



Removal of fluoride ions from aqueous solution using modified attapulgite as adsorbent

Jing Zhang^a, Shaodong Xie^a, Yuh-Shan Ho^{b,c,*}

^a State Key Joint Laboratory of Environmental Simulation and Pollution Control, Department of Environmental Sciences, College of Environmental Science and Engineering, Peking University, Beijing 100871, People's Republic of China

^b Department of Environmental Sciences, College of Environmental Science and Engineering, Peking University, Beijing 100871, People's Republic of China

^c Department of Biotechnology, College of Health Science, Asia University, Taichung 41354, Taiwan

ARTICLE INFO

Article history:

Received 5 June 2008

Received in revised form 24 August 2008

Accepted 25 September 2008

Available online 2 October 2008

Keywords:

Fluorosis

Attapulgite

Modification

Isotherm

Sorption

Anion exchange

ABSTRACT

Adsorption of fluoride ions from water using modified attapulgite with magnesium and aluminum salts was conducted by batch experiments. The effects of temperatures and mass ratios of attapulgite, magnesium and aluminum salts were investigated. Linear and non-linear methods were applied for fitting the adsorption data with Langmuir, Freundlich, and Redlich–Peterson isotherms. Modified attapulgite with a mass ratio attapulgite:MgCl₂·6H₂O:AlCl₃·2H₂O = 2:1:2 had higher fluoride adsorption capacity. In addition, the fluoride adsorption using the modified attapulgite included an anion exchange process.

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1. Introduction

Although a suitable low concentration of fluoride in drinking water is beneficial to health, a high concentration can produce dental and bone fluorosis, which has been early recognized in the 1930s [1,2]. According to the World Health Organization (1993) [3], the acceptable fluoride concentration is generally in the range of 0.5–1.5 mg/L. However, the excess of fluoride in groundwater is found in many regions of the world [4–6]. Except for natural dissolution from geologic formations, significant sources of fluoride in water body are the effluents from the aluminum smelters, electronic device and semiconductor industries [7,8]. It is, therefore, essential that there are technologies for controlling the concentrations of fluoride in aqueous emissions. One effective approach is to use alternative adsorbents. These are low-cost, often naturally occurring, products which have good adsorbent properties. A range of products has been examined precisely, such as alum sludge [9], fly ash [10], clay [11], calcite [12], montmorillonite [13], and charcoal [14]. It has been concluded that the selection of treatment materials should be site specific as per local needs and prevailing conditions.

Attapulgite (palygorskite) is a hydrated magnesium aluminum silicate present in nature as a fibrillar clay mineral containing ribbons of a 2:1 structure [15,16]. Attapulgite has permanent negative charges on its surface, which enable it to be modified by cationic surfactants, to enhance contaminant retention and retard contaminant migration [17]. Numerous studies have been reported on the adsorption of toxic metal, inorganic and organic pollutants from aqueous solution by natural [18–20] or modified attapulgite [21–23].

In this study, the fluoride removal from aqueous solution by adsorption onto modified attapulgite was investigated. The mechanism, the performance of the fluoride uptake under various modification mass ratios, initial fluoride concentrations and temperature were examined in detail. Linear and non-linear methods for Langmuir, Freundlich, and Redlich–Peterson isotherms were applied to determine the best fitting adsorption isotherms.

2. Materials and methods

2.1. Materials and analytical methods

The granular attapulgite samples were of 200 mesh size with a purity of 80%, obtained from the Longwang Hill in Xuyi, in Jiangsu province of China. Elements were analyzed in the form of oxide percentage in Table 1. Attapulgite was modified for the removal

* Corresponding author. Tel.: +866 4 2332 3456x1797; fax: +866 4 2330 5834.
E-mail address: ysho@asia.edu.tw (Y.-S. Ho).

Table 1
The chemical composition of natural attapulgite.

Composition	Percent (%)
SiO ₂	58.38
MgO	12.10
Al ₂ O ₃	9.50
CaO	0.40
TiO ₂	0.56
MnO	0.05
Fe ₂ O ₃ + FeO	5.26
Na ₂ O	1.10
K ₂ O	1.24

of fluoride ions. The samples were dispersed in distilled water, with magnesium and aluminum salts (MgCl₂·6H₂O, AlCl₃·2H₂O) at fixed ratios. The suspensions were shaken at 180 rpm, 30 °C for 4 h, and the pH was adjusted several times by addition of dilute 0.1 M NaOH until pH 7 was obtained. After that, the reaction mixtures were centrifuged and dried in evaporating dishes. Finally, the solid chips were roasted in a furnace at 300 °C, then ground and screened through an 80 mesh sieve (175 μm apertures; B.S. 410/43).

Reagents in all cases were of analytical grade.

The fluoride solutions used in the experiments were prepared by dissolving NaF in deionized water, and placed in polyethylene vessels. A stock fluoride solution (1000 mg/L) was prepared, and all working solutions were prepared by diluting this stock solution with deionized water.

The concentration of fluoride was determined using a selective electrode for fluoride ions. TISAB (Total Ionic Strength Adjustment Buffer) I was added to the solutions to reduce the variation of the ionic intensity. A calibration curve plotted as fluoride concentration (mg/L) versus potential (mV) was obtained using NaF standard solutions with fluoride concentrations from 0.1 to 4 mg/L.

2.2. Experimental procedures

Batch adsorption experiments were carried out at the desired temperature (20, 32, and 40 °C) on a thermostatic shaker at 100 rpm using capped 100 mL polyethylene bottles. In the adsorption isotherm tests, attapulgite (0.20 g) was thoroughly mixed with aqueous solutions of fluoride (50 mL), with initial fluoride concentrations (C₀) ranging from 20 to 200 mg/L. The effects of three modification methods by varying mass ratios of attapulgite, magnesium, and aluminum salts (attapulgite:MgCl₂·6H₂O:AlCl₃·2H₂O = 2:2:1; attapulgite:MgCl₂·6H₂O:AlCl₃·2H₂O = 2:1:2; and attapulgite:MgCl₂·6H₂O:AlCl₃·2H₂O = 4:3:3) were tested. After shaking the flasks for 48 h, the solutions were separated from the adsorbent by centrifugation and the filtrates were analyzed for pH (recorded as pH_e), and the equilibrium concentration of fluoride (C_e).

3. Results and discussion

3.1. Adsorption isotherms

The abilities of three widely used isotherms, the theoretical Langmuir, empirical Freundlich, and Redlich–Peterson isotherms, to model the adsorption equilibrium data were examined.

Langmuir isotherm [24] is perhaps the best known of all isotherms, which is often applied in solid/liquid system to describe the saturated monolayer adsorption. It can be represented as:

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (1)$$

where C_e is the equilibrium concentration (mg/L); q_e is the amount of ion adsorbed (mg/g); q_m is q_e for a complete monolayer (mg/g); K_a is adsorption equilibrium constant (L/mg). The constants q_m and K_a can be determined from a linearised form of Eq. (1), expressed by Langmuir-1 [25]:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m} \quad (2)$$

Langmuir-1 is the most popular of the four linear forms of Langmuir isotherm, as the minimized deviations from the fitted equation result in the best error distribution [25].

The Freundlich isotherm [26] based on adsorption on heterogeneous surface is the earliest known relationship describing the adsorption equilibrium and is given by:

$$q_e = K_F C_e^{1/n} \quad (3)$$

where K_F and 1/n are empirical constants, indicating the adsorption capacity and adsorption intensity, respectively. The equation may be converted to a linear form by taking logarithms:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

The Redlich–Peterson isotherm [27] contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms. It can be described as follows:

$$q_e = \frac{A C_e}{1 + B C_e^g} \quad (5)$$

Eq. (5) can be converted to a linear form by taking logarithms:

$$\ln \left(A \frac{C_e}{q_e} - 1 \right) = g \ln(C_e) + \ln(B) \quad (6)$$

Three isotherm constants, A, B, and g (0 < g < 1), can be evaluated from the linear plot represented by Eq. (6) using a trial and error optimization method [28].

As the linearised form of the experimental data enabled isotherm constants to be calculated, theoretical plots of each isotherm were tested for their correlation with the experimental results. Fig. 1 showed the comparison of three isotherms at the temperature of 305 K. The amount of fluoride adsorbed per unit

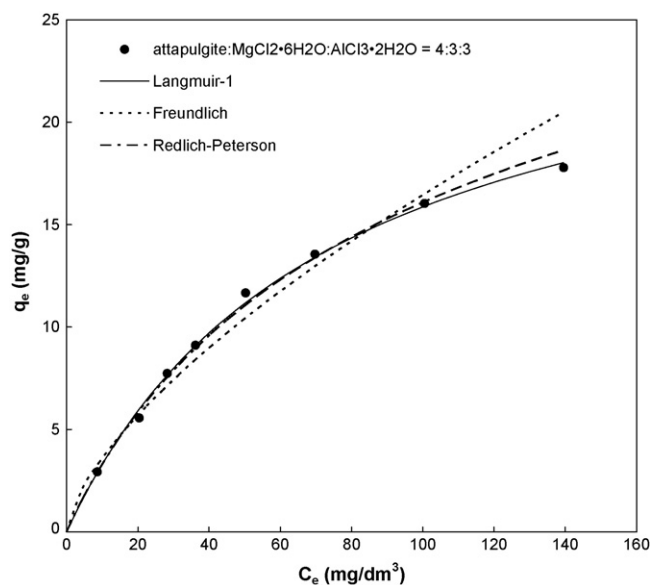


Fig. 1. Isotherms obtained by the linear method for the fluoride adsorption onto modified attapulgite (mass ratio for modification: attapulgite:MgCl₂·6H₂O:AlCl₃·2H₂O = 4:3:3; T: 305 K).

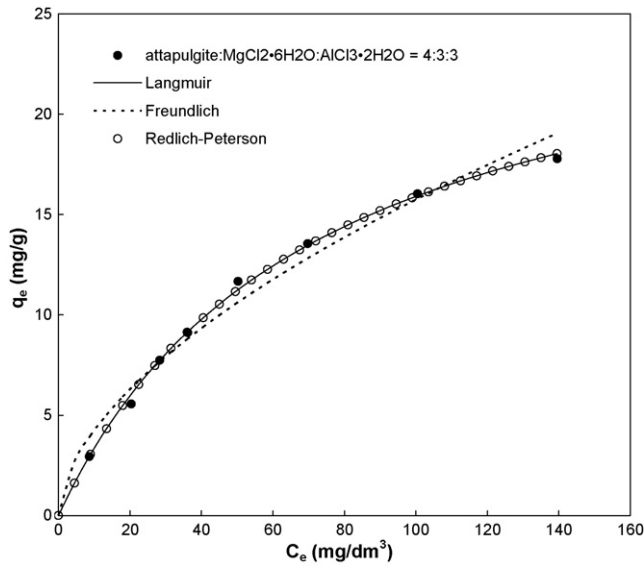


Fig. 2. Isotherms obtained by the non-linear method for the fluoride adsorption onto modified attapulgite (mass ratio for modification: attapulgite: $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}:\text{AlCl}_3 \cdot 2\text{H}_2\text{O} = 4:3:3$; T : 305 K).

mass of modified attapulgite, q_e , was plotted against the concentration of fluoride remaining in solution, C_e . Both the Langmuir ($r^2 = 0.994$) and Redlich–Peterson ($r^2 = 0.983$) isotherms seemed to be the better-fitting models than the Freundlich ($r^2 = 0.976$) isotherm. The adsorption system was more likely monolayer coverage of the modified attapulgite surface by the fluoride ions.

The use of coefficient of determination of linear regression analysis for comparing the best-fitting of different linear isotherms was found not to be appropriate [29,30]. A further analysis of the non-linear method was attempted. Application of computer operation was developed to determine the isotherm parameters using an optimization routine to maximize the coefficient of determination between the experimental data and isotherms in the solver add-in Microsoft Excel [28]. Fig. 2 showed that the Redlich–Peterson and Langmuir isotherms overlapped, and they seemed to be the best-fitting models with the same regression coefficient values ($r^2 = 0.997$). Unlike the linear analysis, different isotherm forms would affect r^2 significantly, and impact the final determination of parameters while non-linear methods would prevent such errors [28].

Non-linear isotherm parameters for three modified adsorbents at 313 K were listed in Table 2. The value of Redlich–Peterson g was almost unity, which meant the isotherms were approaching the Langmuir but not Freundlich isotherm [31]. Langmuir isotherm is a special case of Redlich–Peterson isotherm when constant g is unity, and Redlich–Peterson constant B is the same as Langmuir adsorption equilibrium constant, K_a [31]. In addition, it has been reported that Freundlich isotherm is a special case of Redlich–Peterson isotherm when constants A and B are much greater than unity [29].

The effect of isotherm shape can be used to predict whether an adsorption system is ‘favorable’ or ‘unfavorable’. According to

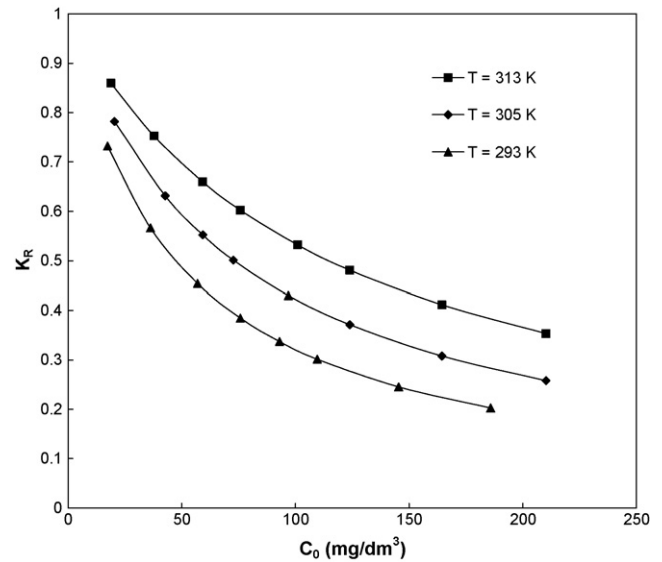


Fig. 3. Values of the separation factor, K_R for the adsorption of fluoride onto modified attapulgite (mass ratio for modification: attapulgite: $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}:\text{AlCl}_3 \cdot 2\text{H}_2\text{O} = 4:3:3$).

Hall et al. the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter K_R which is defined by the following relationship [32]:

$$K_R = \frac{1}{1 + K_a C_0} \quad (7)$$

where K_R is a dimensionless separation factor, C_0 the initial fluoride concentration (mg/L) and K_a the Langmuir constant (L/mg). The parameter K_R indicates the isotherm shape accordingly:

Values of K_R	Type of isotherm
$K_R > 1$	Unfavorable
$K_R = 1$	Linear
$0 < K_R < 1$	Favorable
$K_R = 0$	Irreversible

A figure with a relationship between K_R and C_0 was presented to show the essential features of the Langmuir isotherm [28]. Fig. 3 showed the values of K_R for modified attapulgite (with a mass ratio of attapulgite: $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}:\text{AlCl}_3 \cdot 2\text{H}_2\text{O} = 4:3:3$) at different experiment temperatures. Favorable adsorption was predicted in the present case for higher initial fluoride concentrations but lower temperature.

3.2. Effect of temperature

The effect of temperature on the adsorption isotherms was studied at 293, 305, and 313 K and the results were displayed in Fig. 4. The Langmuir isotherm was applicable to homogeneous adsorption where each fluoride ion/modified attapulgite adsorption process had equal adsorption activation energy [24]. Results

Table 2
Adsorption isotherm constants obtained by the non-linear method (T : 313 K).

Modification mass ratio attapulgite: $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}:$ $\text{AlCl}_3 \cdot 2\text{H}_2\text{O}$	Langmuir			Freundlich			Redlich–Peterson			
	q_m (mg/g)	K_a (L/mg)	r^2	$1/n$	K_F (mg/g) (L/mg) $^{1/n}$	r^2	g (L/mg) $^{1/n}$	B (L/g)	A	r^2
2:1:2	41.5	0.0143	0.995	0.610	1.51	0.983	1.00	0.0143	0.593	0.995
4:3:3	40.1	0.00804	0.997	0.679	0.776	0.992	0.902	0.0140	0.341	0.997
2:2:1	27.6	0.00799	0.989	0.650	0.600	0.981	1.00	0.00799	0.220	0.989

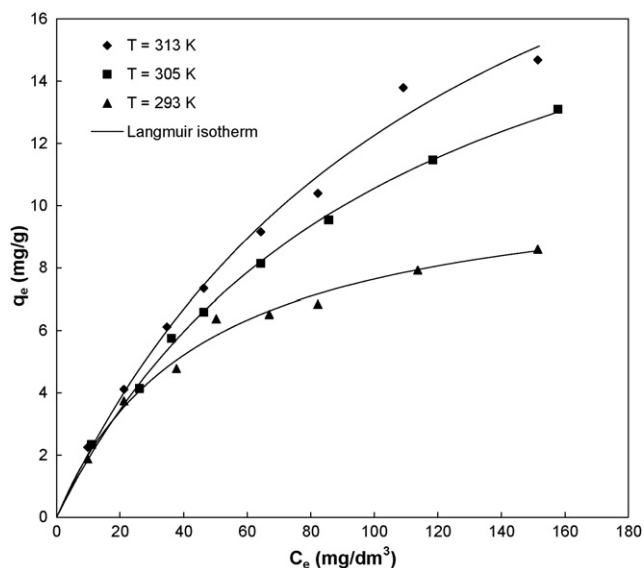


Fig. 4. Langmuir isotherm for the adsorption of fluoride onto modified attapulgite at various temperatures (mass ratio for modification: attapulgite:MgCl₂·6H₂O: AlCl₃·2H₂O = 2:2:1).

indicated that the capacity of modified attapulgite for adsorption of fluoride depended on temperature. At an initial concentration of 210 mg/L, the amount adsorbed by modified attapulgite (mass ratio for modification:attapulgite:MgCl₂·6H₂O:AlCl₃·2H₂O = 2:2:1) increased from 8.60 to 14.7 mg/g with an increase in the solution temperature from 293 to 313 K (Fig. 4). It was clear that the adsorption of fluoride on attapulgite was an endothermic process.

3.3. Effect of modification mass ratio

In order to assess the adsorption efficiency of three modified attapulgites by various mass ratios, the typical Langmuir isotherms at the temperature of 305 K have been shown with the experimental data in Fig. 5. Besides, a comparison of the constants *K_a*, *q_m* and the non-linear coefficients of determination for the Langmuir isotherms were made and listed in Table 3. Modified attapulgites

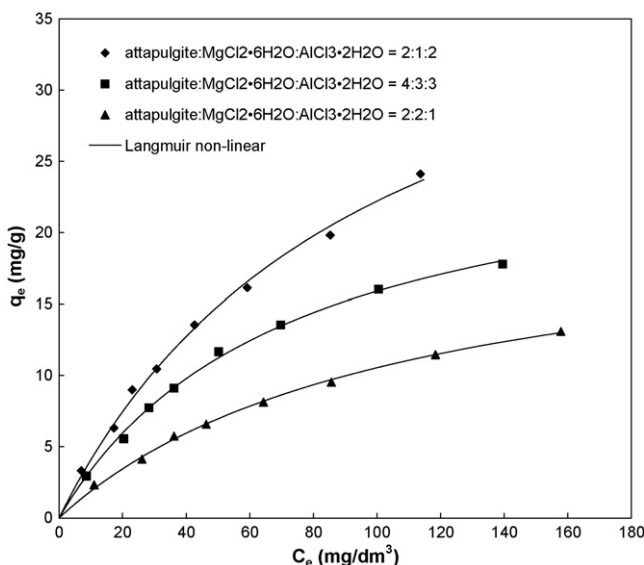


Fig. 5. Langmuir isotherm for the adsorption of fluoride onto three different modified attapulgites (*T*: 305 K).

Table 3
Langmuir isotherm parameters for the adsorption of fluoride onto three modified attapulgites at different temperatures (by the non-linear method).

Modification mass ratio attapulgite:MgCl ₂ ·6H ₂ O: AlCl ₃ ·2H ₂ O	313 K	305 K	293 K
2:1:2			
<i>q_m</i> (mg/g)	41.5	44.0	19.1
<i>K_a</i> (L/mg)	0.0143	0.0102	0.0292
<i>r</i> ²	0.995	0.996	0.990
4:3:3			
<i>q_m</i> (mg/g)	40.1	27.3	17.1
<i>K_a</i> (L/mg)	0.00800	0.0140	0.0205
<i>r</i> ²	0.997	0.997	0.983
2:2:1			
<i>q_m</i> (mg/g)	27.6	21.8	11.1
<i>K_a</i> (L/mg)	0.00800	0.00941	0.0221
<i>r</i> ²	0.989	0.998	0.985

with a mass ratio attapulgite:MgCl₂·6H₂O:AlCl₃·2H₂O = 2:1:2 had the largest adsorption capacity for fluoride uptake at studied temperatures.

3.4. Adsorption mechanism

As tested by previous experiments, the adsorption capacity of the natural attapulgite for fluoride ions from aqueous solution was low, even undetected by the instrument (Fig. 6). Obviously the adsorption capacity of the modified attapulgite was significantly improved.

The fluoride adsorption by the natural attapulgite was negligible probably due to negative charges of the attapulgite surface [17,33]. In order to investigate the attapulgite surface character, a blank experiment was performed with a volume of 50 mL of distilled water (pH = 6.57) placed in a 125 mL conical flask. A change of pH value from 6.57 to 5.43 showed that hydrogen ions were released from the attapulgite into solution. The attapulgite surface was negatively charged. The approach of a fluoride anion would suffer coulombic repulsion from the strong anionic groups in attapulgite. On this basis, it was expected that a cation would have a strong adsorption affinity for natural attapulgite.

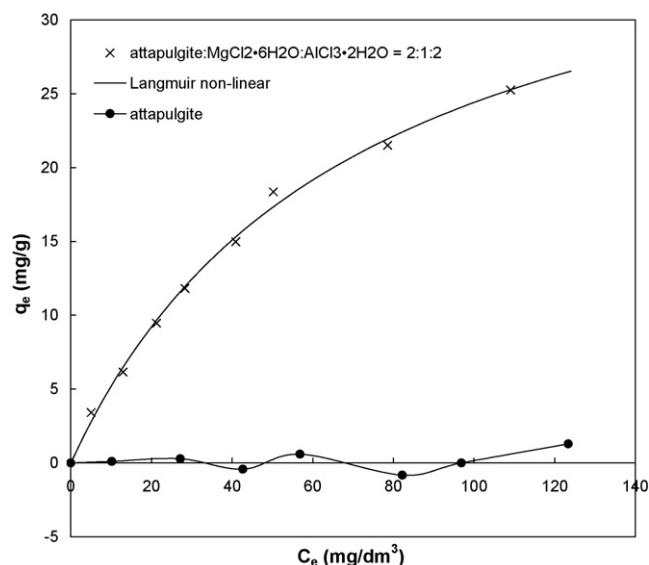


Fig. 6. Adsorption capacities for fluoride ions onto nature and modified attapulgite (*T*: 313 K).

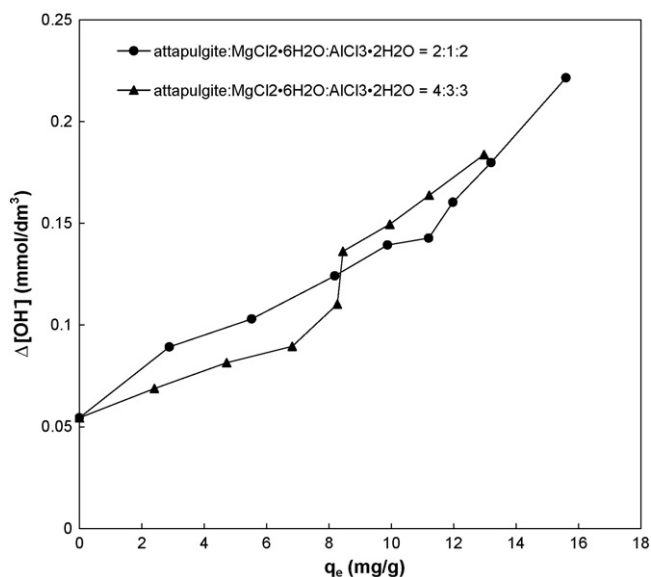


Fig. 7. The relationship between the adsorption capacities and the changes of hydroxyl ion concentration ($T: 293\text{ K}$).

pulgite. The phenomena for the adsorption of divalent metal ions such as Ni(II), Cu(II) and Pb(II) by attapulgite had been reported [19,20].

Fig. 7 illustrated the agreement of the adsorption capacities for the modified attapulgites and changes in the solution hydroxy ion (OH^-) concentration. As more fluoride binded onto the modified attapulgite, more hydroxy ions were released from the adsorbent into the solution. It was clear that anion exchange between fluoride ions and hydroxy groups of the modified attapulgite had occurred in the adsorption system. The anion exchange capacity was influenced by the factor of the initial fluoride ion concentration in the solution, when the temperature and the modified attapulgite dose were fixed [34]. Consequently, higher initial fluoride concentration advanced the anion exchange potential of the adsorbate and resulted in higher adsorption capacity.

4. Conclusions

The use of three different modified attapulgites in fluoride removal from aqueous solution was studied in batch experiments. Two-parameter Langmuir and three-parameter Redlich–Peterson isotherms were the best-fitting models for the experimental data by the non-linear method. An increase in temperature resulted in a higher fluoride loading per unit weight of the adsorbent, suggesting that the adsorption process was endothermic. Fluoride adsorption capacities changed by modification mass ratios of attapulgite, magnesium and aluminum salts. Modified attapulgite with a mass ratio attapulgite: $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}:\text{AlCl}_3 \cdot 2\text{H}_2\text{O} = 2:1:2$ had higher adsorption efficiency than the other two. The agreement of the adsorption capacities and changes of the hydroxy ion concentration indicated that anion exchange reactions occurred in the adsorption process.

Acknowledgments

The authors would like to thank Professor J.S. Sun. from Wuhan Institute of Technology, China for his helpful suggestions in the modification methods.

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