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Fluoride Adsorption Comparison from Aqueous Solutions Using Al- and La-Modified Adsorbent Prepared from *Polygonum orientale* Linn.

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Abstract: Al- and La-modified adsorbent materials (PO-Al, PO-La) were prepared by impregnating *Polygonum orientale* Linn. straw with $\text{Al}_2(\text{SO}_4)_3$ and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ solutions. The potential of removing fluoride using these modified adsorbents was examined. In the PO, PO-Al and PO-La adsorption systems, the fluoride adsorption process followed pseudo-second-order kinetics, and the kinetic constants for k_2 and R^2 were 0.0276 and 0.9609; 0.2070 and 0.9994; 0.1266 and 0.9933, respectively. The adsorption equilibrium results showed the best match with Langmuir isotherms. Moreover, the maximum monolayer adsorption capacity of PO, PO-Al and PO-La are 0.0923, 3.3190 and 1.2514 mg/g, respectively, in 30 °C. The regeneration results show that the effectively regenerating ability of modified adsorbents. Al-modified adsorbent showed the best results in terms of cost-effectiveness and adsorption efficiency for fluoride adsorption.

Keywords: fluoride; *Polygonum orientale* Linn.; modified; adsorption; wastewater



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1. Introduction

As stated by the report of the World Health Organization, the intake of fluoride in drinking water at low concentrations (0.5–1 mg/L) is beneficial, especially in promoting enamel calcification and protecting teeth against teeth decay [1–4]. However, when long-time exposure exceeds 1.5 mg/L fluoride concentrations, it can lead to fluorosis, with a range of serious consequences, including impaired kidney function, bone cancer, reduced immunity, digestive and nervous disorders, endocrine gland lesions, and other conditions [5–8]. Fluorosis caused by high concentrations of fluorine has been reported almost everywhere except in East Asia and Australia [5,9]. Accordingly, excessive fluoride contamination in groundwater has been recognized as an extremely serious problem worldwide.

Various techniques have been developed to remove excess fluoride from drinking water, such as adsorption, coagulation, ion exchange, microbial-induced precipitation [10,11], electrocoagulation [12], electrostatic unit [13] and electrodialysis [5,14]. Among these techniques, adsorption is effective, economical, convenient, and environmentally friendly [3,4,15,16]. Biosorption is a new technology for water treatment using a large amount of available biological materials. The biosorbents for fluoride removal contain chitin, chitosan, etc. The regenerated bone char media was optimized and applied to the defluoridation of drinking water in Tanzania, with the highest fluoride removal and adsorption capacity [17]. Therefore, there is a need to research and develop novel technologies for fluoride removal that use low-cost biomass containing carboxylic acid and amine functional groups that could be applied to water pollution control [18–20].

Polygonum orientale Linn., belonging to *Polygonum* genus, Polygonaceae family, is a fast-growing annual herbage, commonly found in lake edges, drainage ditches, marshes, and other wetlands [21]. It could adsorb large quantities of nutrients and could produce large amounts of biomass at a low cost [22–24]. Therefore, this plant provides a good basis for the study of modified materials as an adsorbent.

The surface adsorption performance of modified adsorbents could be enhanced by changing their surface chemistry and pore structure [4,25]. Many modification methods have been applied to improve affinities towards contaminants in various types of water [26,27], furnishing satisfactory results, particularly using surface-modified adsorbents and/or mineral-based [3].

(1) Modification of alumina with Al^{3+} . Over the years, activated alumina has been proven by researchers to effectively remove fluoride, and a series of explorations have been carried out on it. For example, in order to explore the effects of different experimental conditions on the removal ability of fluoride in water during the experiment, Ku and Chiou [28] studied the conditions of temperature, pH, and initial concentration during the experiment. At the same time, some studies have also explored the interaction process and mechanism between F^- and amorphous $\text{Al}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, and Al_2O_3 [29]. Meanwhile, the researchers also modified the surface of Al_2O_3 to improve the adsorption effect of activated Al_2O_3 , such as adding La^{3+} and Y^{3+} to Al_2O_3 to increase its surface active adsorption sites [30]; using MnO_2 modification is used to prepare $\text{Mn-Al}_2\text{O}_3$ oxide coating (MOCA) for fluorine removal, and Al_2O_3 -supported $\text{La}(\text{OH})_3$ is modified to remove fluoride in water [31,32]. The results have shown that after modification of Al_2O_3 impregnated with $\text{La}(\text{OH})_3$, the adsorption capacity for F^- is the highest, the maximum fluoride uptake capacity for MOCA was found to be 2.85 mg/g [31]. This may be because the ion exchange between fluoride and OH^- on the surface of Al_2O_3 promotes the F^- removal process.

(2) Modification of alumina with La^{3+} . The biomass materials are widely used as adsorbents because of their large reserves, low cost, and good adsorption capacity. So, some researchers reported that the use of lanthanide compounds to modify the surface of chitosan can improve the ability to remove F^- [33].

In addition, Kamble et al. [32] and Parmar et al. [34] studied the difference in the adsorption of fluoride with $\text{La}(\text{OH})_3$ and AlCl_3 modification; the results showed that after $\text{La}(\text{OH})_3$ and AlCl_3 modification, the treatment had better adsorption ability of F^- . Similar research also includes the use of agricultural biomass materials such as coconut husk and rice husk to remove fluoride [35]. Therefore, this study aimed to assess the feasibility and adsorption capacity of $\text{Al}_2(\text{SO}_4)_3$ - and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ -modified biomaterials derived from *P. orientale* (PO, PO-Al, PO-La) to remove fluoride in aqueous solutions. Furthermore, the ability of these adsorbents to perform desorption test was examined for potential industrial application.

2. Materials and Methods

2.1. Preparation of Modified Adsorbents

Polygonum orientale Linn. was gathered from Fenhe river (Shanxi province, northern China), after the process of cutting, washing, and drying in an oven (101A-3, Boxun, Shanghai, China), the samples were ground into powder by a grinder and then sieved through a standard sieve to obtain 160–200 mesh particles. This precursor (2 g) was added to $\text{Al}_2(\text{SO}_4)_3$ (3%) or $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (5%) aqueous solutions (200 mL). After soaking for 24 h, the solution was filtered by vacuum filtration and the resultant modified adsorbents of $\text{Al}_2(\text{SO}_4)_3$ -modified (PO-Al) and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ -modified (PO-La) were obtained after washed with distilled water until the pH was 7.0 and dried at 120 °C for 8 h.

2.2. Adsorption Experiments

Fluoride stock solution was prepared by dissolving NaF (2.21 g) in 1000 mL deionized water. The solution pH was adjusted by adding 0.5 M NaOH or 0.5 M HNO_3 solutions.

Adsorption experiments were performed by shaking prepared modified adsorbent (2.0 g) with NaF experimental solutions (100 mL) of different concentrations (10, 20, and 30 mg/L). Continuous stirring was performed throughout the experiment at a constant speed of 120 rpm. In addition, the adsorption isotherm tests were performed at 10, 20, and 30 °C, simultaneously, other things being equal. Then, the supernatant liquids were filtered by a disposable injector and syringe filter (13 mm × 0.45 µm, Millipore, Billerica, MA, USA), and the F[−] concentration was measured by F[−] concentration meter (PXSJ-216F, Leici, Shanghai, China), the F[−] concentration in each flask was determined three times.

In this study, two isotherm models of Langmuir and Freundlich were utilized to analyze the experimental equilibrium data for fluoride adsorption by PO, PO–Al, and PO–La. The adsorption isotherm model is a basic model describing the interactions between adsorbate and adsorbent.

2.2.1. Langmuir Isotherm

The Langmuir isotherm model formula as shown in the following Equation (1) [36]:

$$\frac{C_e}{q_e} = \frac{1}{Q_m b} + \frac{1}{Q_m} C_e \quad (1)$$

where C_e (mg/L) represents the equilibrium concentration of the adsorbate, q_e (mg/g) is the maximum adsorption capacity on the equilibrium phase, b (L/mg) is the Langmuir adsorption constant, and Q_m (mg/g) is the maximum amount adsorbed of adsorbent. However, a dimensionless equilibrium parameter R_L could be defined according to Equation (7) to determine whether adsorption is beneficial [37]:

$$R_L = \frac{1}{1 + bC_0} \quad (2)$$

where R_L indicates whether the isotherm is favorable ($0 < R_L < 1$), irreversible ($R_L = 0$), linear ($R_L = 1$), or unfavorable ($R_L > 1$). b (L/mg) is the Langmuir isotherm constant, and C_0 (mg/L) is the initial fluoride concentration.

2.2.2. Freundlich Isotherm

The Freundlich isotherm model could be expressed in Equation (3) [38]:

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (3)$$

where K_F ((mg/g) (L/mg)^{1/n}) indicates the adsorption capacity of the adsorbent, with a larger K_F value indicating a larger adsorption capacity. The Freundlich isotherm constant n indicates the favorable degree of the adsorption process, with $1/n < 1$ indicating the normal Freundlich isotherm and cooperative adsorption process.

2.3. Adsorption Kinetic Models

2.3.1. Pseudo-First-Order Model

The pseudo-first-order kinetic model is shown in Equation (4) [39].

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (4)$$

When $q_t = 0$ at $t = 0$, Equation (4) could be integrated to give Equation (5):

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (5)$$

where q_e and q_t (mg/g) are the adsorption capacity of fluoride at equilibrium and time t , respectively, t (min) is the adsorption time, and k_1 (min^{-1}) is a rate constant for this equation.

2.3.2. Pseudo-Second-Order Model

The pseudo-second-order kinetic model as shown in Equation (6) [40]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (6)$$

when Equation (6) is simplified and $q_t = 0$ at $t = 0$, the new equation could be rearranged into Equation (7):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

$$h = k_2 q_e^2 \quad (8)$$

where h (mg/(g min)) represents the product of the pseudo-second-order kinetic constant k_2 (g/(mg min)) and the maximum adsorption capacity on the equilibrium phase q_e (mg/g), and it represents the initial adsorption rate.

2.4. Desorption Studies

The modified adsorbents (PO, PO-Al, PO-La) was inputted to a 100 mg/L NaF solution and kept at a constant temperature in a shaker at 150 rpm until equilibrium was reached. The concentration C_{ad} of fluoride was defined as the difference between the initial and equilibrium fluoride concentration ($C_o - C_e$). The spent adsorbent powder was washed with deionized water, over dried at 40 °C, 10 h and mixed with H₂O, 0.1 M HCl, NaOH, and 95% ethanol to desorb the fluoride. The fluoride concentration C_{de} (mg/L) in the solution was determined after the desorption process. The desorption capacity of fluoride was calculated using Equation (9):

$$\text{Desorption (\%)} = \frac{C_{de}}{C_{ad}} \times 100 \quad (9)$$

3. Results

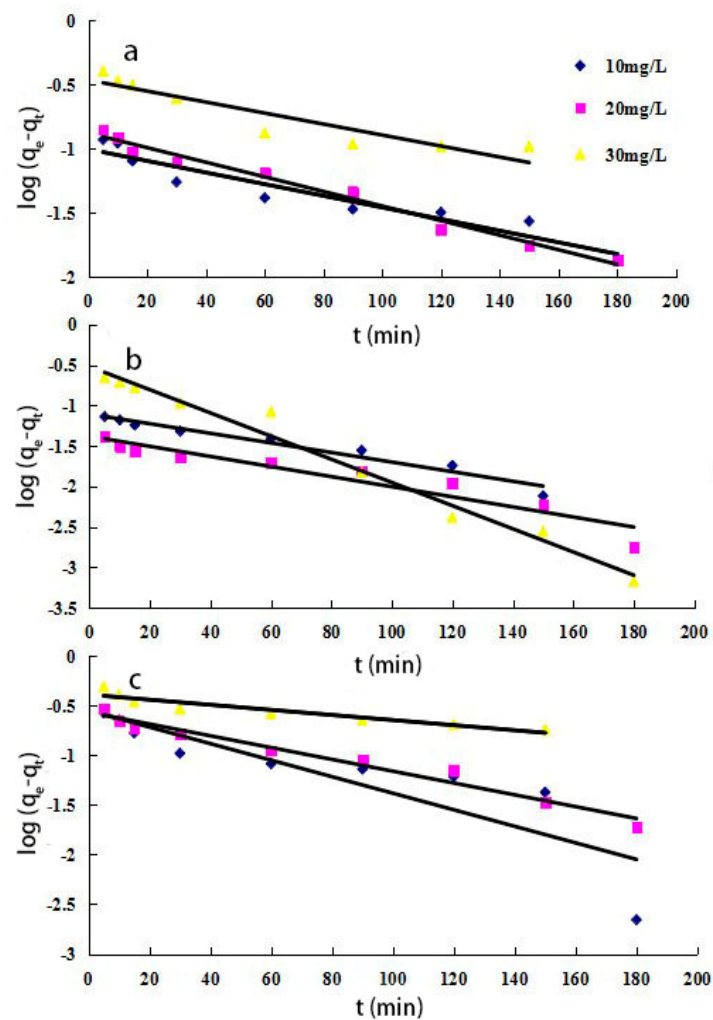
3.1. Adsorption Kinetics

By surface modification of the adsorbent, the adsorption capacity and strength of the adsorbent can be improved without a significant increase in cost. These modified adsorbents were prepared by impregnating *P. orientale* with Al₂(SO₄)₃ and La(NO₃)₃·6H₂O solutions for removing fluoride in aqueous solutions.

In this section, pseudo-first-order and pseudo-second-order kinetic models are used to fit the adsorption process of fluoride onto three types of adsorbents. Meanwhile, kinetic process fitting is very important to elucidate the adsorption kinetic mechanism and diffusion process. The parameters of the pseudo-first-order and pseudo-second models are shown in Table 1. The comparison of different kinetic models for the adsorption of fluorine at different concentrations of PO, PO-Al, and PO-La are shown in Figures 1 and 2. The pseudo-first-order kinetic curves were poorly fitted to the experimental kinetic data. This disagreement was also confirmed by the low R^2 . Therefore, it was suggested that fluoride adsorption onto the biochar activated carbon did not conform to the pseudo-first-order model. In contrast, the results showed a high degree fitting degree with the pseudo-second-order model. This great agreement was further supported by the similar calculated and experimental values of q_e .

Table 1. Pseudo-first-order and pseudo-second-order kinetic parameters.

C_e (mg/L)	Pseudo-First-Order					Pseudo-Second-Order			
	q_e (exp) (mg/g)	$k_1 \times 10^{-2}$ (min ⁻¹)	q_e (cal) (mg/g)	R^2		k_2 (g/mg·min)	q_e (cal) (mg/g)	h (mg/g·min)	R^2
PO									
10	0.2935	0.0104	0.0993	0.9111		0.3970	0.2963	0.0349	0.9962
20	0.6469	0.0131	0.1326	0.9808		0.3615	0.6525	0.1539	0.9993
30	0.4075	0.0099	0.3435	0.8585		0.0276	0.5208	0.0075	0.9609
PO-Al									
10	0.4778	0.0136	0.0779	0.9564		0.5947	0.4829	0.1387	0.9994
20	0.9432	0.0956	0.0415	0.9031		1.2770	0.9445	1.1391	0.9996
30	0.0758	0.0329	0.3016	0.9805		0.2070	1.4255	0.4207	0.9994
PO-La									
10	0.3980	0.0191	0.2812	0.7620		0.1874	0.3980	0.0297	0.7445
20	0.7967	0.0136	0.2707	0.9672		0.2196	0.7844	0.1351	0.9056
30	0.5647	0.0060	0.4069	0.8810		0.1266	0.4209	0.0224	0.9933

**Figure 1.** Pseudo-first-order results for fluoride adsorption in (a) PO, (b) PO-Al, and (c) PO-La systems.

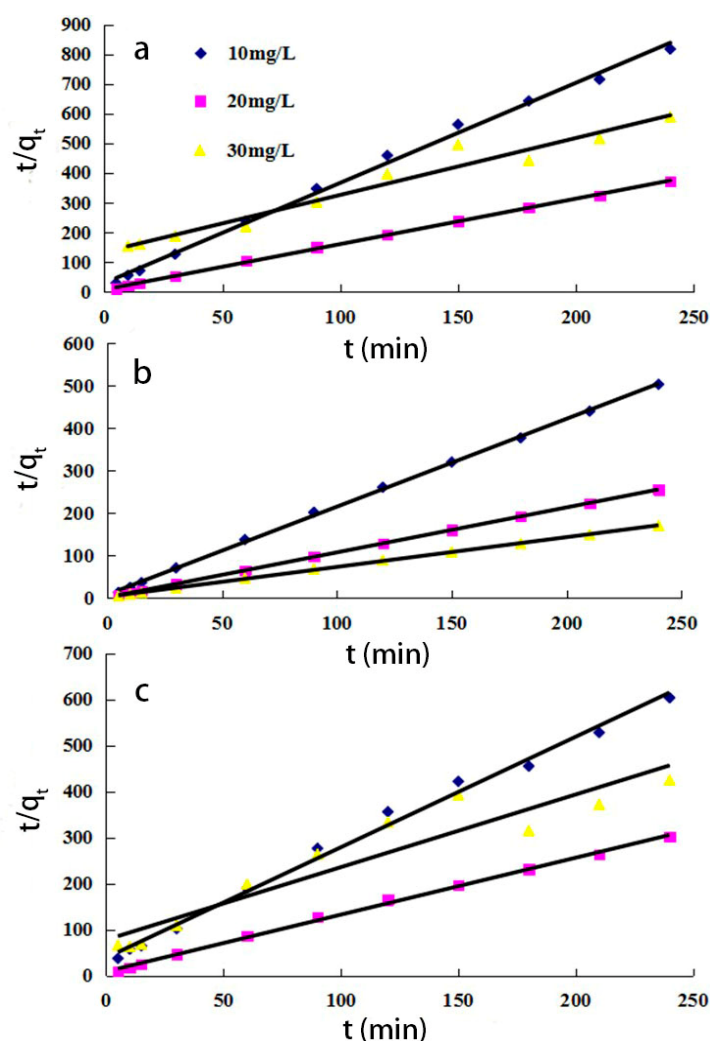


Figure 2. Pseudo-second-order results for fluoride adsorption in (a) PO, (b) PO-Al, and (c) PO-La systems.

These results show that the adsorption mechanism may rely not only on the interaction with fluoride, but also on the role of adsorbent [41], and the rate-limiting step might be chemisorption, involving valence forces by the exchange or sharing of electrons [26,27].

3.2. Adsorption Isotherms

The adsorption isotherm of fluoride adsorption onto PO, PO-Al, and PO-La at 283, 293 and 303 K, respectively, based on the linear forms of the Langmuir and Freundlich isotherms are shown in Figures 3 and 4, respectively. The isotherm constants and correlation coefficients calculated from the linear forms of the two isotherms are summarized in Table 2. The experimental data of fluoride adsorption onto PO and PO-La were fitted to the Langmuir isotherm model. The adsorption of F^- on PO-Al was fitted well by both the Langmuir and Freundlich isotherm models, while a better fit with the Langmuir equation was statistically confirmed by the larger R^2 values closer to unity. Furthermore, the results show that the adsorption process is favorable, because the Langmuir isotherm value of R_L was between 0 and 1. In addition, the maximum adsorption capacity of Q_m , improved with increasing temperature, revealing an endothermic process. Adsorption capacity showed that PO, PO-Al, and PO-La could be employed as promising adsorbents to remove fluoride from an aqueous solution. In addition, Table 3 lists the comparison of the fluoride adsorption capacity in this study and reported in other literature. These values are based on the Langmuir adsorption capacity of the adsorbent. The results show that in

the field of low-cost adsorbents, the adsorbents prepared in this study are superior to most of the adsorbents in removing fluoride.

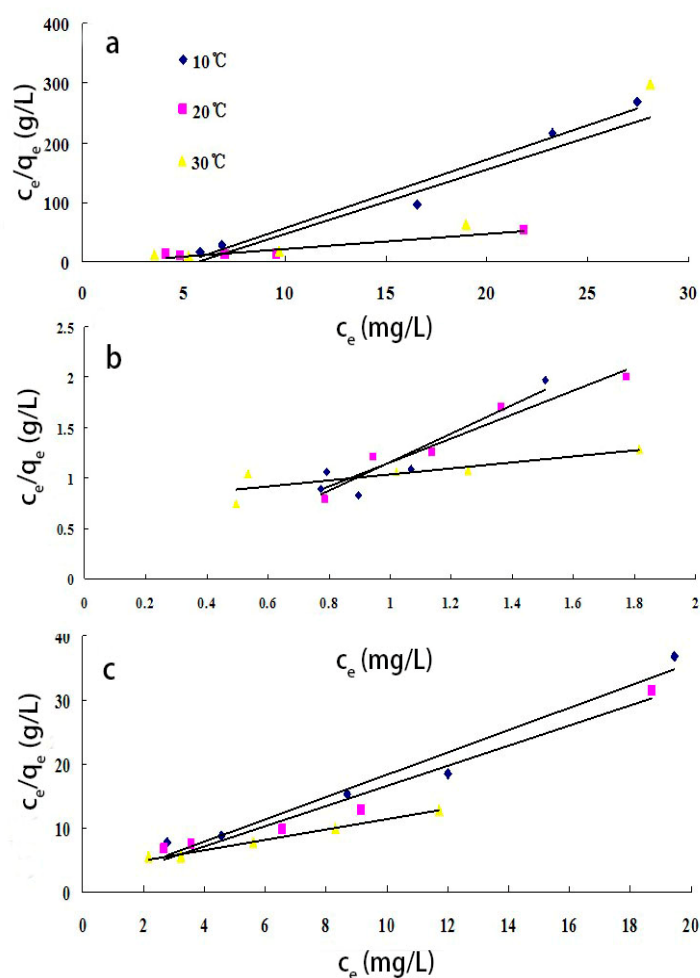


Figure 3. Langmuir isotherms for fluoride adsorption onto (a) PO, (b) PO-Al, and (c) PO-La at different temperatures.

Table 2. Langmuir and Freundlich isotherm parameters for fluoride adsorption in PO, PO-Al and PO-La systems.

T (K)	Langmuir				Freundlich		
	Q_m (mg/g)	b (L/mg)	R_L	R^2	K_F (mg/g (L/mg) ^{1/n})	$1/n$	R^2
PO							
283	0.0916	0.2211	$0 < R_L < 1$	0.8641	0.9714	0.6631	0.6577
293	0.4042	0.7331	$0 < R_L < 1$	0.9049	0.3989	0.1063	0.0341
303	0.0923	0.1758	$0 < R_L < 1$	0.8094	1.0214	0.539	0.4606
PO-Al							
283	0.7060	5.4251	$0 < R_L < 1$	0.8687	0.9041	1.4115	0.7420
293	0.8403	3.0912	$0 < R_L < 1$	0.9462	0.7702	1.3838	0.9477
303	3.3190	0.4114	$0 < R_L < 1$	0.7108	0.9506	0.7306	0.9028
PO-La							
283	0.5735	2.0291	$0 < R_L < 1$	0.9644	0.3398	0.206	0.5367
293	0.6645	1.1717	$0 < R_L < 1$	0.9686	0.5398	0.3086	0.4247
303	1.2514	0.2378	$0 < R_L < 1$	0.9890	0.3016	0.4758	0.9328

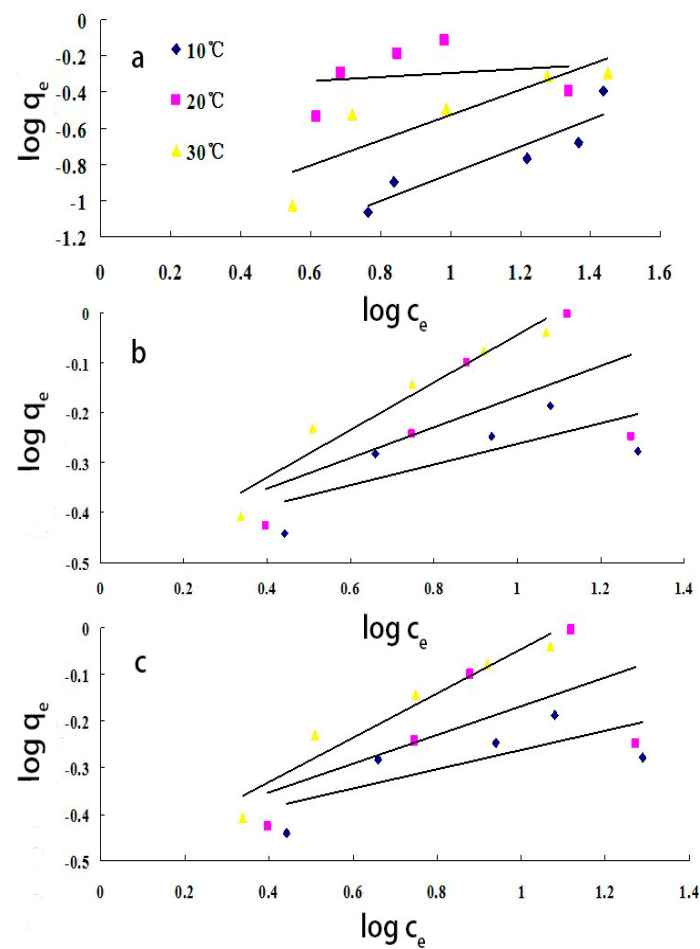


Figure 4. Freundlich isotherms for fluoride adsorption onto (a) PO, (b) PO-Al, and (c) PO-La at different temperatures.

Table 3. Comparison of the fluoride adsorption capacity in this study and reported in the literature.

Adsorbents	Adsorption Capacity (mg/g)	References
Chi-Pr	8.20	[42]
Hydrous iron(III)–tin(IV) bimetal	10	[43]
Nano-alumina	14	[44]
o-WM	4.2	[45]
CR	3.72	[46]
CL	3.16	[46]
MOCA	2.85	[31]
MWCNTs	2.83	[47]
a-WM	2.8	[45]
SWCNTs	2.40	[47]
Fe(III)-STI	2.31	[48]
Ceramic	2.16	[49]
AC-CMCSL	2.01	[50]
ZrO ₂ -Ze	0.34	[51]
PO-Al	3.32	This study

3.3. Desorption

A suitable defluorine adsorbent should not only have high defluorine removal capacity and cost efficiency, but also be easy to desorb F^- and be able to be regenerated efficiently so that the adsorbent can be reused many times. The desorbent should not cause any

damage to the adsorbent, resulting in a decline in adsorption capacity. For economic and environmental reasons, the only reusable sorbent can be of practical value in practical systems.

Desorption of F^- is performed by leaching of adsorbed F^- by different solvents as eluants, which could contribute to elucidate the mechanism of adsorption and assess the stability of the loaded adsorbents. The elution of fluoride from the adsorbent by water, strong base or acid, and organic substance symbolized the adsorption of fluoride onto PO by the weak force, ion exchange, and chemical adsorptions, behaviors, respectively. Figure 5 showed the results of the desorption percentages using 0.1 M NaOH, deionized water, 0.1 M HCl, and 95% ethanol were measured for PO, PO-Al, PO-La, respectively. If the strong acid or base could desorb a large amount of adsorbate from the adsorbent, the adsorbate is attached to the adsorbent by ion exchange. The organic solvent, for instance, ethanol, could elute F^- from PO-Al easily and indicated that chemical adsorption is the main phenomenon of PO-Al adsorption of F^- . Strong chemical bonds between the adsorbate molecules and the adsorbent surface may not be broken by the eluting agents. NaOH displayed certain desorption effect on F^- . This indicated F^- has a strong chemical attachment to PO-Al, which can be broken by thermal forces.

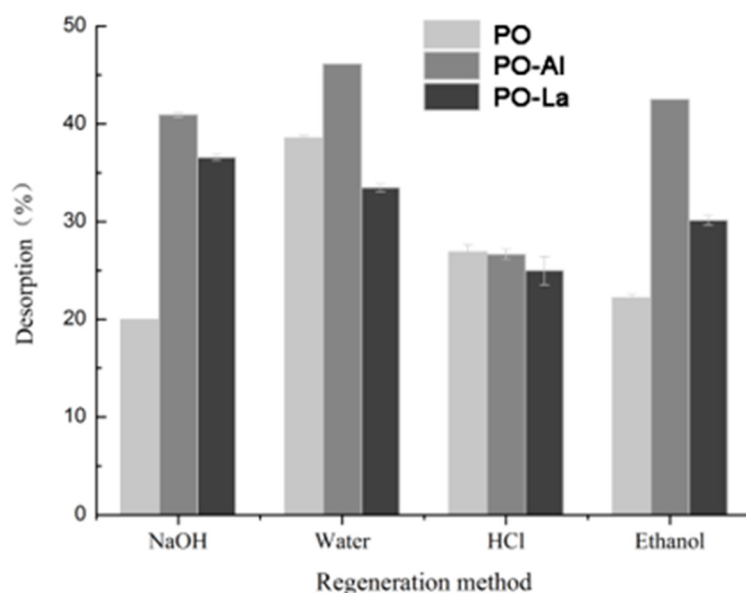


Figure 5. Resorption of fluoride on PO, PO-Al, PO-La desorbed by NaOH, HCl, deionized water, and ethanol.

4. Conclusions

The modified adsorbent showed the most potential as an economic and efficient adsorbent for fluoride adsorption from aqueous solutions. Meanwhile, the pseudo-second-order kinetic and Langmuir model indicated that the adsorption process of fluoride ions was mainly chemical adsorption. The Langmuir model showing that adsorption was a spontaneous and endothermic process. The increasing temperature was beneficial to adsorption. In the reusability test, ethanol and NaOH were effective materials for regenerating the adsorbent. Furthermore, desorbed PO-Al was highly effective in fluoride resorption. Despite these, more research is needed to translate the process to an industrial scale. In addition, regeneration studies need to be carried out to more extent to recover the adsorbent and improve the economic viability of the process.

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