Research Article

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Optimization for removal efficiency of fluoride using La(III)–Al(III)-activated carbon modified by chemical route

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Abstract: A simple chemical route was adopted for the preparation of adsorbent to remove fluoride in the simulation solution. In this study, commercially activated carbon (CAC) was used as the raw material, HNO_3 (20 wt%), $\text{La}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ (0.05 mol/L), and $\text{Al}(\text{NO}_3)_3$ (0.10 mol/L) were employed as modification reagents to successfully prepare the CAC adsorbent loaded with the elements La and Al (La(III)–Al(III)–CAC). The modified adsorbent was characterized by scanning electron microscopy, energy-dispersive spectroscopy, and Fourier-transform infrared spectroscopy measurements. The effects of variables such as solution pH, adsorption time, initial concentrations, and volume of solution were investigated on adsorption efficiency by the response surface method (RSM). Under optimum conditions, specified as a pH value of 6, an adsorption time of 1.2 h, an initial concentration of 30 mg/L, a solution volume of 25 mL, and the value of R_F can reach at 74.11%. From the RSM analysis, the pH value was a significant factor in the adsorption process and the order for these key factors was as follows: pH > adsorption time > solution volume. Meanwhile, there were interactions among these factors. Chemical modification had an important role in pore structure generation and functional group of adsorbent to improve the adsorption efficiency. The removal performance of adsorbent on simulation solution of fluoride also showed the feasibility of adsorbent to be applied in industrial purposes.

Keywords: activated carbon modification, loaded with La and Al, simulation solution of fluoride, removal rate, optimum conditions

Abbreviations

A	Concentration of HNO_3
AC	Activated carbon
B	Concentration of $\text{La}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$
C	Concentration of $\text{Al}(\text{NO}_3)_3$
CAC	Commercially activated carbon
D	Solution volume ratio of $\text{La}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3$
E	Adsorption time
F	pH
EDS	Energy-dispersive spectroscopy
F^-	Fluoride ion
FT-IR	Fourier-transform infrared spectroscopy
G	Solution volume
La(III)–Al(III)–CAC	La(III)–Al(III) loaded on CAC
MCAC	Acid-modified activated carbon
R^2	Correlation coefficient
RF	Removal rate of fluoride
RSM	Response surface method
SEM	Scanning electron microscopy
TISBS	Total ionic strength buffer solution.

1 Introduction

Fluoride is a very important trace element for our human body because it has great significance for the body's growth and development [1,2]. But it has harmful effects such as endocrine disorders [3], the formation of fluoride plaque [4], and even bone cancer [5] when the intake is excessive. Given that the source of fluorine is mainly drinking water, many people are drinking water with an

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excess amount of fluoride [6–8]. Fluoride pollution attracted great attention because it has become a worldwide problem, so it is very much necessary to carry out the research on defluoridation.

There are several methods to remove the fluoride ion (F^-), such as limestone precipitation method, ion exchange method, membrane separation method, and adsorption method. Among these strategies, adsorption method is one of the most effective and commonly used methods as it is environmentally friendly [9]. Various adsorbents have been used in the literature for defluoridation of aqueous solution such as activated carbon (AC), activated alumina, zeolites, alumina-based Zr-MOFs, iron-based adsorbents, or some biosorbents. Theoretically, they can be used as adsorbents for fluoride removal because of their unique physical or chemical composition [10–12]; however, there are some disadvantages such as highly pH-dependent in regeneration, material loss in adsorption process, and a gap between adsorption properties and desired effect by these strategies. AC is supposed to be a sustainable material for elimination of pollutants from drinking water.

Recently, to improve the adsorption capacity of AC, a number of metal oxides were employed to remove the anionic contaminants [13]; Fe_2O_3 , ZrO_2 , SnO_2 , MnO_2 , and $MnFe_2O_4$ can be good choice due to their biocompatibility and chemical stability [14–17]. Meanwhile, some modified methods of graphene oxide can be referred from previous studies [18–20]. Lanthanum is a kind of a rare-earth element, and some compounds of lanthanum were reported to be excellent adsorbents of fluoride [21], such as nano-adsorbent of Al–Fe–La [22] and triple-metal composite of Fe–Mg–La [23]. Oxides and hydroxides of aluminum have also been reported to remove fluoride effectively with comparatively low cost [24–26]. Thus, a novel La-based and La–Al-based composite or a modified adsorbent will be a good choice for removing fluoride. However, few studies on La–Al adsorbents were reported.

In this work, the cheap AC, the low-cost reagent, and an experimental design technique were combined to explore an easier to handle, faster, more efficient, and cost-effective method to treat the simulation solution of fluoride. RSM is a statistical method used for optimization of the process and evaluation of the significance of the variables and their effects on the response [27]. The results of this study confirm the great potential and applicability of adsorbents for the removal of other ions from industrial wastewater.

2 Experimental methods

2.1 Materials

Commercially activated carbon (CAC) was employed as a raw material in this experiment. The properties of CAC are listed in Table A1 in the Appendix. After being ground and screened until the particle size was less than 0.425 mm, the CAC will be washed five times and dried.

2.2 Methods and design

Preparation of La(III)–Al(III)–CAC included two steps: the acid modification process (I) and the La(III)–Al(III) loading process (II). A specific mass fraction of nitric acid (HNO_3) was involved in process I. A total of 100 mL of HNO_3 and CAC (20 g) were mixed in a flask, which was placed in a water bath at a constant temperature of 75°C for 2 h. Then, the CAC was washed to neutral and dried at 100°C for 3 h and the acid-modified activated carbon (MCAC) was obtained. $La(NO_3)_3 \cdot 2H_2O$ and $Al(NO_3)_3$ were employed to load La(III) and Al(III) on MCAC. A 10 g MCAC was stirred in 100 mL of mixed solution of $La(NO_3)_3 \cdot 2H_2O$ and $Al(NO_3)_3$ for 24 h. Then, the solid product was carbonized in a tube furnace at 300°C under a N_2 atmosphere for 2 h, and after cooling to room temperature, the preparation of La(III)–Al(III)–CAC was completed. La(III)–Al(III)–CAC will be used as an adsorbent for fluoride. The La(III)–Al(III)–CAC was put into the simulation solution of fluoride for a certain time period to perform the adsorption process. Illustration of La(III)–Al(III)–CAC preparation and adsorption processes is shown in Figure 1.

An experimental design for the preparation of La(III)–Al(III)–CAC was required to reduce the experimental cost [28]. Factors adopted here were solution concentration (mass fraction) of HNO_3 (A), concentration (mass fraction) of $La(NO_3)_3 \cdot 2H_2O$ (B), concentration (mass fraction) of $Al(NO_3)_3$ (C), and solution volume ratio of $La(NO_3)_3 \cdot 2H_2O$ and $Al(NO_3)_3$ (D), each having three levels, as shown in Table 1. The orthogonal array designed by the JMP method (a kind of statistical analysis software designed by SAS company) is listed in Table 2. This reduced the experimental number from $3^4 = 81$ to $L_{15}(3^4) = 15$.

Figure 1: Illustration of preparation and adsorption processes.

Table 1: Factors and levels for the experimental design

Factor	Level		
	1	2	3
A (%)	0.1	0.2	0.3
B (mol/L)	0.01	0.03	0.05
C (mol/L)	0.05	0.10	0.15
D (-)	0.5	1	2

Table 2: Orthogonal array for the experiment

No.	A	B	C	D
1	1	1	1	1
2	2	3	2	2
3	2	1	3	1
4	1	3	1	1
5	3	3	1	3
6	1	2	2	1
7	2	2	3	3
8	3	3	3	1
9	1	3	2	3
10	1	3	3	2
11	3	1	2	2
12	1	1	3	3
13	1	2	1	2
14	3	2	1	1
15	2	1	1	3

2.3 Calculation of R_F

Ion-selective electrode method was explored to calculate the concentration of F⁻, and a standard curve can be obtained by this method, which is detailed in the Appendix. According to the standard curve, R_F can be calculated by the following equation:

$$R_F = \frac{C_0 - C_1}{C_0} \times 100\%, \quad (1)$$

where R_F, C₀, and C₁ are the removal rate of F⁻ (%), concentration of F⁻ before and after adsorption processes, respectively (mg/L).

3 Results and discussion

3.1 Confirmation of preparation parameters

The higher the value of R_F, the better the adsorption efficiency of La(III)–Al(III)–CAC. Table 3 shows the results for 15 runs, and it is easy to find that No. 2 sample got the maximum value of R_F, indicating that the optimal preparation parameters were confirmed as A2B3C2D2.

Table 3: R_F of samples with different conditions

No.	Condition	R_F (%)
1	A1B1C1D1	0.25
2	A2B3C2D2	0.58
3	A2B1C3D1	0.41
4	A1B3C1D1	0.23
5	A3B3C1D3	0.27
6	A1B2C2D1	0.18
7	A2B2C3D3	0.41
8	A3B3C3D1	0.38
9	A1B3C2D3	0.21
10	A1B3C3D2	0.32
11	A3B1C2D2	0.27
12	A1B1C3D3	0.38
13	A1B2C1D2	0.15
14	A3B2C1D1	0.29
15	A2B1C1D3	0.44

3.1.1 SEM-EDS analysis of adsorbent

Scanning electron microscopy (SEM) was adopted to show the micromorphology of samples and the corresponding energy-dispersive spectroscopy (EDS) images to prove the successful loading of La(III) or Al(III) on La(III)-Al(III)-CAC, which were prepared under optimized conditions.

As shown in Figure 2, there were more and denser pore structures on MCAC, indicating that the modification of HNO_3 was beneficial for generating the pores. The SEM images of La(III)-CAC and La(III)-Al(III)-CAC are shown in Figure 3. There were many oval pores in Figure 3a which were marked as 1. The surface of La(III)-CAC was coarse, and finer porous structures were marked as 2. However, the pore structures of La(III)-

Al(III)-CAC were changed in Figure 3b. The pore structure marked as 1 became a little more regular circle, the finer pore size marked as 2 became larger, and the pores distributed more uniformly, which were suitable for better adsorption capability. The presence of elements La(III) and Al(III) were detected from the samples in Figures 3a1, a2 and b1, b2. The weight percentage of La(III) was 0.86%, which increased obviously to 2.55% after the modification of La $(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3$. More La(III) content in adsorbent will show better adsorption performance, which was probably caused by the synergistic effect of the two elements in the modification process.

3.1.2 FT-IR analysis of adsorbent

The Fourier-transform infrared spectroscopy (FT-IR) spectra of La(III)-Al(III)-CAC are shown in Figure 4. Six kinds of absorption peaks in curves were observed at 3,457, 2,905, 2,350, 1,630–1,365, 605, and 425 cm^{-1} , which correspond to the stretching vibration of hydroxyl ($-\text{OH}$), stretching vibration of $-\text{CH}_2-$, telescopic vibration of $-\text{C}\equiv\text{N}$, deformation vibration of $\text{C}=\text{O}$, stretching vibration of $\text{La}-\text{O}$, and bending vibration of $\text{Al}-\text{O}$. According to FT-IR analysis of La(III)-Al(III)-CAC, the number of oxygen-containing functional groups on adsorbent was increased, and La(III) and Al(III) were successfully loaded on CAC and existed in the form of oxide. The reaction equations that may be involved in the modification process are as follows:

Figure 2: The SEM images of (a) CAC and (b) MCAC.

Figure 3: The SEM and EDS analyses of La(III)-Al(III)-CAC: (a, a1, a2) La(III)-CAC and (b, b1, b2) La(III)-Al(III)-CAC.

Figure 4: FT-IR spectra of La(III)-Al(III)-CAC.

3.2 Single-factor experiment for adsorption process

3.2.1 Effect of initial concentration

The concentration of F^- plays an important role in the adsorption process because it can affect the capacity of adsorbents. Seven different concentrations (10, 20, 30, 40, 50, 60, and 70 mg/L) were selected to explore the effect of the initial concentration on the adsorption process of La(III)-Al(III)-CAC. The other parameters of adsorption process were fixed as follows: the solution volume was 30 mL, the dosage of La(III)-Al(III)-CAC was 1 g, the adsorption time was 1.4 h, and the pH value was 6. R_F was calculated after the end of the adsorption process, as shown in Figure 5. R_F was improved at the first increase in the initial concentration; it can reach the value of 53.82% when the concentration was 30 mg/L, which was also the maximum value. R_F decreases continuously with the increase in concentration, this is because the limited adsorption capacity of adsorbent, which can't absorb more ions [29,30], therefore, the maximum concentration that the La(III)-Al(III)-CAC can be loaded was 30 mg/L.

3.2.2 Effect of adsorption time

The adsorption process means the contact process, and all transfer phenomena such as adsorption are inseparable from contact; therefore, the adsorption time is a fundamental parameter. The other parameters of adsorption process were fixed as follows: the initial

Figure 5: Effect of initial concentration on R_F .

concentration was 30 mg/L, the solution volume was 30 mL, the dosage of La(III)-Al(III)-CAC was 1 g, and the pH value was 6. The effects of the adsorption time on R_F are shown in Figure 6. Clearly, R_F of solution increased quickly at the value of 71.2% in the initial stages of the contact period until 1.0 h, and then gradually increased to 71.6% with a prolonged contact time of 1.4 h until equilibrium was reached. There are usually three steps for the adsorption process as follows: external surface adsorption stage, internal surface adsorption stage, and adsorption reaction stage. The adsorption reaction stage is a chemical reaction, which is not involved here, so the decisive step is the other two physical adsorption stages. The increase in R_F in initial stages before 1.0 h was contributed to the external surface adsorption process, as all of the active sites on the La(III)-Al(III)-CAC were vacant at the first stage of adsorption process and the concentration of solution was also high, so it is easy to

Figure 6: Effect of adsorption time on R_F .

increase the amount of adsorption. However, after that stage, the adsorption process mainly depends on the internal surface adsorption. Few surface active sites were available, which lead to the observation of small increase in the uptake of R_F . Hence, the suitable time to reach equilibrium was selected as the adsorption time for further experiments.

3.2.3 Effect of solution volume

The solution volume is also a very important factor of adsorption process because of the relationship between the capacity of an adsorbent and a given initial concentration of solution. Studies were conducted to learn the effect of La(III)–Al(III)–CAC on NaF solution with the concentration of 30 mg/L, which was confirmed by experiments before. Seven different solution volumes were employed in the study (10, 25, 40, 55, 70, 85, and 100 mL), the dosage of La(III)–Al(III)–CAC was 1 g, the adsorption time was 1.4 h, and the pH value was 6. The R_F obtained from experiments is shown in Figure 7. There was a sharply increasing trend as the solution volume increased from 10 to 25 mL, then continued to decline, and the maximum R_F was 70.6% at the solution volume of 25 mL. The higher removal percentage in the present experiment contributed to the greater availability of exchangeable sites and larger surface area [31]. More solution volume provided more contact area of La(III)–Al(III)–CAC in order to promote the effective adsorption process. However, because of the limited adsorption capacity of La(III)–Al(III)–CAC, R_F decreased when the solution volume was more than 25 mL. Therefore, 25 mL was used as the optimal solution volume of the adsorption.

Figure 7: Effect of solution volume on R_F .

3.2.4 Effect of pH

It is necessary to analyze the effect of pH as a single factor because the pH value of an aqueous solution is one of the most important factors during the adsorption process, especially when it can affect the existence form of fluorine. The effect of pH was investigated for pH values of 3, 4, 5, 6, 7, 9, and 11. The pH value was adjusted during the experiments by adding a few drops of HCl (1 mol/L) and NaOH (1 mol/L). All other parameters in the adsorption process were kept constant (the dosage of La(III)–Al(III)–CAC was 1 g, the initial concentration of NaF solution was 30 mg/L, and the solution volume was 25 mL). The effect of pH value on R_F is shown in Figure 8. Figure 7 shows that an uptake of R_F significantly increased with an increase in pH value in the solution; it can achieve the peak point at 72.1% when the pH value was 6, and then followed by a downward trend until the pH value was 11. In the pH range of 0–7, fluorine exists in the form of F^- , HF, and HF^{2-} , and mainly in the form of HF when $pH < 3$; therefore, the concentration of F^- will not increase at the condition of $pH > 3$ theoretically. However, there is similarity in chemical bond between F^- and OH^- , and the OH^- will affect the adsorption of F^- , making the higher adsorption efficiency to be obtained at a higher pH value and the suitable pH was 6.

3.3 Response surface method experiment

3.3.1 Design and result

The response surface method (RSM) was adopted to optimize the adsorption process and get a higher R_F .

Figure 8: Effect of pH on R_F .

Experimental design was carried out by the custom design method in JMP software, and the response item was R_F . Three parameters, including adsorption time (E), pH (F), and solution volume (G), were studied and each parameter was set according to single-factor experiment results, as shown in Table 4. In addition, R_F is also shown in the last column of this table, which will be discussed later.

3.3.2 Analysis of model

The stepwise regression method was adopted to analyze the experimental data in Table 4. Analysis of variance and significance test for the regression model are listed in Tables 5 and 6, respectively.

The smaller the P value and the larger the F value, the more significant the model. In Table 5, the value of R^2 is 0.9488, the F value is 12.3555, and the P value is 0.0031, which indicated that the stepwise regression model was suitable for the analysis of experimental data. Hence, the model can be used to analyze and optimize the adsorption process. When the P value of index was <0.0100 , the factor can be interpreted as the extremely significant factor. In Table 6, the significant factor was the pH value, as well as the

Table 4: Experimental design and results

No.	E (h)	F (–)	G (mL)	R_F (%)
1	1	9	10	59.74
2	1	3	40	62.75
3	1.2	6	25	73.87
4	1.4	6	25	69.45
5	1.2	6	40	72.32
6	1	9	40	60.31
7	1	3	10	64.32
8	1.2	3	25	70.84
9	1.4	3	10	65.73
10	1.2	6	25	73.80
11	1.4	9	40	60.41
12	1.4	3	40	65.23
13	1.2	9	25	64.74
14	1.4	9	10	59.33
15	1	6	25	67.20
16	1.2	6	10	68.42

Table 5: Analysis of variance for the regression model ($R^2 = 0.9488$)

Source	Df	Sum of square	Mean square	F value	P value
Model	9	408.346	45.3718	12.3555	0.0031
Error	6	22.033	3.6722		
Total	15	430.379			

Table 6: Significance test for the regression coefficients

Source	Df	Sum of square	F value	P value
E	1	3.3640	0.9161	0.3755
F	1	59.0490	16.0800	0.0070 ^a
G	1	1.2250	0.3336	0.5846
E^2E	1	51.3203	13.9754	0.0096 ^a
E^2F	1	2.2050	0.6005	0.4687
F^2F	1	64.9128	17.6768	0.0057 ^a
E^2G	1	0.3200	0.0871	0.7778
F^2G	1	1.8050	0.4915	0.5095
G^2G	1	14.7092	4.0056	0.0922

^aSignificant influence factor.

F (pH) squared and the E (adsorption time) squared, which means the interaction of three factors among them was not a simple linear relationship. The order for these key factors was $F > E > G$ (solution volume).

3.3.3 RSM optimization and verification

The RSM method was employed to analyze the experimental data in Table 6. The quadratic regression surface model was established after eliminating the non-significant items. The model for removal rate (R_F) can be calculated by the obtained quadratic regression equation given by:

$$R_F = 73.69 + 0.58X_1 - 2.43X_2 + 0.35X_3 - 4.41X_1^2 - 0.53X_1X_2 - 4.96X_2^2 + 0.2X_1X_3 + 0.475X_2X_3 - 2.36X_3^2, \quad (5)$$

where X_1 , X_2 , and X_3 are equal to (adsorption time: 1.2)/0.2, (pH value: 6)/3, and (solution volume: 25)/15.

In order to get the optimization conditions for adsorption, interaction effect among three factors was explored by three-dimensional RSM of the quadratic polynomial regression equation, as shown in Figures 9–11.

The convex surfaces can be seen on the response surface in Figures 9–11, which means that the model has a stable maximum point in the test range. When the adsorption time was 1.2 h and the pH value was 6, the R_F was 74.05%; when the pH value was 6 and the solution volume was 25 mL, the R_F was 74.00%; when the adsorption time was 1.2 h and the solution volume was 25 mL, the R_F was 73.72%. The maximum R_F value was 74.05% by the prediction of Equation 2 and RSM. Therefore, the optimal adsorption process conditions are determined as the adsorption time was 1.2 h, the pH value was 6, and the solution volume was 25 mL. Three parallel adsorption experiments (No. 17, No. 18, and No.

Figure 9: Interaction of adsorption time and pH on the response surface.

19) were performed in the laboratory with the optimal parameters and the R_F was 74.03%, 73.94%, and 74.37%, respectively, and the average R_F was 74.11%.

4 Conclusion

La(III)–Al(III)–CAC was successfully modified with 20 wt% HNO_3 , 0.05 mol/L $La(NO_3)_3 \cdot 2H_2O$, and 0.10 mol/L $Al(NO_3)_3$ in a fast and simple process used for adsorption of F^- . Modification increased the number of oxygen-containing functional groups on adsorbent, and La(III) and Al(III) were successfully loaded on CAC, which is

Figure 10: Interaction of pH and solution volume on the response surface.

Figure 11: Interaction of adsorption time and solution volume on the response surface.

confirmed by the EDS and FTIR analyses. Experiments were set as a function of the selected variables, concluding the initial concentration of 30 mg/L, the adsorption time of 1.2 h, the pH value of 6, and the solution volume of 25 mL by the optimized method of RSM to obtain the R_F value at 74.11%. According to the analysis, the pH value was an extremely significant factor in the adsorption process; meanwhile, the order for these key factors was $pH > \text{adsorption time} > \text{solution volume}$. The verification equation was

$$R_F = 73.69 + 0.58X_1 - 2.43X_2 + 0.35X_3 - 4.41X_1^2 - 0.53X_1X_2 - 4.96X_2^2 + 0.2X_1X_3 + 0.475X_2X_3 - 2.36X_3^2.$$

The higher removal efficiency of this adsorbent in simulation solution of fluoride confirmed the great potential and applicability of adsorbent for the removal of other ions from industrial wastewater.

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Appendix

Calculation of R_F

Electrode is made of LaF₃ single crystal, and the potential measured by the electrode is linear with the logarithm of the F⁻ concentration. To draw a standard curve, the standard solution and total ionic strength buffer solution (TISBS) are necessary. Standard solution was NaF (100 mg/L); TISBS was prepared from three reagents such as Na₃C₆H₅O₇·2H₂O (12 g), NaNO₃ (58 g), and C₂H₄O₂ (58 mL); and HCl (1 mol/L) and NaOH (1 mol/L) were used to adjust the pH at 5–6. Pipette a certain volume of standard solution and TISBS, insert the electrode into the test solution, and record the potential value when the digital stable, as shown in Table A2, and the standard curve is shown in Figure A1.

Table A1: Properties of CAC

Item	Data	Item	Data
Raw materials	Apricot shell	Iodine number	980
		(mg/g)	
Place of production	Zhengzhou/HeNan province	Methylene blue value (mg/g)	120
Moisture (%)	≤5	Bulk density (g/cm	0.42
Strength (%)	≤90	pH	7

Table A2: Data record

Item	Data						
NaF concentration (mg/L)	2	4	6	8	10	12	14
Log C (-)	0.30	0.60	0.78	0.90	1.0	1.07	1.15
Potential value (mv)	204	197	189	182	175	169	163

Figure A1: Standard curve of F⁻.