Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.966278

56 (2015) 3067–3074
December

Taylor & Francis
Taylor & Francis Group

Adsorptive removal of fluoride from aqueous solution by a PES/LDH blend flat-sheet membrane

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Received 3 March 2014; Accepted 5 September 2014

ABSTRACT

Adsorption of fluoride by PES/LDH (layered double hydroxide) blend flat-sheet membrane was investigated. The SEM, AFM, and fluoride adsorption capacity of the membrane were evaluated. The addition of LDH led to a significant enhancement in the adsorption capacity of the membrane. The batch adsorption experiments demonstrated that the membrane effectively removed fluoride in a wide pH ranging from 2–10. The adsorption equilibrium could be established in 30 min, and the maximum adsorption capacity was 2.63 mg/g. The pseudo-second-order kinetics was observed for the adsorption process which followed the Langmuir-type adsorption isotherm. The membrane can be regenerated with 0.1 M NaOH. This work provides a new method to the adsorptive removal of hazardous substance in aqueous solutions.

Keywords: PES/LDH blend membrane; Fluoride; Adsorption; Removal; Kinetics

1. Introduction

Fluoride is present in the effluents of semiconductor manufacturing, electroplating, mining and fertilizer industries, and electroplating. It causes fluorosis, which is a chronic disease characterized by mottling of teeth and softening of bones, ossification of tendons, and ligaments. The chronic toxic effects on human health of excessive intake of fluoride have been studied intensively and the fluoride concentration in the range 0.5–1.5 mg/L is generally considered to be beneficial to human beings [1]. The magnitude of fluorine in the environment is accentuated by the increase in discharge of fluoride-containing waste. Thus, it is imperative and significant to remove excessive fluorides from aqueous solution.

The conventional technologies of fluoride removal from aqueous solution include adsorption [2], ion exchange [3], electrodialysis [4], and precipitation [5]. Among these methods, adsorption attracts considerable attentions because of its convenience, high efficiency, and low-energy consumption [6–11].

Layered double hydroxides (LDHs) are lamellar mixed hydroxides containing positively charged main layers with the general formula: $[M_x^{2+}M_x^{3+}(OH)_{2(x\ +\ y)}]A_{y/n}^{n-}\cdot mH_2O$, where M^{2+} is bivalent metal ion (Zn, Mg, Cu, Co, Ni, etc.), M^{3+} is trivalent metal ion (Al, Fe, Cr, etc.), and A^{n-} is the exchangeable anion. Considerable interest has been shown in LDHs recently as a result of their large interlayer spaces and significant number of exchangeable anions in different industrially relevant processes, particularly as ion exchanger and adsorbent to remove organic and inorganic wastes [12–20].

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It was reported that LDH could effectively remove fluoride [21–23]. However, the size of the sorbent particle is too small and always floats on water surface, which makes it difficult to fully contact with aqueous solution. Thus additional separation becomes necessary. As a result, it cannot conveniently be used in water treatment.

In the present study, a PES/LDH blend flat-sheet membrane was successfully prepared to remove fluoride conveniently. The surface and cross-sectional morphology were evaluated. The kinetic adsorption characterizations of PES/LDH membrane and pH effect on their fluoride adsorption capacity were also conducted.

2. Materials and methods

2.1. Materials

Poly(ether sulfone) (PES) with *Mw* of 58,000, N,N-dimethylacetamide (DMAc), and the other chemicals used were purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents were of the highest purity available and were used without purification. Milli-Q water (Millipore, integrated ultrapure water system) with a resistivity of 18.2 MΩ cm was used.

2.2. Synthesis of Mg–Al LDH

Mg–Al LDH was synthesized by blending aqueous solution of magnesium sulfate and aluminum sulfate at the molar ratio of Mg:Al = 3:1, then mixed with sodium hydroxide and sodium carbonate. The mixture was stirred in an airtight container at 130˚C for 24 h. The crystallized Mg–Al LDH was isolated by centrifugation and further dried in oven at 100˚C. Then the LDH was calcinated at 400˚C and stored in a desiccator over fused $CaCl_2$ for the subsequent experiments.

2.3. Preparation of membranes

LDH particles prepared above were added into homogeneous casting solution consisting of PES and DMAc. The resultant mixture was kept stirring for 24 h at 70˚C so that the LDH particles could be homogeneously dispersed in the PES/DMAc solution. The PES/LDH blend flat-sheet membranes were prepared by casting the solution on the clean glass plate with a slit thickness of 150 μm, and then the liquid membranes were immediately immersed in DI water for 24 h. DI water was changed every 8 h to thoroughly remove the organic solvent from the membranes. Finally, the membranes were dried at room temperature.

2.4. Batch adsorption study

Fluoride solutions with various initial concentrations were prepared by dissolving NaF in DI water. All the sorption experiments were conducted by adding the membranes into airtight bottles containing the fluoride solution. The effect of pH on the adsorption was investigated by adjusting the pH with 1 M HCl or NaOH. The concentration of fluoride ions in the solutions was determined using a selective electrode for fluoride ions [24].

3. Results and discussion

To select appropriate candidate, four different PES/LDH blend flat-sheet membranes (M0, M14, M18, and M21) were prepared and the fluoride adsorption data are shown in Table 1. Obviously, M18 shows the highest adsorption amount of 2.63 mg/g. Therefore, further experiments were conducted with M18 only.

3.1. Characterization of the PES/LDH blend membrane

The SEM images of the top surface and cross section of the membranes with different mass of LDH particles are shown in Fig. 1. The pure PES film is smooth and empty. When more LDH particles were added to the membrane, more particles can be seen at the membrane surface. The cross-sectional SEM images embedded in the surface images of the membranes show that more and more finger-like pores across the whole thickness damaged the LDH particles thereby increasing its amount .

Fig. 2 shows the surface morphologies of LDH incorporated PES membranes by AFM. Similar trend can be observed that the distribution of LDH particles becomes more and more accumulated with the increase in LDH percentage.

Table 1
Effect of the ratio of LDH and PES on the removal of fluoride

Membrane	Casting solution compositions (wt%)			Adsorption capacity
	PES	Mg–Al LDH	DMAc	(mg/g)
M0	12	0	88	0
M14	12	14	74	1.86
M18	12	18	70	2.63
M21	12	21	67	2.07

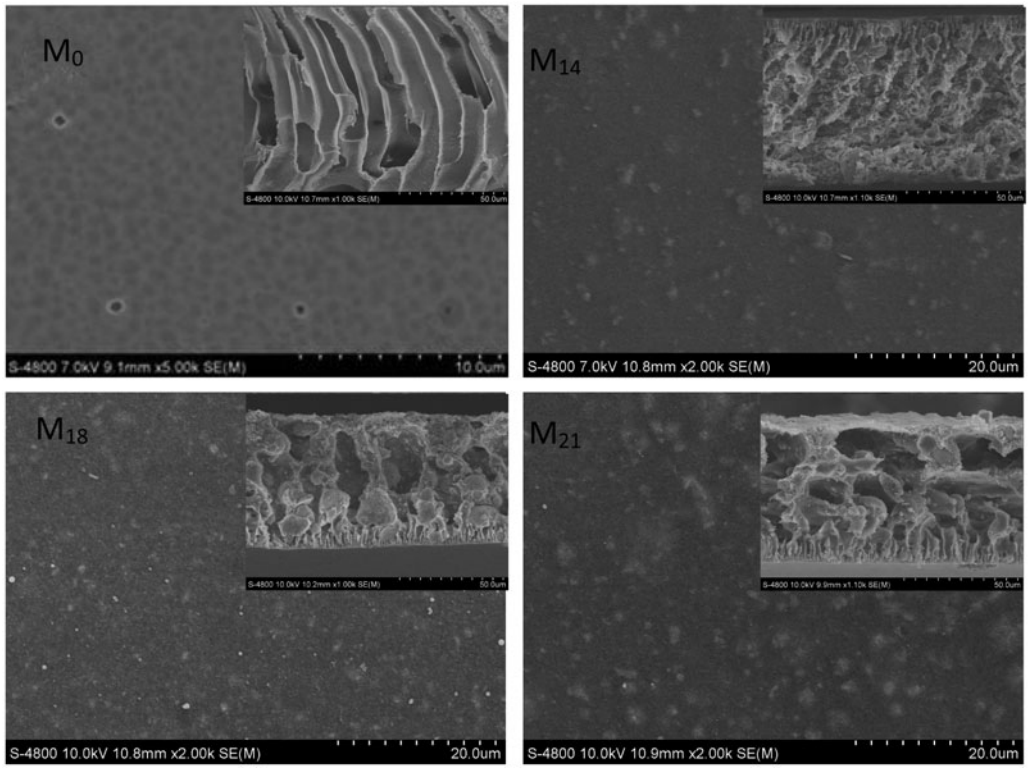

Fig. 1. SEM images of top surface and cross section of membranes.

3.2. Adsorption study of the PES/LDH blend membrane

3.2.1. Effect of adsorption temperature

Fig. 3 shows the effect of temperature on removal of fluoride. It showed that the adsorption was not obviously influenced by temperature, which means the thermal effect is negligible.

3.2.2. Effect of initial fluoride concentration

Fig. 4 shows the effect of initial fluoride concentration on removal of fluoride. It is evident that by increasing the initial concentration, the percentage removal of fluoride decreased and the actual amount of fluoride adsorbed per unit mass of the membrane increased. As the initial concentrations increased from 10 to 120 mg/L, the percentage of the removed fluoride decreased from 56 to 14%. The adsorption capacity increased with the initial fluoride concentration and reached a plateau at about 50 mg/L, at which the concentration of other experiment conditions is investigated.

3.2.3. Effect of contact time

The effect of contact time on adsorption is presented in Fig. 5. Apparently, with the contact time increasing, the amount of adsorbed fluoride is increased. The results showed that the adsorption of fluoride is faster during initial stages; then became slower and finally reached equilibrium at approximately 30 min. The fast adsorption rate during the initial phase is probably due to the availability of a large number of vacant sites on the surface of adsorbent and with the gradual occupancy of these sites, the adsorption became less efficient [25].

3.2.4. Effect of the membrane dosage

Fig. 6 shows the effect of the membrane dose on removal of fluoride. The mass of the membrane increased from 0.1 to 0.8 g, which can be attributed to the availability of more vacant sites of the membrane. The increase in the membrane dose can result in increased pollutant removal, but this elevation leads to decrease in adsorbed fluoride per unit of adsorbent from 3.2 to 2.26 mg/g.

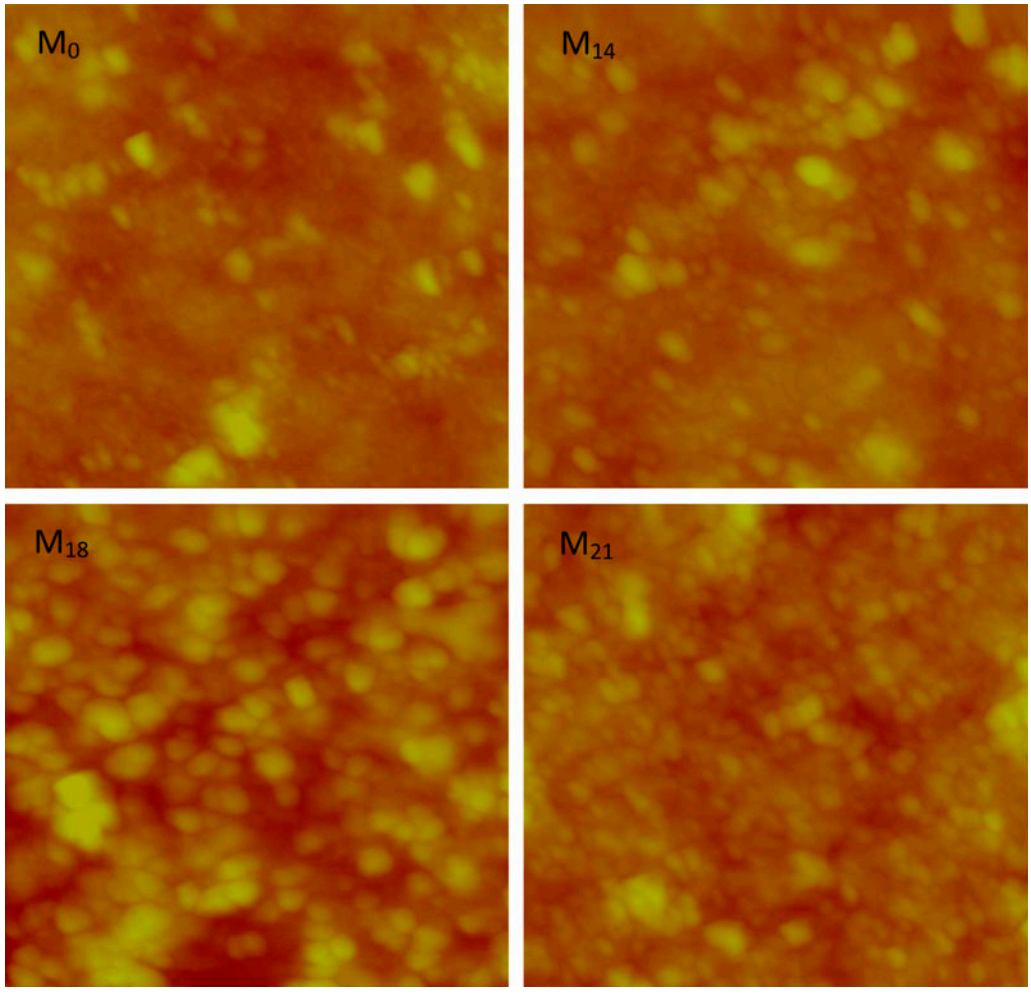

Fig. 2. AFM images of the membranes (size: 5 × 5 μm and *z* scal: 150 nm).

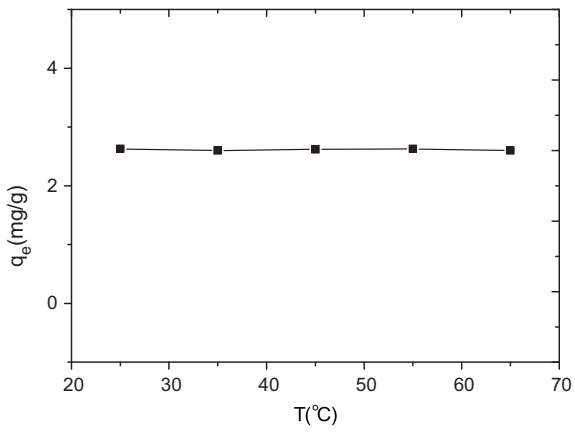

Fig. 3. Effect of adsorption temperature on the removal of fluoride (membrane sample mass = 0.35 g, pH 6, and initial concentration = 50 mg/L).

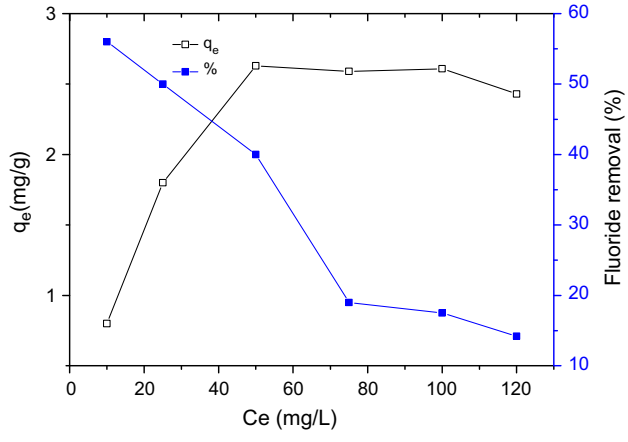

Fig. 4. Effect of initial fluoride concentration on the removal of fluoride with different adsorbent dosage (membrane sample mass = 0.35 g, *T* = 25℃, and pH 6).

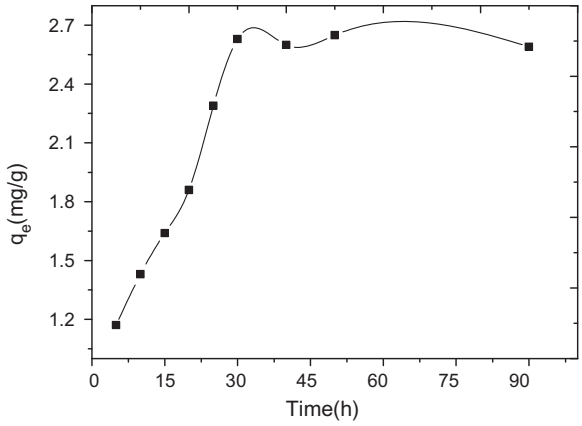

Fig. 5. Effect of contact time on the removal of fluoride (membrane sample mass = 0.35 g, T = 25°C, pH 6, and initial concentration = 50 mg/L).

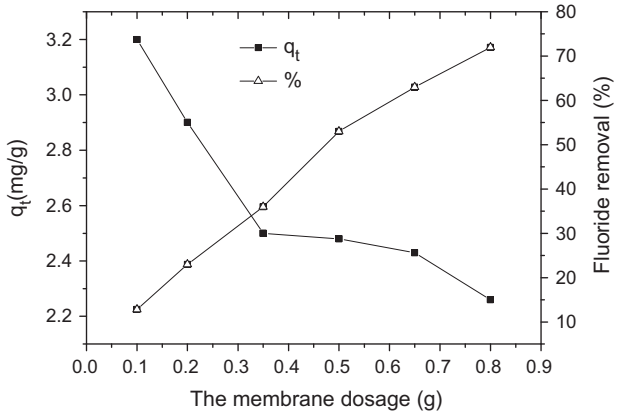

Fig. 6. Effect of membrane dosage on the removal of fluoride (T = 25°C, pH 6, and initial concentration = 50 mg/L).

3.2.5. Effect of solution pH

Fig. 7 shows the effect of pH on the fluoride adsorption on the PES/LDH blend membrane under the initial pH ranging from 2.0 to 10.0. More fluoride is removed at lower pH. This result can be attributed to the increase in the concentration of competing anions OH^- at higher pH. With hydroxyl released from LDH in the membrane during the adsorption process, the pH of the solution increased after adsorption. Our experiments were conducted under pH 6, as the pH of ground water is 6–8.

3.2.6. Effect of coexisting ions

The practical wastewater often contains more anions and the influences of six diverse ions were

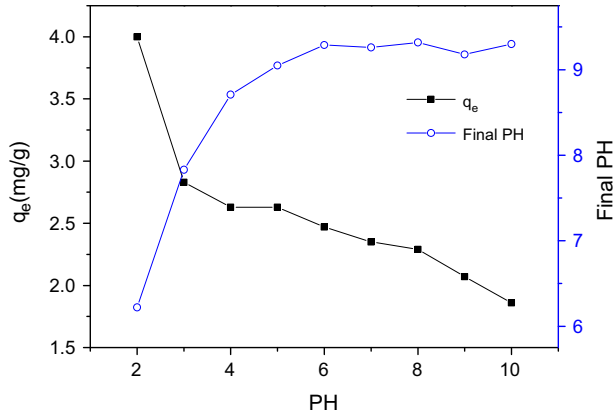

Fig. 7. Effect of initial pH on the removal of fluoride (membrane sample mass = 0.35 g and T = 25°C).

examined; the relevant results were presented in Fig. 8.

Referring to the figure, the concentration of PO_4^{3-} has the largest influence for its highest charge. CO_3^{2-} and SO_4^{2-} comes second; they had ion exchange with LDH in the membranes and occupied the limited adsorptive sites, which decreases the F^- exchange capacity. The effects of monovalent ion on fluorine adsorption are inferior to bivalent ions. NO_3^- and HCO_3^- were equally effective in the adsorption owing to their steric hindrance. Chloride minimally affects the sorption, because its polarity is similar to fluoride.

3.3. Adsorption isotherms

The adsorption isotherm indicates how the adsorbates interact with adsorbents. It is basically important

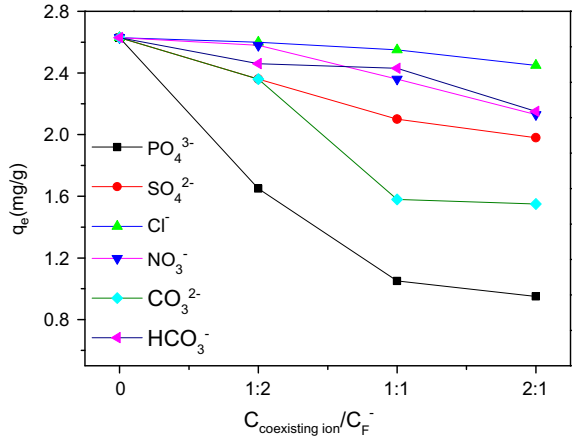

Fig. 8. Effect of coexisting ions on removal efficiency of fluoride (membrane sample mass = 0.35 g, T = 25°C, and pH 6).

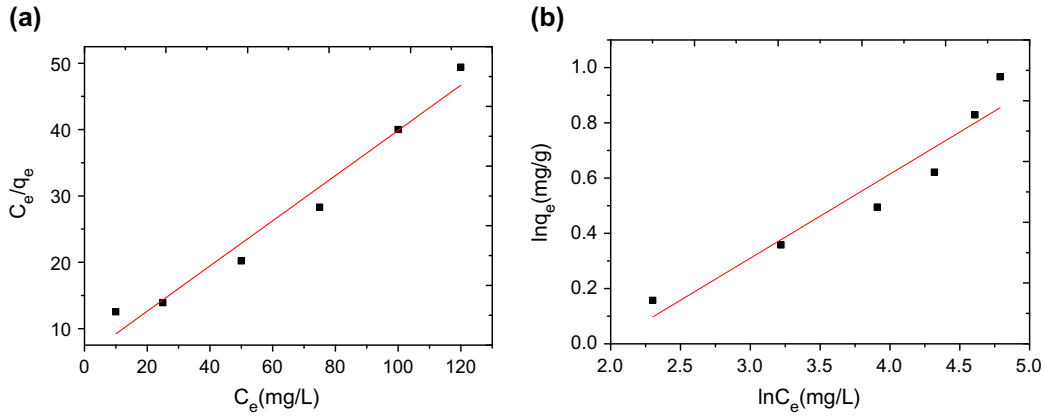

Fig. 9. Adsorption isotherms of Langmuir (a) and Freundlich (b) (membrane sample mass = 0.35 g, pH 6, and T = 25℃).

Table 2
The parameters of Langmuir and Freundlich isotherm models

	Langmuir			Freundlich		
T (℃)	K	R^2	q_m (mg/g)	K_f	R^2	n
25	0.088	0.980	2.43	1.513	0.918	8.47

to describe how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches equilibrium, which will give some valuable information to optimize the design of new adsorption systems [26,27]. Two general-purpose equilibrium models, Langmuir and Freundlich, were used to fit the experimental data at equilibrium. The isotherm diagrams are given in Fig. 9 and the parameters are given in Table 2.

Based on the correlation coefficient (R^2), it can be seen that the adsorption of fluoride onto the membrane is better fitted to the Langmuir isotherm. The maximum adsorption capacity obtained from the Langmuir isotherm is 2.43 mg/g, which is very close to the experimental one.

3.4. Adsorption kinetics

The adsorption kinetics data can be further analyzed by the pseudo-first-order rate model [28] and the pseudo-second-order rate model [29], expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_{e1} - q_t) \quad (1)$$

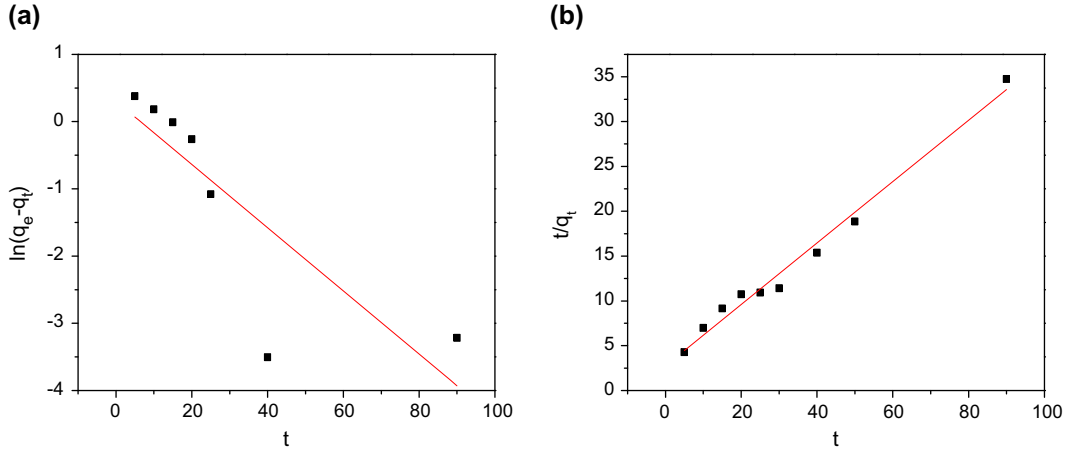

Fig. 10. Kinetics adsorption models of pseudo-first-order (a) and pseudo-second-order (b) fitting curves.

Table 3
Adsorption kinetic parameters obtained by different models

q_e exp (mg/g)	First-order kinetic model			Second-order kinetic model		
	q_{e1} (mg/g)	k_1 (min^{-1})	R^2	q_{e2} (mg/g)	k_2 (g/mg min)	R^2
2.63	1.35	0.047	0.701	2.92	0.0424	0.985

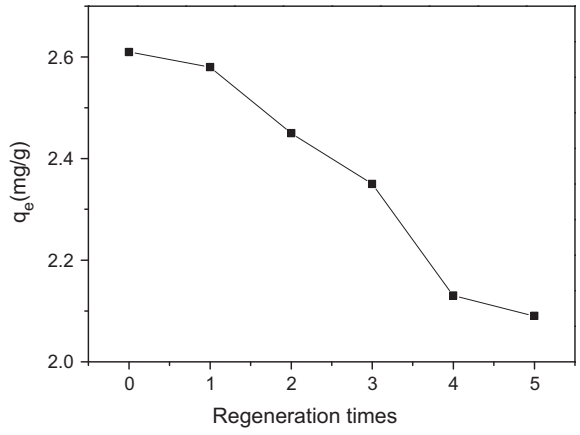

Fig. 11. Effect of regeneration frequencies on the removal of fluoride.

$$\frac{dq_t}{dt} = k_2(q_{e2} - q_t)^2 \quad (2)$$

where k_1 and k_2 are rate constants for the pseudo-first-order (1/min) and the pseudo-second-order adsorptions (g/mg min), respectively. While q_t and q_e are the amounts of fluoride adsorbed (mg/g) at time t and at equilibrium, respectively.

The classic pseudo-first/second fitting curves are shown in Fig. 10 and the model parameters are summarized in Table 3. As discussed above, one can draw a conclusion that the adsorption kinetics data can be well described by the pseudo-second-order rate model with a correlation coefficient R^2 above 0.98. The equilibrated adsorption capacity obtained from the pseudo-second-order rate model is 2.92 mg/g, which is very close to the experimental one.

3.5. Regeneration of the membrane

We regenerated the membrane after adsorption by soaking the membranes in 0.1 M NaOH and the results are shown in Fig. 11. The adsorption capacity of LDH reduced to 2.09 mg/g after they were regenerated five times; the defluorination efficiency of the membrane slightly declined with increase in regeneration times.

4. Conclusions

A PES/LDH blend flat-sheet membrane was successfully prepared by phase inversion process for adsorptive removal fluoride applications. The optimum conditions were obtained through the experiments: initial fluoride concentration is 50 mg/L, contact time is 30 min, the adsorption temperature is 25℃, and the maximum adsorption capacity of the membrane is 2.63 mg/g.

The kinetics adsorption experiment indicated that the adsorption equilibrium can be obtained within 30 min, and pseudo-second-order rate model can be well used to describe the adsorption kinetics. The Langmuir model gave a better fit of the adsorption data compared to the Freundlich model. The membrane can be regenerated with 0.1 M NaOH, and defluorination efficiency was slightly reduced with increase in regeneration times.

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