Possible reasons for this and efforts required to make Donnan dialysis industrially attractive are discussed below.

A predominant factor is the current price of IEMs which is around $300 per m^2 compared with $10–20 per m^2 for RO and $30–60 per m^2 for UF-MF membranes. Also, industrial membrane modules suitable for Donnan dialysis are not available. Clearly industrial application of Donnan dialysis separations requires resolution of these drawbacks.

Another factor slowing down practical application of Donnan separations may be due to lack of simple design methods. Most studies tend to analyze experimental results using rigorous complex modeling as opposed to design-oriented modeling. The currently available simplified design oriented models for single component systems reviewed in this paper are seen to be in good agreement with experimental data. There is need to expand such design oriented models to multi-component ion separations.

Recalling the history of RO membranes which started with prices in the range of hundreds of dollars per m^2 and then plunged to tens of dollars per m^2 with a concomitant sharp growth in industrial application, Donnan dialysis may hopefully follow such a course.

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