

Removal of fluoride from water using anion-exchange membrane under Donnan dialysis condition

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Abstract

The transport of fluoride through Neosepta-ACM anion-exchange membrane has been studied as a function of feed phase and receiver phase concentration and co-existence anions under Donnan dialysis condition. It was observed that the transport of fluoride was maximum at pH 6 of feed phase and at pH 1 of receiver phase. Moreover, transport of fluoride increased with increase of feed and receiver phase concentration and decreased in the presence of other co-existence anions in the feed phase. The transport of fluoride was also correlated with the flux data and explained according to structure of membrane.

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1. Introduction

Fluoride in drinking water can be either beneficial or detrimental to health depending upon its concentration. Namely, dietary intake of fluoride with the concentration of 1 mg/L can prevent particularly skeletal and dental problems. Contrary, when the fluoride concentration is above this level, it leads to many bone diseases, mottling of teeth and lesions of the endocrine glands, thyroid, liver, and other organs. Owing to these adverse effects of fluoride, World Health Organization (WHO) accepted the maximum fluoride concentration in drinking water as 1.5 mg/L [1]. In the literatures, it was reported that many countries have regions where the water contains more than 1.5 mg/L of fluoride. For example, in some regions of North Africa the fluoride concentration of ground water reaches 20 mg/L. In Southern California Lakeland the fluoride concentration in ground water is about 5 mg/L [2] and in the some parts of Anatolia water contains over 1.5 mg/L fluoride [3].

Many methods, i.e. adsorption [4,5], ion exchange [6,7], precipitation [8], Donnan dialysis [9–11], and electrodialysis [12] have been investigated to remove excessive fluoride from water.

Donnan dialysis is a membrane-based equilibrium process and is different from the classical dialysis technique; its theory and principle are reviewed in textbooks [13,14]. Many studies on the diffusion of ions and molecules through ion-exchange membranes have been reported [15–20]. Although Donnan dialysis has slow kinetics compared to electrodialysis, it has some advantages, i.e. economical, energy saving and need simple technology, etc. [21].

Donnan dialysis has been used for fluoride removal from diluted solutions with the anion-exchange membranes including DSV, AFX, AMX, ACS, AFN, AHA, and SB-6407 [9–11]. In the present work, it was aimed that ACM anion-exchange membrane, not considered previously, was tested for the removal of fluoride from water under Donnan dialysis. The effects of feed phase concentration, pH of feed phase, the accompanying anions in feed phase and the concentration and pH of receiver phase on the removal of fluoride were investigated and discussed in detail.

2. Materials and methods

NaF, NaCl, NaOH, HCl, and CH₃COOH were of analytical grade obtained from Merck Co. (Darmstadt, Germany) and their solutions were prepared without further purification with deionized water. Neosepta-ACM anion-exchange membrane

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manufactured by Tokuyama Soda Co. Ltd. was kindly provided by Eurodia. ACM membrane has quaternary ammonium as a functional group. The ion-exchange capacity and water content of ACM membrane is 1.4–1.7 mequiv./g and 13–18%, respectively. The membrane is supplied in the chloride ion form. To remove impurities, the membrane was conditioned by a cycle of equilibrations with HCl, distilled water, NaOH, distilled water again, and then 1.0 M NaCl.

In order to carry out the experiments, the cell consisting of two detachable compartments made of Teflon was used, as described in Ref. [21]. The exposed membrane area was 7.07 cm² and the volume of feed and receiver solution was 500 mL. The experiments were performed at 25 ± 1 °C and the flow rate of solutions was kept constant as 20 mL/min.

The fluoride concentration was determined with a specific ion electrode (Metler-Toledo, Type 15 215 3000) by use of total ionic strength adjustment buffer (TISAB) solution (58 g of sodium chloride, 57 mL of glacial acetic acid and approximately 150 mL of 6 M NaOH in a volume of 1000 mL) to maintain pH 6 and to eliminate the interference effect of complex ion. The fluoride samples and the fluoride standard solutions were diluted 1:1 with a total ionic strength adjustment buffer solution [22]. Fluoride concentration and pH were determined by an Orion EA940 ion meter.

In specific experiments, the compositions of feed and receiver phase were chosen as below:

- Feed phase: only F⁻ solution as single at 0.1 M concentration with different pH ranging from 1 to 9, receiver phase: 0.1 M NaCl (pH 6.5),
- Feed phase: only F⁻ solution as single at 0.1 M concentration with pH at 6, receiver phase: 0.1 M NaCl with pH at 1 and 6 and 0.2 M NaCl with pH at 6.
- Feed phase: only F⁻ solution as single at 0.1, 0.01 and 0.01 M concentrations with pH at 6, receiver phase: 0.1 M NaCl with pH at 6.
- Feed phase: F⁻ solution at 0.1 M concentration with its corresponding Cl⁻ and SO₄²⁻ ions (pH 6), receiver phase: 0.1 M NaCl with pH at 6.

3. Results and discussion

The flux values were evaluated for all experimental conditions in order to compare to transport of fluoride ion from feed to receiver phase. The fluoride ion flux (J) can be obtained by using the following equation:

$$J = \left(\frac{V}{A} \right) \left(\frac{dC^{n+}}{dt} \right)_{t \rightarrow 0} \quad (1)$$

where V is the volume of receiver phase and A is the effective membrane area. In fact, J is calculated by differentiating the curve-fit polynomials of the time profiles and the obtained results were given in Table 1.

Table 1

Flux values of fluoride through ACM anion-exchange membrane with respect to feed and receiver phase composition

Feed phase	Receiver phase	J ($\times 10^{-8}$ mol/cm ² s)
0.1 M NaF, pH 1	0.1 M NaCl, pH 6.5	0.671 ± 0.020
0.1 M NaF, pH 3		0.997 ± 0.026
0.1 M NaF, pH 6		1.482 ± 0.031
0.1 M NaF, pH 9		0.321 ± 0.005
0.1 M NaF, pH 6	0.1 M NaCl, pH 1	2.354 ± 0.036
	0.2 M NaCl, pH 6	1.879 ± 0.016
0.1 M (NaF + NaCl), pH 6	0.1 M NaCl, pH 6	0.901 ± 0.015
0.1 M (NaF + Na ₂ SO ₄), pH 6		0.448 ± 0.016
0.01 M NaF, pH 6		0.791 ± 0.015
0.001 M NaF, pH 6		0.347 ± 0.011

3.1. Effect of initial pH of feed phase

The transport of fluoride through ACM anion-exchange membrane was studied at four different pH values ranging from 1 to 9. The variation of fluoride ion flux for different initial pH was presented in Fig. 1, which reveals that the transport of fluoride increased with increasing of pH up to 6. This can be attributed to the dependency of the ionic fraction of hydrofluoric acid estimated from the hydrofluoric acid dissociation equilibrium (Eq. (2)) and its dissociation constant, pK_a (Eq. (3)):



$$\text{pH} = \text{p}K_a + \log \left[\frac{\text{F}^-}{\text{HF}} \right] \quad (3)$$

As can be obviously seen in Eq. (3), the fraction of fluoride ion increases as the pH value increased. This led to increase the fluoride transport toward receiver phase. Considering pK_a of 3.16 of hydrofluoric acid [23], fluoride ions are the dominant species in aqueous phase when pH is higher than 3.16. However, at a pH above 6, transport of fluoride decreases sharply

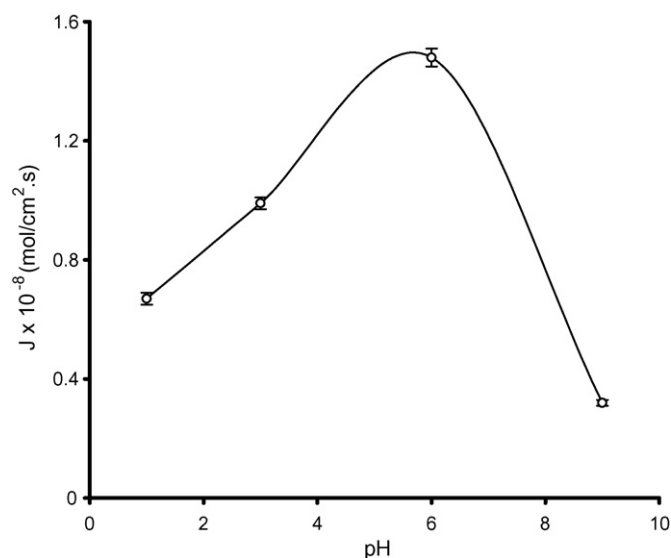


Fig. 1. The effect of initial pH of feed phase on fluoride transport (feed phase: 0.1 M NaF, receiver phase: 0.1 M NaCl, pH of receiver phase: 6.5).

because of a competition between fluoride and hydroxide ions to reach the receiver phase. The obtained result with regard to effect of initial pH on transport of fluoride ion is in agreement with previous studies about the adsorptive removal of fluoride from aqueous phase. For example, maximum adsorption of fluoride ion take places at pH 6 on alum sludge [24], at pH 6.5 on mixed rare earth oxides [25] and at pH 5.5 on red mud [26].

Decreasing of pH of the feed phase with HCl also causes the increasing Cl^- ion which is an accompanying anion for fluoride ion [27,28]. The influence of accompanying Cl^- ion on the fluoride transported can be seen as flux value in Table 1, which indicates that presence of Cl^- ion in feed phase decreases the transport of fluoride ion toward receiver phase because of the competition. Therefore, it has to be also investigated whether the decreasing of flux is owing to the increasing of H_3O^+ or Cl^- ions when pH of the feed phase adjusted to 1 with concentrated HCl. Adding NaCl in feed phase with the concentration of 0.1 M gives the same Cl^- concentration as decreasing of pH to 1. As shown in Table 1, decreasing of the pH of feed phase to 1 was of the lowest flux value compared to the feed phase with the composition of 0.1 M ($\text{F}^- + \text{Cl}^-$).

3.2. Effect of initial pH of receiver phase

The transport of fluoride ion through anion-exchange membrane continues to reach an equilibrium, which depends on the concentration of the F^- in the feed and receiver phase. The equilibrium in ion exchangers is generally reached within one or several days. However, this time can be shortened with increasing of the ion flux through membrane. The association or complexation of transported ion in receiver phase causes an increasing the fluxes. For instance, Hichour et al. [10] studied the fluoride removal by Donnan dialysis. They reported that using Al^{3+} as a chelating agent in the receiver phase resulted in increasing the fluoride transport compared to without Al^{3+} . It was considered that decreasing of pH of receiver phase with HCl causes the similar effect for F^- ion due to the hydrofluoric acid dissociation equilibrium (Eq. (2)).

When decreasing of the pH to 1 with HCl, the molecule form of hydrofluoric acid becomes dominant species in receiver phase and the flux of F^- from feed to receiver obtains speed in order to reach the equilibrium. Decreasing of pH of the receiver phase with HCl also cause the increasing of Cl^- ion which is a pumping ion for anion-exchange membrane in Donnan dialysis. In other words, increasing of pumping ion, in this case Cl^- ion, led to effective transport of fluoride toward receiver phase. Changing the concentration of NaCl in receiver phase from 0.1 to 0.2 M gives the same Cl^- concentration as decreasing of pH to 1. Therefore, it was also investigated whether the increasing of flux is owing to the increasing of H_3O^+ or Cl^- ions when pH of the receiver phase adjusted to 1 with concentrated HCl. As can be seen in Table 1 and Fig. 2, decreasing of the pH to 1 in receiver phase was of the highest flux and transported amount compared to the receiver phase of 0.1 and 0.2 M NaCl. This can be explained by the association equilibrium of F^- and H_3O^+ . Namely, F^- which reaches to the receiver solution came across the H_3O^+ and constitutes the non-ionic molecule of hydrofluoric

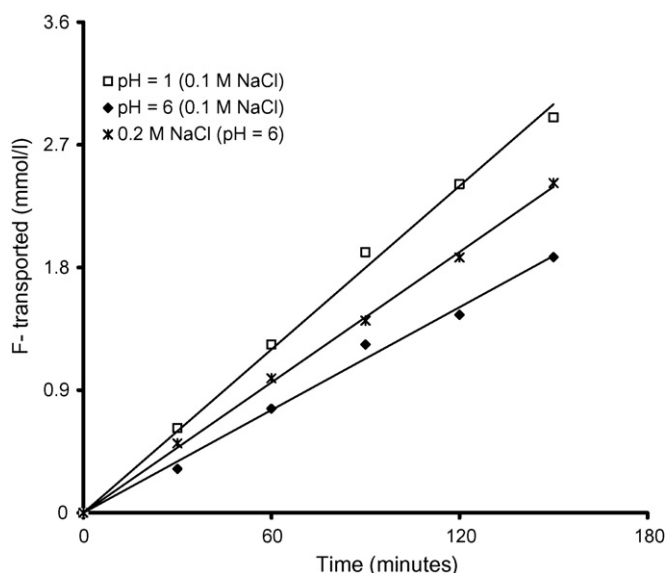


Fig. 2. Time dependence of transported fluoride for different pH of receiver phase (feed phase: 0.1 M NaF, pH of feed phase: 6).

acid. Consequently, free F^- ion in receiver phase was decreased by this association. Therefore, flux of F^- from feed to receiver phase speeds up in order to reach the concentration equilibrium. This explanation can also be supported by the time dependence of pH of the receiver phase. It can be clearly seen in Fig. 3, at the beginning of the Donnan dialysis system, pH of receiver phase (0.1 M NaCl) was 1.10. During the transport of fluoride, pH was increased because of the association of F^- and H_3O^+ as described above.

3.3. Effects of feed phase concentration and accompanying anions

The transport of fluoride is expected to depend on the fluoride concentration and other co-existence anions in the feed phase.

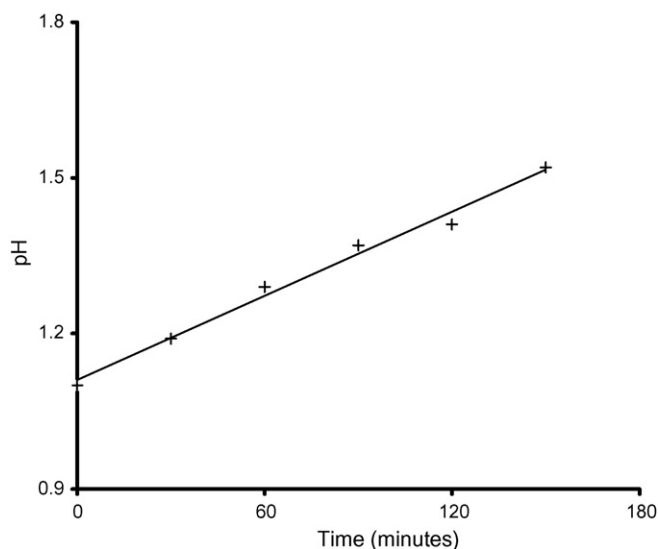


Fig. 3. Time dependence of pH value of receiver phase (0.1 M NaCl, pH 1) (feed phase: 0.1 M NaF, pH of feed phase: 6).

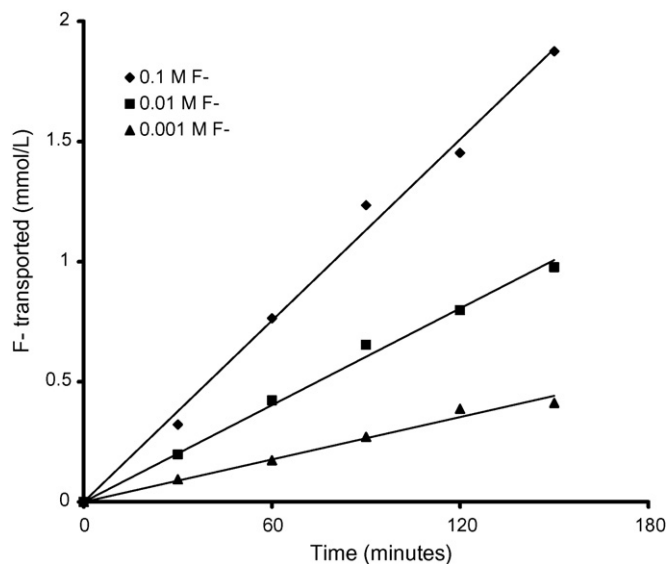


Fig. 4. Time dependence of transported fluoride for different concentration of receiver phase (pH of feed phase: 6, receiver phase: 0.1 M NaCl, pH of receiver phase: 6).

That is why, further work was conducted by using the single fluoride solution with different concentrations and binary equal molar mixtures of (F^- and Cl^-) and (F^- and SO_4^{2-}) solutions. Taking into account of single fluoride solution with different concentrations in feed phase, as seen in Table 1 and Fig. 4, when the fluoride concentration was diluted from 0.1 to 0.01 and 0.001 M, the fluxes decreased. These results are consistent with other publications [26,29]. Thus, the concentration of ion in feed phase could be considered to be the controlling factor in Donnan dialysis process for transport of target anion or cation.

As shown in Fig. 5, a comparison of the influence of the co-existence anion on the transport of fluoride through ACM anion-exchange membrane gave the sequence as $F^- \text{ only} > (F^- + Cl^-) > (F^- + SO_4^{2-})$. These results are in agree-

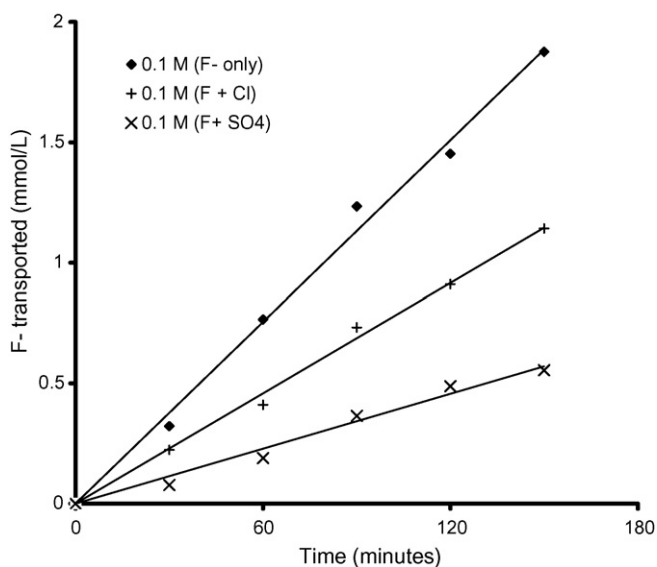


Fig. 5. Time dependence of transported fluoride in presence of mono and bivalences of anions (pH of feed phase: 6, receiver phase: 0.1 M NaCl, pH of receiver phase: 6).

ment with the flux values of fluoride given in Table 1. It is noticed that the single fluoride ion flux is always higher than that of fluoride ion in the presence of Cl^- and SO_4^{2-} in feed phase. The charged membranes contain many ions or ionizable groups in their structure, the fixed charge on the membrane mainly plays role for transport of electrolytes. On the other hand, the mobility of the ions is strongly influenced by the fixed charges in the membranes. The mobility of the monovalent and bivalent ions in an ion-exchange membrane was investigated by Miyoshi [30], who reported that a monovalent ion makes an ion pair with a fixed ion in the ion-exchange membrane and transfer step by step between neighbor fixed ions. In case of bivalent ions and transfer from two fixed ions to other two neighbor fixed ions. For this reason, a set of two fixed ions is needed for transfer of one bivalent ion in the membrane. In other words monovalent ion needs only one fixed charged ion that is corresponding of a half set of a bivalent ion. The results obtained were in agreement with this explanation. Under these circumstances, the motion of fluoride was decreased by increasing valence of co-existence anion.

3.4. Effect of receiver phase concentration

The transport of fluoride ion was examined as a function of NaCl concentration in receiver phase and some typical curves for transport on the NaCl side versus time are shown in Fig. 2. The results from both Fig. 2 and Table 1 suggest that the flux of fluoride ion through anion-exchange membrane increases with increasing of NaCl concentration from 0.1 to 0.2 M. The basic mechanism of the Donnan dialysis process was described in Ref. [29]. In this process, the transport of fluoride ions is balanced by the pumping ion: in this case Cl^- ion moving in the counter-balance. During the Donnan dialysis, the transported flux of F^- from feed to receiver phase is equal to that of the pumping ion. Namely, increasing of the NaCl concentration of receiver phase increase the pumping ion, and this led to effective transport of F^- toward receiver phase. The experimental finding is in agreement with results of Ref. [26], which reported the recovery of metals from red mud by using homogenous SA₃S polysulfonated cation exchange membrane under Donnan Dialysis condition and the influence of the H_3O^+ ion concentration, which is pumping ion for cation exchange membranes, on the recovery of metals and it was reported that the flux of ions increased with increase of H_3O^+ ion concentration in the receiver phase. The similar result was also reported in Ref. [28].

3.5. Effect of membrane structure

Neosepta-ACM anion-exchange membrane is homogeneous and contains quaternary ammonium bases as ionic groups. Durmaz et al. [11] studied the removal of fluoride with Neosepta AFN and AHA membranes under Donnan dialysis conditions and they reported that the flux of fluoride transport on the receiver phase for AHA and AFN membranes was determined as 3.71×10^{-8} and 9.47×10^{-8} mol/cm² s, respectively.

In the present study, under the same experimental conditions reported by Durmaz et al. (feed phase: 0.1 M NaF, pH of feed

phase: 6 and receiver phase: 0.1 M NaCl), the flux of fluoride for ACM membrane was obtained to be 1.48×10^{-8} mol/cm² s. It is clearly seen that the transport efficiency of ACM membrane is lower than that of AFN and AHA membranes. This can be attributed to the nature and ion-exchange capacity of membranes [31].

The nature of the Neosepta AFN and AHA membranes is also homogenous and contains quaternary ammonium groups. However, ACM, AFN and AHA membranes are different from each other by means of the amount of cross-linking agent and water content. The AFN membrane has a structure that contains a cross-linking agent, and its water content is about 40–55%. The water content of the AHA is also around 13–20% [11]. The low water content of the membrane indicates that its structure contains more cross-linking agent. In addition, an increase in cross-linking degree decreases the ion-exchange capacity [31]. Therefore, it can be assumed that highest exchange capacity and higher water content causes high conductivity. That is why the ACM membrane has lower transport efficiency than AFN and AHA membranes.

Ion-exchange capacity of the membrane is very important factor for the ion transport through ion-exchange membrane. This feature was emphasized by Wen and Hamil [32], who investigated the transport of metals, Co(II), Ni(II), Mg(II), and Fe(III) ions through sulfonated styrene-grafted and acrylic acid-grafted membranes, and they reported that transport rate increased with increasing of membrane ion-exchange capacity. Ion-exchange capacity of ACM anion-exchange membrane (1.4–1.7 mequiv./g) is lower than that of AFN (2.3–3.5 mequiv./g) and AHA (0.5–3.0 mequiv./g) membranes. This may be also another reason why ACM gives low transport efficiency compared to AFN and AHA membranes.

4. Conclusion

The results indicated that fluoride transport depends on initial pH of the feed and receiver phase, initial fluoride concentration as well as membrane structure.

The obtained results can be concluded as follows:

- i. When pH of feed phase is at 6, the highest transport of fluoride was obtained.
- ii. Decreasing pH to 1 in receiver phase increased the fluoride transport through membrane.
- iii. Decreasing effect of two valences of co-existence anion on the fluoride transport was more than monovalent co-existence anion.
- iv. Decreasing fluoride concentration in feed phase caused decreasing fluoride transport.

The results of the experiments demonstrated that removal of fluoride from water with Donnan dialysis is viable. A higher

transport of fluoride could be achieved by applying an external electrical field to the external phases. Further studies are now under way with membrane systems by applying an electrical field.

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