Supplementary Material

Fluoride Removal from Water Using High-Activity Aluminum Hydroxide Prepared by the Ultrasonic Method

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1. Adsorption dynamics

The adsorption kinetics describes the rate of adsorbate uptake on adsorbent, which determines the adsorption equilibrium time. Understanding of adsorption kinetics is helpful for modeling the adsorption process and designing adsorption-based water treatment systems. Pseudo-first-order and pseudo-second-order adsorption kinetic models were used to analyze the experimental data for the F^- adsorption onto UAH.

The pseudo-first-order adsorption kinetic model is expressed as follows[1]

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{S1}$$

where q_e and q_t are the amounts of F$^-$ adsorbed (mg/g) at equilibrium and at time t, respectively, and k_1 is the adsorption rate constant, which can be determined from the slope of linear plot of $\log(q_e - q_t)$ versus t.

The pseudo-second-order adsorption kinetic model is expressed as follows[1]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{S2}$$

where k_2 is the adsorption rate constant, which can be determined by plotting t/q_t versus t.

Fig. S1 shows the pseudo-first-order and pseudo-second-order kinetic plots for the fluoride removal from solution with different initial F$^-$ concentration using UAH at 25°C. The kinetic parameters for pseudo-first-order and pseudo-second-order kinetic models are given in Table S1. From the correlation coefficient R^2, it can be seen that the adsorption kinetics data for UAH fit better with the pseudo-second-order kinetic model, indicating that F$^-$ adsorption onto UAH follows the second-order adsorption.

2. Adsorption isotherm

Langmuir, Freundlich and Dubinin-Radushkevich (D-R) adsorption isotherm models were used to analyze the experimental data for F$^-$ adsorption onto UAH. The Langmuir isotherm model assumes that adsorption takes place on a homogenous surface by monolayer adsorption without interaction between adsorbate species, which is given by the following equation[2]

$$\frac{1}{q_e} = (\frac{1}{q_{max}K_L})\frac{1}{C_e} + \frac{1}{q_{max}} \tag{S3}$$

where q_{max} is the maximum theoretical amount of F⁻ adsorbed on adsorbent, C_e is the equilibrium concentration of F⁻ in solution and K_L is the binding energy constant.

The Freundlich isotherm is based on non-ideal adsorption on heterogeneous surfaces as well as for multilayer adsorption, which is given by the following equation[2]

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{S4}$$

where K_F is isotherm constant, and n is the Freundlich constant related to the favorable degree of adsorption. When the value of n is between 1 and 10, the adsorption is beneficial.

Fig. S2 shows Langmuir and Freundlich adsorption isotherm plots for the fluoride removal from aqueous solution using UAH at 25°C. The parameters of Langmuir and Freundlich adsorption isotherms for F⁻ adsorption onto UAH are given in Table S2. It can be seen that the adsorption experimental data fit better with Freundlich isotherm model, indicating that F⁻ adsorption on UAH is multilayer adsorption. The value of n is 3.054, implying that F⁻ adsorption onto UAH is beneficial.

In order to analyze whether the adsorption is physical or chemical adsorption, D-R adsorption isotherm model was used to analyze the experimental data, which is described by the following equation[2]

$$\ln q_e = \ln q_{max} - K\varepsilon^2 \tag{S5}$$

where K is a constant related to the adsorption energy, and the Polanyi potential ε is

given by

$$\varepsilon = RT \ln(1 + \frac{1}{C_e}) \tag{S6}$$

where R is the gas constant and T is the adsorption temperature.

Fig. S3 shows D-R isotherm plots for the fluoride removal using UAH at different temperatures. The parameters of D-R adsorption isotherms for F^- adsorption onto UAH are given in Table S3. From the value of R^2, it can be seen that the experimental data fit well with the D-R isotherm model. The value of q_{max} decreases with increasing the temperature, also indicating that F^- adsorption onto UAH is an exothermic process.

The K values can be used to calculate the adsorption energy, E, using the following equation[2]

$$E = (2K)^{-1/2} \tag{S7}$$

and E can be used to estimate the adsorption type. If the value of E is between 8 and 16 kJ/mol, the adsorption process is chemical adsorption; if E is below 8 kJ/mol, the adsorption process is physical adsorption.[2] The calculated adsorption energy E for UAH is ~ 10 kJ/mol, indicating that F^- adsorption onto UAH is a chemical adsorption process.

3. Thermodynamic study

To evaluate the thermodynamic feasibility of the adsorption process, three basic thermodynamic parameters, standard enthalpy (ΔH^0), standard entropy (ΔS^0) and standard free energy (ΔG^0) were calculated using the following equations[3]

$$\log(\frac{q_e}{C_e}) = \frac{\Delta S^0}{2.303R} - (\frac{\Delta H^0}{2.303R})\frac{1}{T} \tag{S8}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{S9}$$

where q_e/C_e is the adsorption affinity. The thermodynamic parameters were calculated

from the plot of $\log(q_e/C_e)$ versus $1/T$ for defluoridation test using UAH at an initial F⁻

concentration of 20 mg/L, as shown in Table S4. The ΔH^0 for F⁻ adsorption onto UAH

is -9.113 kJ/mol, indicating that F⁻ adsorption is an exothermic process. The ΔG^0 for

F⁻ adsorption is about -18 kJ/mol, and the negative value of ΔG^0 suggests that F⁻

adsorption onto UAH is favorable and spontaneous in nature.

References

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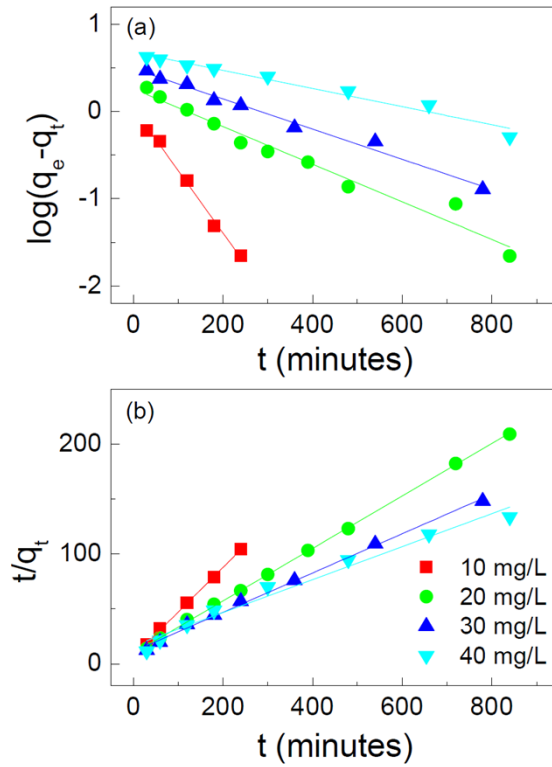
Fig. S1. (a) Pseudo-first order kinetic and (b) pseudo-second order kinetic plots for fluoride removal from aqueous solution with different initial F⁻ concentrations using UAH at 25°C.
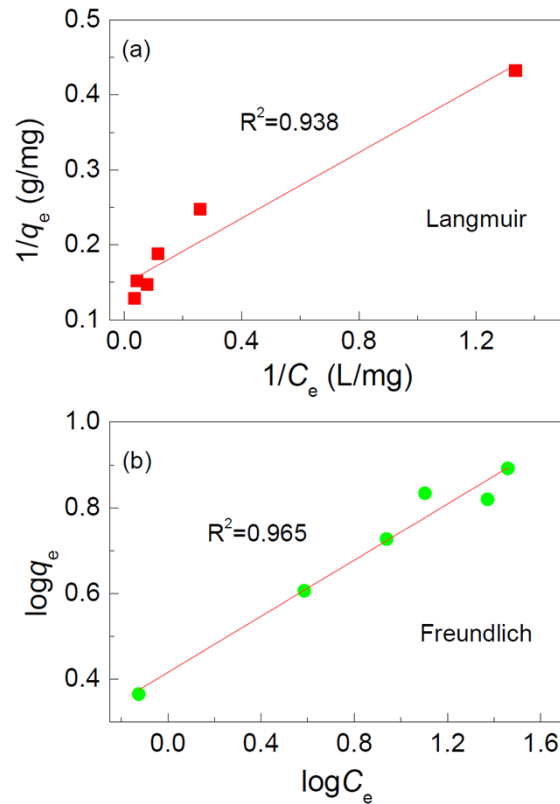

Fig. S2. (a) Langmuir adsorption isotherm and (b) Freundlich adsorption isotherm plots for fluoride removal from aqueous solution using UAH at 25°C.
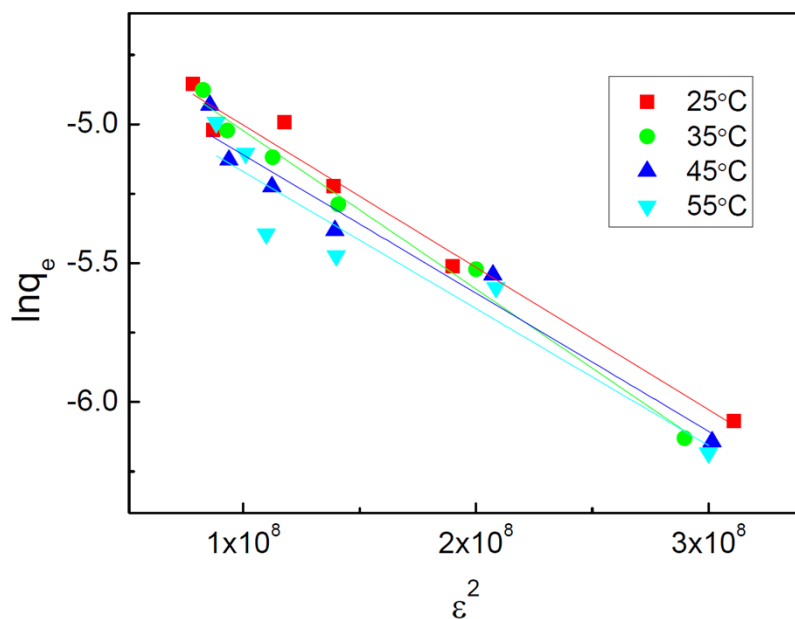
Fig. S3. Dubinin-Radushkevich isotherm plots for fluoride removal from aqueous solution using UAH.

Table S1 Kinetic parameters of pseudo-first-order and pseudo-second-order models for F^- adsorption by UAH at 25°C.

C_0 (mg/L)*	Pseudo-first-order			Pseudo-second-order		
	k_1 (min^{-1})	q_e (mg/g)	R^2	k_2 (g/mg min)	q_e (mg/g)	R^2
10	0.016	1.091	0.992	1.044	2.459	0.999
20	0.005	1.813	0.967	0.541	4.186	0.999
30	0.004	3.089	0.985	0.357	5.594	0.996
40	0.002	4.771	0.963	0.374	6.664	0.963

*C_0 is the initial F^- concentration in aqueous solution.

Table S2 Parameters for Langmuir and Freundlich isotherm models for F⁻ adsorption by UAH at 25°C.

Langmuir parameters			Freundlich parameters		
q_{max} (mg/g)	K_L (L/mg)	R^2	K_F	n	R^2
6.776	0.674	0.938	2.604	3.054	0.965

Table S3 Parameters for D-R isotherm model for F⁻ adsorption by UAH.

Temperature (K)	q_m (mg/g)	K	R^2	E (kJ/mol)
298	11.2	5.13×10^{-9}	0.974	9.88
308	10.5	5.70×10^{-9}	0.986	9.36
318	9.9	4.98×10^{-9}	0.953	10.02
328	9.3	4.93×10^{-9}	0.893	10.07

Table S4 Thermodynamic parameters for F⁻ adsorption by UAH.

ΔH^0 (kJ/mol)	ΔS^0 (J/mol K)	R^2	ΔG^0 (kJ/mol)			
			25°C	35°C	45°C	55°C
-9.113	-9.688	0.857	-17.325	-17.600	-17.876	-18.151