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Research Article

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Removal of fluoride from water by NiAl layered double hydroxide prepared by solvothermal method

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ABSTRACT

NiAl layered hydrotalcite was prepared by solvothermal method and the adsorption performance of F^- in water was studied. According to the experimental results of single factors, heat treatment can increase the adsorption performance of the samples, but the higher roasting temperature can cause hydrotalcite layered structure destroyed, in this study, optimal calcination temperature is 150℃. As-prepared absorbent was calcinated at 150℃, various conditions such as initial fluorine ion concentration, adsorbent dosage, solution pH value, interfering ion survived together, adsorption temperature and adsorption time etc, were investigated. The sample was characterised by XRD and TEM, and the adsorption kinetics and adsorption isotherms were also analyzed. The adsorption equilibrium was achieved within 24 h on the adsorption reaction of fluoride ion in water. Adsorption isotherms fitted the Freundlich model. The adsorption kinetic fitted well the second-order dynamics model.

Keywords: solvothermal method, NiAl layered hydrotalcite, F^-, adsorption

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INTRODUCTION

Fluoride is the most abundant anions present in groundwater worldwide and creates a major problem in safe drinking water supply. Excess fluoride ingestion for a long time would lead to dental and skeletal fluorosis, bone disease, and nonskeletal fluorosis[1]. According to the World Health Origanization, the maximum acceptable concentration of fluoride in the drinking water is 0.5-1.0 mg/L[2]. Thus, the removal of fluoride ions from nature water is becoming a crucial issue. Various treatment technologies have been applied to water contaminated, including chemical precipitation, adsorption, ion exchange, membrane techniques and so on[1, 3-4]. Among the innumerable presented technologies, adsorption is an effective method for fluoride ion removal. In particular, it is a low-cost, simple, easy to perform [5]. Many materials such as activated carbon fibers[6], zirconyl silicate[7], bone char, calcite[8], Li-Al layered double hydroxides[9] have been tried for defluorination by adsorption. However, most of them have low sorption efficiency.

Layered double hydroxides (LDHs) are one of the most useful classes of inorganic layered compounds and have recently received considerable attention in the fields of catalysts, adsorbents[10], drug carriers[11], flame-retardant filler[12] and ect. The general formula of hydrotalcite-like compounds is $[M_{1-x}^{II}M_x^{III}\ (OH_2)]A_{x/n}^{n-}\cdot mH_2O$, where M^{II} and M^{III} are respectively divalent and trivalent cations, the value of the coefficient x is equal to the molar ratio $M^{III}/(M^{II}+M^{III})$, and A^{n-} is an anion with charge n. Replacement of some fraction of the divalent ions by a trivalent ion of comparable size leads to a net positive charge on the layers. These positive charge is balanced by anions in the interlayer. Ling zhao et al. successfully synthesized NiAl mixed oxides by urea hydrolysis approach[13]. Jinbo Wei et al. synthesis of self-assembled layered double hydroxides/carbon composites by in suit solvothermal method[14]. In addition, reduction-oxidation and microwave-assisted methods have also been extensively used.

In this paper, NiAl LDHs was synthesized by solvothermal method. XRD, TEM, were well employed to characterize the phase, morphology, and adsorption properties of the as-prepared samples. The resulting exhibits fine applicability for the removal of fluoride ion from water and a possible removal mechanism is proposed in the present work.

EXPERIMENTAL SECTION

2.1 Materials

Analytical-grade chemicals ($Ni(NO_3)_2·6H_2O$, $Al(NO_3)_3·9H_2O$, NaF, $NH_3·H_2O$, $C_6H_5Na_3O_7·2H_2O$, $NaNO_3$) were used for Ni/Al LDH preparation. Total ionic strength adjustment buffer solution (TISAB) was prepared by $NaNO_3$ and $C_6H_5Na_3O_7·2H_2O$ at pH ranging from 5 to 6. Deionized water was used to prepare all solutions used in this study.

2.2 Preparation of NiAl LDHs

NiAl LDHs was prepared by the coprecipitation method. In a typical procedure, A total of 0.009 mol Ni $(NO_3)_2·6H_2O$, 0.003 mol Al $(NO_3)_3·9H_2O$ and 0.04 mol urea were dissolved in 80 mL absolute ethyl alcohol. The solution was magnetically stirred for 20 min in air at room temperature. Subsequently, the solution was transferred to the Teflon-lined stainless steel autoclave, sealed and heated at 140 ºC for 24 hours, then the green product was recovered and washed in deionized water and absolute ethyl alcohol a few times ,finally dried at 80℃ for 12 h, the sample was denoted as NiAl-LDHs.

2.3 Characterization

The crystalline structure of the LDHs was characterized using an X–ray diffraction analyzer (D/MAX–2500/PC), X-ray diffractometer from 5° to 80° (2θ) at a scanning rate of 5° (2θ) per min. The surface morphology of the samples was monitored with TEM (JEM–2010).

2.4 Kinetic studies

In our previous work, the optimal calcination temperature condition was 150℃, and adsorption experiments were carried out in a batch equilibrium mode. The effect of pH, co-anions and contact time were studied.

The kinetic studies were carried out as follows: 0.4 g adsorbent material was added into 200 mL sodium fluoride at initial concentrations 100 mg/L and the mixture was under well agitated. The fluoride ion uptake by samples was calculated by the following equation:

$$q_t = (C_0 - C_t)V/m \qquad (1)$$

where q_t is the amount of adsorbed F^- at time t (mg/g); V the volume of solution (L), C_0 and C_t are the initial and at time t F^- concentration respectively (mg/L)，and m is the mass of adsorbent (g).

2.5 Thermodynamic experiments

The equilibrium adsorption isotherm was determined using batch studies: 0.1 g adsorbent and 50mL fluoride solution of various initial concentrations (10 – 140 mg/L) were poured into the beaker. The time required to reach equilibrium as determined in equilibrium studies was 24 h. A series of isotherms were determined at the temperatures of 298 K, 318 K and 338K, respectively. The adsorption capacity (q_e) was obtained using the following equation:

$$q_e = (C_0 - C_e)V/m \qquad (2)$$

Where C_0 and C_e (mg/L) are initial and equilibrium F^- concentration respectively; V (L) is the volume of the solution, and m (g) is the adsorbent mass. All adsorption tests were carried out by a Fluoride ion selective electrode (pF-1).

RESULTS AND DISCUSSION

3.1 Characterization of NiAl-LDHs

The XRD patterns of as-prepared NiAl LDHs were shown in Fig.1; All of the reflections can be directly indexed to a typical rhombohedral phase NiAl hydrotalcite (JCPDS No. 15-0087). These diffraction peaks are sharp, narrow and symmetrical with a stable baseline, indicating that the sample is well-crystallized.

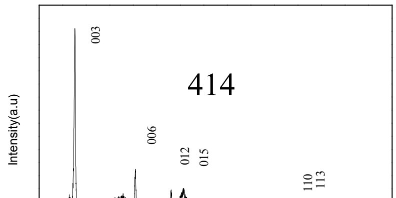

Fig.1 XRD pattern of NiAl LDHs

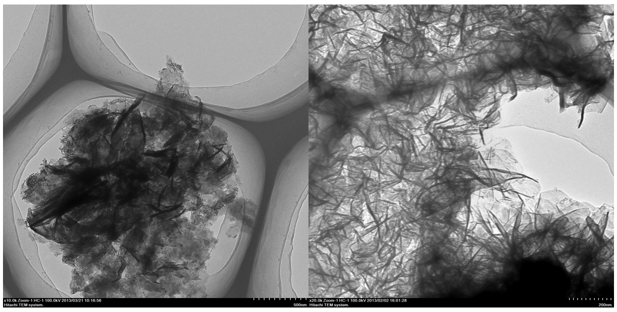

Fig.2 TEM images of NiAl LDHs

TEM images were important tools to understand the morphology evolution process of NiAl LDHs crystals in this system. Fig.2 shows the flowerlike porous structures were obtained. The surface of the compound is rough and contains flexible nanosheets that bend and connect with each other. The nanosheets distribute uniformly in all directions and extend from the center.

3.2 Effect of pH

Generally pH is considered to be an important parameter which controls the adsorption at water-adsorbent interfaces. In this view, the adsorption of F^- (10mg/L) by NiAl LDHs (0.1g) was studied at different pH values ranging from 2 to 12 at an ambient temperature of 25℃. Fig.3 shows the effect of initial solution pH on fluoride removal on LDHs, and it can be observed that pH values had a significant effect on fluoride adsorption. The results revealed that the uptake decreased with the increase of OH^- in solutions, indicating that high pH is not in favour of the adsorption of F^- because of the competition between OH^- excess and F^-. There was a decrease in F^- adsorption when the equilibrium solution pH was less than 3, which was partially caused by the dissolution of LDHs at this solution pH. The best pH is ranging from 3 to 6. Thus, all the experiments were performed at pH 6.

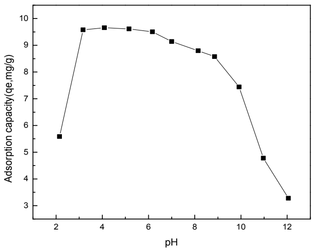

Fig.3 Effect of solution pH on the removal of fluoride (initial concentration: 100 mg/L, adsorbent dosage:2 g/L, adsorption time: 24 h, adsorption temperature: 25℃)

3.3 Kinetic studies

To examine the controlling mechanism of the adsorption process, kinetic models are used to test experimental data from the adsorption of fluoride onto Ni/Al LDHs. These models include the pseudo-first-order model, pseudo-second-order model, and intraparticle diffusion. The kinetic models can be linearized as shown in Table 1.

Table 1. Kinetic model parameters for adsorption of fluoride

Kinetic models	Ni/Al=3:1			
Pseudo-first-order	R^2	$K_1(min^{-1})$	$q_{e(exp)}$（mg/g）	$q_{e(cal)}$（mg/g）
10 mg/L	0.9546	0.08515	4.817	1.320
20 mg/L	0.9374	0.07527	9.238	2.641
40 mg/L	0.9161	0.07572	17.20	3.151
Pseudo-second-order	R^2	$K_2(gmg^{-1} min^{-1})$	$q_{e(exp)}$（mg/g）	$q_{e(cal)}$（mg/g）
10 mg/L	0.9999	0.2853	4.817	4.845
20 mg/L	0.9999	0.1299	9.238	9.291
40 mg/L	0.9999	0.1155	17.20	17.26
Intraparticle-diffusion	R^2		$k(mg\ g^{-1}\ min^{-1/2})$	
10 mg/L	0.6773		0.2049	
20 mg/L	0.6954		0.4173	
40 mg/L	0.7243		0.4610	

From the slope and intercept of the straight line obtained, the kinetic parameters for the removal of fluoride were determined, as compiled in Table 1. It can be seen from Table 1, the experimental data of kinetic model fit well with the pseudo-second-order reaction ($R^2 \approx 1$). The pseudo-second-order model means that the rate-controlling step is a chemical reaction involving valency forces change through sharing or exchange of electrons between adsorbate and adsorbent. The value of the equilibrium adsorption capacity is found to be in good agreement with the value of the experimental adsorption capacity. It was found the adsorption capacity increase from 4.817 to 17.20 mg/g with increase of F^- concentration from 10 to 40mg/L. This indicate that increasing the F^- concentration of the solution seems to reduce the rate of diffusion of fluoride in the boundary layer and to enhance the diffusion in the solid. These results are consistent with literature[7].

3.4 Equilibrium adsorption isotherms

For solid-liquid system, the equilibrium of adsorption is one of the important physic-chemical aspects in the description of adsorption behavior. In this work, three well-know models of Langmuir, FreÜndlich and Dubinin-Radushkevich isotherm are evaluated. The parameters obtained from the different models provide important information on the surface properties and affinities of the sorbent. The models are represented in Table 2.

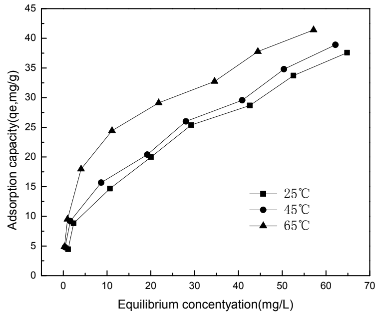

Fig.4 Adsorption isotherms of fluoride ion adsorption onto NiAl-LDHs (adsorbent dosage: 0.1g, adsorption time: 24 h and pH: 6-7)

Effect of temperature was studied at 298 K, 318 K, 338 K at initial fluoride concentrations of 10 mg/L- 140 mg/L. The adsorption isotherms are shown in Fig.4. These isotherms indicate that F^- has a high affinity for LDH surfaces. The structure of LDHs consist of positively charged hydroxide sheets, when F^- is removed from aqueous solution by LDHs, the adsorption may occur probably, primarily in response to Coulomb attractions between the anionic adsorbent and the positively charged external and interlayer surfaces of LDHs via memory effect[7]. The increase in the initial concentration and adsorption temperature led to an increase in fluoride adsorption capacity. This indicated that the adsorption process of LDHs was endothermic. Table 2 shows the results of a linear fit. It can be seen that the experiment data were better fitted by the Freundlich isotherm with correlation coefficient R^2 higher than 0.9800, indicating the homogeneous nature of sample surfaces and formation monolayer coverage of F^- on the surface of adsorbent.

Table.2 Langmuir, Freündlich, Dubinin-Radushkevich isotherm model constants and correlation coefficients for adsorption of F^- on prepared sample

Isotherm models	Ni/Al=3:1		
Langmuir	R^2	K_L(L/mg)	q_{max}(mg/g)
25°C	0.9401	0.06322	42.86
45°C	0.9287	0.09132	41.19
65°C	0.9754	0.1742	42.37
Freundlich	R^2	n	K_F(mg/g (L/mg)$^{1/n}$)
25°C	0.9847	2.050	4.807
45°C	0.9919	2.517	6.989
65°C	0.9873	2.620	9.113
Dubunin-Radushkevich	R^2		
25°C	0.7583		
45°C	0.6910		
65°C	0.7852		

CONCLUSION

The NiAl LDHs with high sorption capacity for fluoride have been successfully synthesized by solvothermal method. It was found that the samples have a high sorption capacity at broad range pH. Kinetic data of adsorption were well-represented by the pseudo-second-order model, and the isotherm data were well fitted by the Freundlich models. The prepared sample is under a promising for the removal of fluoride ion in environmental treatment.

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