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

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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:$MgCl_2{\cdot}6H_2O$:$AlCl_3{\cdot}2H_2O$ = 2:1:2 had higher fluoride adsorption capacity. In addition, the fluoride adsorption using the modified attapulgite included an anion exchange process.

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 preciously, 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

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Table 1
The chemical composition of natural attapulgite.

Composition	Percent (%)
SiO_2	58.38
MgO	12.10
Al_2O_3	9.50
CaO	0.40
TiO_2	0.56
MnO	0.05
Fe_2O_3 + FeO	5.26
Na_2O	1.10
K_2O	1.24

of fluoride ions. The samples were dispersed in distilled water, with magnesium and aluminum salts ($MgCl_2{\cdot}6H_2O$, $AlCl_3{\cdot}2H_2O$) 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 though 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 polyethene 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 polyethene bottles. In the adsorption isotherm tests, attapulgite (0.20 g) was thoroughly mixed with aqueous solutions of fluoride (50 mL), with initial fluoride concentrations (C_0) ranging from 20 to 200 mg/L. The effects of three modification methods by varying mass ratios of attapulgite, magnesium, and aluminum salts (attapulgite:$MgCl_2{\cdot}6H_2O$:$AlCl_3{\cdot}2H_2O$ = 2:2:1; attapulgite:$MgCl_2{\cdot}6H_2O$:$AlCl_3{\cdot}2H_2O$ = 2:1:2; and attapulgite:$MgCl_2{\cdot}6H_2O$:$AlCl_3{\cdot}2H_2O$ = 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:

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \tag{1}$$

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]:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m} \tag{2}$$

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:

$$q_e = K_F C_e^{1/n} \tag{3}$$

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:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

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:

$$q_e = \frac{A C_e}{1 + B C_e^g} \tag{5}$$

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

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

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

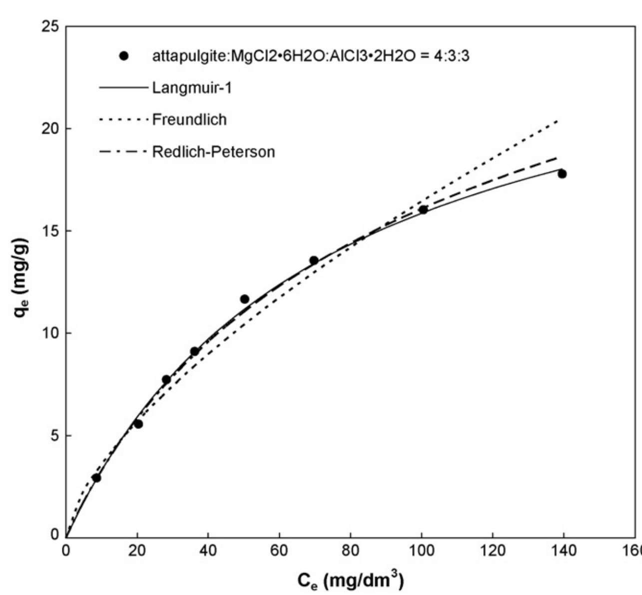

Fig. 1. Isotherms obtained by the linear method for the fluoride adsorption onto modified attapulgite (mass ratio for modification: attapulgite:$MgCl_2{\cdot}6H_2O$:$AlCl_3{\cdot}2H_2O$ = 4:3:3; T: 305 K).