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Removal of fluorions from trifluoroacetic acid by reverse osmosis

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ABSTRACT

The separation characteristics of fluorions and trifluoroacetic acid (TFA) by reverse osmosis (RO) were investigated in detail. Separation results revealed that the fluorion rejection depended strongly on pH of the feed solution. The fluorion rejection could be very low by adjusting pH of the feed solution to acidic condition. Under operating pressure of 2.5 MPa, the fluorion rejection decreased sharply from 96% to 17.71% with the feed pH decreased from 6.7 to 2.75. Experimental results illustrated that RO separation can effectively remove fluorions from TFA solutions. Multi-stage RO separation can decrease the fluorion concentration to desirable level. Therefore, RO separation is an efficient and alternative method to remove fluorions from waste effluents or other fluorine compounds.

Keywords: Fluorion; Reverse osmosis; Trifluoroacetic acid; Hydrofluoric acid

1. Introduction

Fluoride ions can be found in wastewaters derived from semiconductor, metal processing, fertilizer and glass-manufacturing industries. Treating high fluoride-content wastewater efficiently has been an important issue for environmental engineers because of the dramatic development of the semiconductor industry which uses a large amount of hydrofluoric acid (HF) in etching and quartz cleaning operations. There are several defluorination processes tested or employed globally, such as coagulation [1], adsorption [2–6], chemical precipitation [7–9], and electrochemical method [10,11]. Membrane technology [12–15] was also widely used in defluorination application, especially the reverse osmosis (RO) membrane separation process. Reverse osmosis is a pressure driven membrane process that does not involve phase change or the use of high temperature. Since it has many advantages including low temperature operation, lower energy consumption, use of compact installations and easy operation, RO membranes are utilized in a wide range of fluoride ions removal from brackish water and wastewater [16–18]. However, in these defluorination applications, RO membranes exhibited high fluorion rejection, i.e., fluorions were almost completely rejected by RO membranes, which limited the application of RO membranes in fluorions removal to a certain extent. For example, during organic fluorine synthesis process, fluorocarbon products with a relatively large molecular weight are always mixed with fluorions. Thus, it is necessary to separate fluorions from the fluorocarbon products. These kinds of fluorocarbon products are usually rejected by RO membranes. Under such conditions, fluorions are expected to permeate RO membranes rather than be rejected. A mixture containing fluorions and trifluoroacetic acid, produced during hexafluoropropene oxide (HFPO)

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production process, belongs to the fluorocarbon products mentioned above. We hope that both TFA and fluorions can be reused. TFA with a relatively large molecular weight might be rejected by RO membranes. Therefore, fluorions are expected to permeate RO membranes.

In our work, by adjusting pH value of the feed solution, most fluorions would permeate through the RO membrane. Therefore, RO membranes can be used to separate fluorions with other fluorine compounds. Our study revealed that RO is an efficient method to separate fluorions with TFA.

2. Materials and methods

2.1. Chemicals and materials

All chemicals used in these experiments were of analytical grade. Sodium fluoride and trifluoroacetic acid were from Sinopharm Chemcial Reagent Co., Ltd., Shanghai, China.

2.2. Analytical methods

The fluorion concentration was measured by PF-1 fluorine electrode (Shanghai Kangning Electrooptical Technology Co., Ltd., Shanghai, China). pH was measured by a Digital Acidimeter (pHS-3C precision acidimeter, Shanghai Precision Science Equipment Co., Ltd., Shanghai, China). TOC was measured by TOC Analyzer from Elementar, Germany.

2.3. Experimental set-up

The experimental set-up was a batch cross-flow RO system shown in Fig. 1. The RO membrane was positioned in a stainless permeation cell to form the membrane separation unit. In order to stabilize the system pressure and avoid impulse, one buffer was fixed before the membrane unit. The feed was pumped from the feed tank to the membrane unit by a flow control pump. The concentrate solution (residue in Fig. 1) was recycled into the feed tank, and the concentrate flow was measured by a flowmeter. The permeate solution was reserved by a container. All membranes used were polyamide RO membranes for desalination of seawater from Development Center of Water Treatment Technology, SOAF, Hangzhou, China. The total membrane surface area was 40 cm^2. The experiments were conducted using different kinds of prepared solutions. The temperature was kept at 298 K in all experiments.

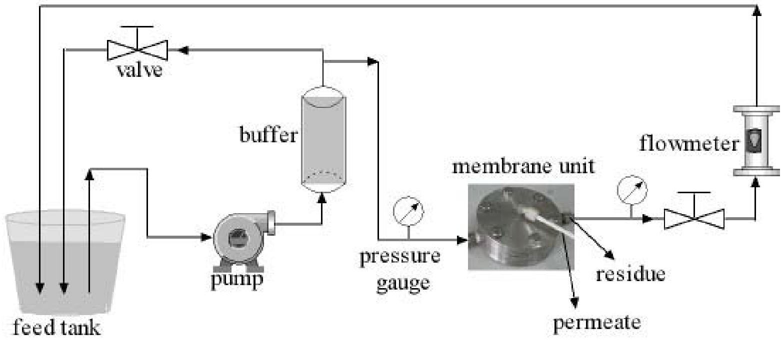

Fig. 1. RO experimental set-up.

3. Results and discussion

The volume flux from the experiment can be described as:

$$F = \frac{V}{At} \tag{1}$$

The fluorion rejection is defined as:

$$\text{Fluorion rejection (\%)} = \frac{[\text{F}^-]_f - [\text{F}^-]_p}{[\text{F}^-]_f} \times 100 \tag{2}$$

In this study, TOC (total organic carbon) rejection represents the TFA rejection, and can be defined as below:

$$\text{TOC rejection (\%)} = \frac{\text{TOC}_f - \text{TOC}_p}{\text{TOC}_f} \times 100 \tag{3}$$

where F, V, A and t represent flux (L m^{-2} h^{-1}), permeate volume (L), membrane area (m^2), and operating time (h) respectively; $[\text{F}^-]_f$ and $[\text{F}^-]_p$ represent fluorion concentration of the feed solution and permeate solution, respectively; TOC_f and TOC_p represent TOC value of the feed solution and permeate solution, respectively.

3.1. Separation characteristics of NaF solution

In this study, three NaF solutions were prepared with different initial concentrations, that is, two low concentration solutions A and B with the concentration of 100 mg L^{-1} and 200 mg L^{-1}, respectively, and one high concentration solution C with the concentration of 1000 mg L^{-1}. The characteristics of three solutions are shown in Table 1.

Table 1
The characteristics of three solutions

	A	B	C
NaF concentration (mg L^{-1})	100	200	1000
F$^-$ (mg L^{-1})	32	67	349
pH	6.70	6.72	6.76
Conductivity (ms cm^{-1})	0.432	0.448	1.793
Volume (L)	2	2	2

The separation results of NaF solutions at low and high concentrations by RO are illustrated in Figs. 2–4. The operating pressure was kept at 1.5 MPa, and the concentrate flow was of 2.2 LPM (L/min). From Fig. 2, it can be seen that the fluorion concentration in the permeate side was below 2 mg L^{-1} at a low initial NaF concentration, while it reached 12–13 mg L^{-1} at a high initial NaF concentration. The fluorion rejection rate came to above 96% whether the initial NaF concentration was low or not. It means that the RO membrane used has high rejection of fluorions when pH is about 7.

The conductivity in the permeate side also demonstrated the high fluorion rejection of the RO membrane. As shown in Fig. 3, the conductivity in the permeate side increased with the increasing of the initial NaF concentration. Fig. 4 reveals that the flux changed little at different initial NaF concentrations and kept at the range of 33–39 L m^{-2} h^{-1}.

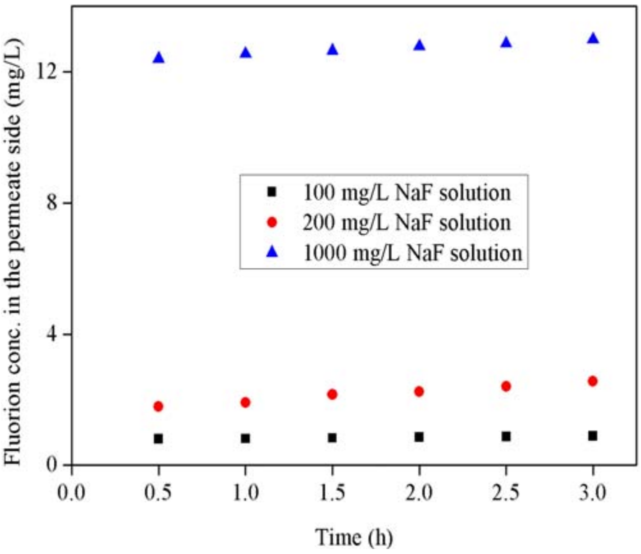

Fig. 2. Fluorion concentration in the permeate side at different initial NaF concentrations in RO (operating pressure — 1.5 MPa, concentrate flow — 2.2 LPM).

3.2. *Separation characteristics of TFA solution*

In this section, 9.21 g/L TFA solution was prepared by diluting TFA with de-ionized water. The characteristics of TFA feed solution were: pH 1.83, conductivity 8.44 ms cm^{-1}, TOC 740.5 mg L^{-1}, volume 2 L. The separation results of TFA by RO are depicted in Table 2 and Fig. 5. TOC rejection increased as the operating pressure increased. The flux changed towards the similar trends, which agreed with the theoretical relationship between flux and operating pressure in the following:

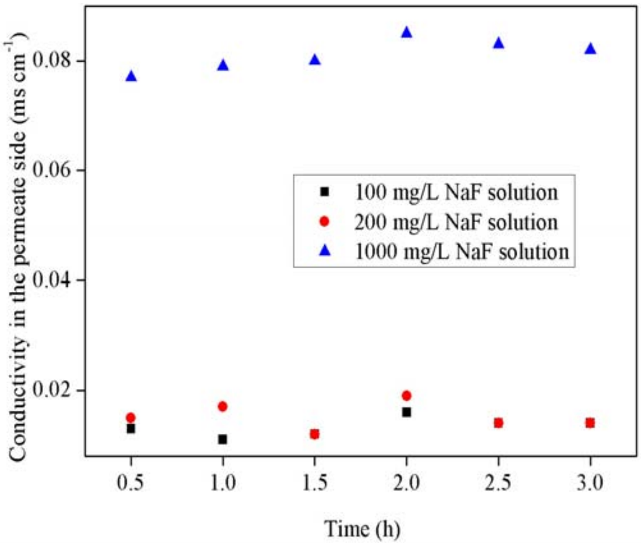

Fig. 3. Conductivity in the permeate side at different initial NaF concentrations in RO (operating pressure — 1.5 MPa, concentrate flow — 2.2 LPM).

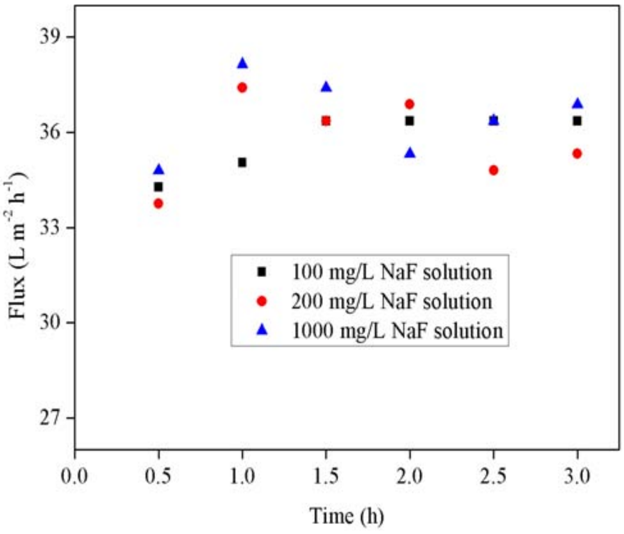

Fig. 4. Flux at different initial NaF concentrations in RO (operating pressure — 1.5 MPa, concentrate flow — 2.2 LPM).

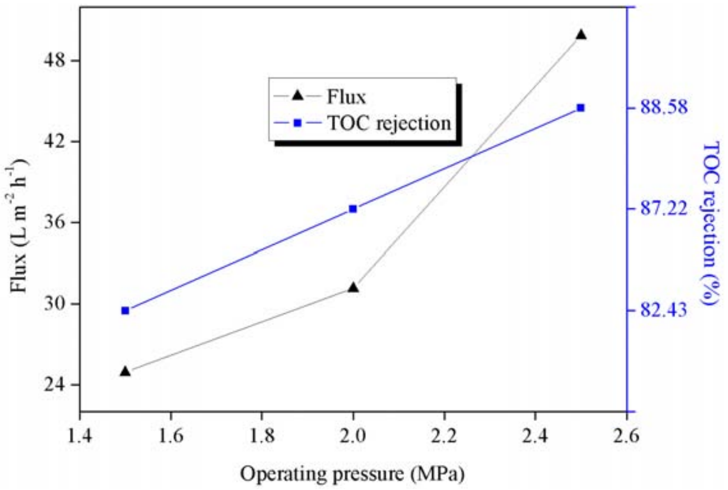

Fig. 5. Flux and TOC rejection vs. operating pressure for TFA solution.

Table 2
Separation results of TFA solution by RO

Operating pressure (MPa)	1.5	2	2.5
pH of permeate solution	2.38	2.47	2.48
Conductivity of permeate solution (ms cm^{-1})	1.87	1.41	1.4
Flux (L m^{-2} h^{-1})	24.93	31.16	49.87
TOC of permeate solution (mg L^{-1})	130.1	94.6	84.6

$$F = L_p(\Delta P - \sigma\Delta\pi) \tag{4}$$

where F represents volume flux (m^3/m^2 s), L_p is water permeate coefficient of the RO membrane (g/s bar m^2), ΔP and $\Delta\pi$ represent the pressure and osmostic pressure difference between the two sides of membrane (bar), respectively, while s is the solute rejection coefficient of the membrane.

Under operating pressure of 2.5 MPa, the flux was as high as 49.87 L m^{-2} h^{-1}, and the TOC rejection was above 88%. In other words, at operating pressure of 2.5 MPa, nearly 88% TFA was rejected by the RO membrane, which shows the high TFA rejection of the RO membrane.

3.3. Separation characteristics of TFA and NaF solution

From section 3.1 and 3.2, it can be deduced that the RO membrane has high rejection for both fluorions and TFA at pH of about 7. However, for some system such as hexafluoropropane oxide production wastewater, it is necessary to separate TFA from HF. In our work, separation characteristics of the solution containing both TFA and NaF (the characteristics of solution were: TFA concentration of 9.21 g/L, NaF concentration of 1000 mg L^{-1}, F$^-$ of 350 mg L^{-1}, acidity of 0.27%, pH of 2.75, conductivity of 3.63 ms cm^{-1}, TOC of 740.5 mg L^{-1}, volume of 2 L) by RO was studied, and the separation results are shown in Table 3 and Fig. 6. The separation results revealed that when the operating pressure increased, the TOC rejection increased with a sharp decrease of fluorion rejection. Under the operating pressure of 2.5 MPa, the TOC rejection was above 90% and the fluorion rejection was 17.71%. Compared with the results of section 3.2, it can be seen that the TOC rejection changed little; while compared with that of section 3.1, an interesting phenomenon was found that the fluorion rejection decreased sharply from 96% to 17.71% when the pH of the solution change from 6.7 to 2.75. It can also be deduced that the fluorion rejection of the RO membrane depends largely on the pH of the feed solution. The lower the pH, the more fluorions permeate through the membrane. Fluorions show significant permeability under acidic conditions. In acidic solution, fluorions can easily be dissolved in the RO membrane matrix due to the strong hydrogen-bonding formation with the membrane materials, and hence the permeability of the fluorions is increased.

Table 3
Separation results of TFA + NaF solution by RO

Operating pressure (MPa)	1.5	2	2.5
Conductivity of permeate solution (ms cm^{-1})	1.48	1.6	1.67
F$^-$ of permeate solution (mg L^{-1})	225	259	288
Acidity# (%)	–0.023	–0.027	0.03
Flux (L m^{-2} h^{-1})	29.61	60.77	84.15
Fluorion rejection (%)	35.71	26	17.71
TOC of permeate solution (mg L^{-1})	53.20	45.70	40.00
TOC rejection (%)	88.18	89.84	91.11

Acidity was measured by acid-base titration and calculated on the basis of HF.

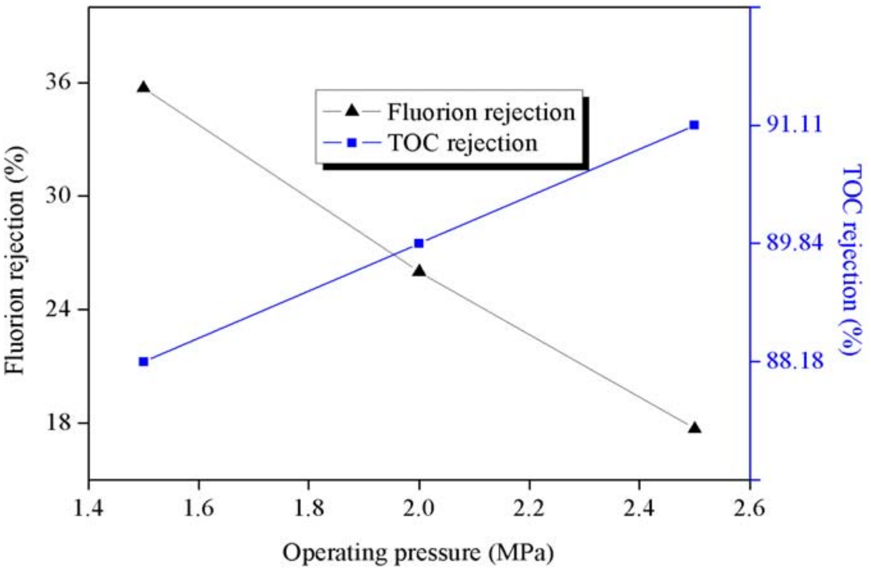

Fig. 6. Fluorion rejection and TOC rejection vs. operating pressure for TFA and NaF solution.

3.4. Multi-stage RO system

From section 3.3, it can be seen that fluorions do not permeate completely through the RO membrane, thus, the solutions after a single RO separation process also contain a certain fluorions. Therefore, multi-stage RO separation is necessary to remove fluorions to a desirable level. Table 4 shows the calculating results of multi-stage RO separation under the condition and results obtained from the above sections: the operating pressure 2.5 MPa, the fluorion rejection of RO membrane 18%, the TOC rejection of RO membrane 90%. For instance, if the fluorion concentration of the feed TFA solution was of 0.1% (1000 mg L^{-1}), two-stage RO separation can decrease the fluorion concentration to 0.00324% (32.4 mg L^{-1}), and the TFA recovery rate would be 81%. A lower operating pressure or solutions containing higher fluorion concentration would need more stages RO separation to decrease the fluorion concentration below 50 mg L^{-1}. In addition, the optimal feed pH and pressure in designing RO membrane separation processes depends on the membrane stability and the required flow rate of the permeate stream.

3.5. RO membrane fouling and operation cost

From the pure water study, it was observed that the pure water flux decreased by 21% after the separation experiment (see section 3.3) for 40 h, which declared that the membrane fouling was serious. In our work, the membrane needed to be washed by alkali solution to alleviate the membrane fouling, following de-ionized water to recover the water flux of the membrane. After washing, the flux could be recovered about 92%.

Although the RO membrane seems not cheap, the recovered valuable products such as TFA decreased the operation cost a lot. In addition, good experiment maintenance will prolong the membrane life-time.

Table 4
Calculating results of multi-stage RO treatment

Stages	Components of concentrate side	Components of permeate side
First	90%TFA + 18%F-	10%TFA + 82%F-
Second	81%TFA + 3.24%F-	19%TFA + 96.76%F-
Third	72.9%TFA + 0.58%F-	27.1%TFA + 99.42%F-
Fourth	65.61%TFA + 0.1%F-	34.39%TFA + 99.9%F-
Fifth	59.05%TFA + 0.018%F-	40.95%TFA + 99.982%F-
Sixth	53.144%TFA + 0.00324%F-	46.856%TFA + 99.99676%F-

4. Conclusion

The fluorion rejection of the RO membrane depends strongly on pH of the feed solution. The fluorion rejection could be very low by adjusting pH of the feed solution to acidic condition. Under the operating pressure of 2.5 MPa and pH of 2.75, the fluorion rejection and TFA rejection were 17.71% and 91.11%, respectively. Multi-stage RO separation can decrease the fluorion concentration to a desirable level. RO separation is an efficient and alternative method to remove fluorions from waste effluents or other fluorine compounds.

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