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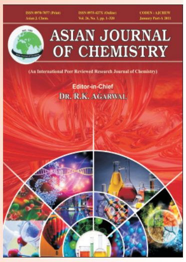

Removal of Cr(VI) from Aqueous Solution by Baritite Clay Adsorption

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Among the investigated clays and minerals (kaolinite, natural zeolite, manual zeolite, bentonite, sepiolite, sepiolite amianthus, tremolite amianthus, vermiculite and baritite), the baritite clay was selected as the optimal adsorbent for aqueous Cr(VI). The adsorption capacity of Cr(VI) on baritite clay reached as high as 39.01 mg g^{-1} at 20 °C. Then the adsorption kinetics and thermodynamics of Cr(VI) by the baritite clay were studied. Results showed that the pseudo-second-order model was a suitable description for the adsorption kinetics and fitted well with the experimental data. The calculated values of entropy ($\Delta S°$) and enthalpy ($\Delta H°$) changes of the adsorption process were $\Delta H° = -9.653$ kJ/mol and $\Delta S° = -22.57$ J mol^{-1} K^{-1}. This indicated that the adsorption of Cr(VI) on baritite clay was an exothermic process with chemical reactions. Finally, a hypothetical chemical adsorption mechanism of Cr(VI) was proposed.

Keywords: Chromate, Baritite clay, Adsorption, Kinetics, Thermodynamics.

INTRODUCTION

It is particularly important to maintain safe aquatic environments, where toxic metals are considered to cause health problems to animals and human beings[1]. Removal of heavy metals is currently a matter of great concern. As the chromate is present in the effluents of electroplating, tanning, mining and fertilizer industries, the hexavalent chromium Cr(VI) pollution has become a major environmental problem. Cr(VI) is a strong mutagenic substance which can cause lung cancer and nasopharyngeal cancer[2,3].

The harmful effects of Cr(VI) necessitate its removal from wastewater before release into streams. The removal of Cr(VI) has considerable ecological and economic interest and the selection of a removal method is based on the concentration of the metal ions, efficiency/cost ratio and adsorption capacity of the adsorbent[4]. Some strategies have been proposed for the removal of Cr(VI) from effluents, such as chemical precipitation, conventional coagulation, reverse osmosis[5], ion exchange[6] and adsorption on activated carbon[7]. However, most of these methods have some disadvantages such as complicated process, high cost and high energy consumption. Hence, there is a crucial need for the development of a method that is not only cost-effective and economic but can also be easily implemented. This leads to a search for low-cost, easily obtainable materials for the adsorption of heavy metals worldwide[8-10].

So far, there was little report about the adsorption of aqueous Cr(VI) by the baritite clay. In this paper, it was found that the baritite clay is an efficient adsorbent for Cr(VI). As the baritite clay is low-cost and available with large quantity, applications of the baritite clay in the treatment of Cr(VI) wastewater have great promising prospects.

EXPERIMENTAL

The baritite clay, kaolinite, bentonite, sepiolite, sepiolite amianthus, natural zeolite, manual zeolite, tremolite amianthus and vermiculite were procured from Non-metallic Mining Co., Ltd of Jiacheng, Zhejiang in China. All the clays and minerals were screened at 80-100 mesh screens and calcined at 500 °C for 24 h before using them as adsorbents. Other compounds used in the adsorption process, such as K_2CrO_4, $BaSO_4$, hydrochloric acid and deionized water, were supplied by Hangzhou Chemical Reagents Company (China).

Adsorption experiments: The adsorption experiments were carried out by using aqueous Cr(VI) solution, which was prepared by dissolving K_2CrO_4 in deionized water and the concentration of the stock solution is about 50 mg Cr(VI) per liter. Firstly, blank experiments were conducted without any clays or minerals on the similar conditions with the actual experiments, by taking 100 mL of 50 mg/L Cr(VI) solutions in quartz flasks at 20 °C water bath and shaking the flasks in the frequency of 220 Hz for 1 h. The results showed that there was not any measurable adsorption of Cr(VI) by the quartz flasks walls.

The adsorption of Cr(VI) by different clays and minerals were carried out in the same quartz flasks, by mixing together 0.1 g of adsorbent with 100 mL of 50 mg/L Cr(VI) aqueous solution. The flasks were shaked gently at 20 °C water bath in the frequency of 220 Hz for 1 h. Then the suspensions were centrifuged at 3,000 rpm for 10 min. The Cr(VI) ions remaining unadsorbed in the supernatant were determined by atomic absorption spectrophotometer (Shimadzu, Spectr AA 6300 with air-acetylene oxidizing flame).

The adsorption experiments by kaolinite, natural zeolite, manual zeolite, bentonite, sepiolite, sepiolite amianthus, tremolite amianthus, baritite and vermiculite were carried out under the same initial conditions. At 20 °C for 60 min, each adsorbent is 0.1 g and the initial Cr(VI) ion concentration is 50 mg/L. The results for different adsorbents are shown in Table-1.

Samples were run in duplicates and used as the curve dots. The amounts of Cr(VI) adsorbed were calculated by using the following formula:

$$Q_t = \frac{(C_0 - C_t).V/1000}{W} \tag{1}$$

where Q_t (mg g^{-1}) is the adsorption capacity of Cr(VI) adsorbed on the baritite clay at time *t*, C_0 (mg L^{-1}) is the initial Cr(VI) concentration, C_t (mg L^{-1}) is the concentration of Cr(VI) in solution at time *t*, V (mL) is the volume of metal ion solution used and W (g) is the weight of the adsorbent used.

Furthermore, the adsorption of Cr(VI) by baritite clay was studied in details, including the adsorption kinetics and the temperature effects. Adsorption experiments data were shown in Fig. 1.

RESULTS AND DISCUSSION

Adsorption of Cr(VI) on various adsorbents: The result of Cr(VI) adsorption on various adsorbents was shown in Table-1. The considered adsorbents included baritite clay, kaolinite, bentonite, sepiolite, sepiolite amianthus, natural zeolite, manual zeolite, tremolite amianthus and vermiculite.

TABLE-1
Cr(VI) ADSORPTION USING DIFFERENT ADSORBENTS

Adsorbents	Adsorption capacity (mg g^{-1})
Natural zeolite	29.62
Manual zeolite	31.79
Sepiolite amianthus	32.55
Sepiolite	30.78
Bentonite	26.93
Kaolinite	32.72
Tremolite amianthus	31.88
Vermiculite	26.94
Baritite	39.01

As it was shown in Table-1, the baritite clay is the best adsorbent for Cr(VI) in aqueous solution among these studied adsorbents. The adsorption capacity of Cr(VI) reaches 39.01 mg g^{-1}, far more than other clays and minerals adsorbents. Therefore, the baritite clay was selected as the optimal adsorbent for Cr(VI), the adsorption of Cr(VI) in aqueous solution was investigated in present study.

Kinetics of Cr(VI) adsorption on the baritite clay: The results of the dynamic analysis usually were performed by the pseudo-first-order and pseudo-second-order rate equations. While Unuabonah *et al.*[11] regarded pseudo-second-order kinetic as the proper expression for metal/sorbent sorption systems such as divalent metal ions using sphagnum moss peat[12].

Therefore, the pseudo-second-order rate equation was used to study the adsorption kinetics of the adsorption of Cr(VI) by the baritite clay.

The pseudo-second-order model is represented by eqn. 2

$$\frac{dQ_t}{dt} = k(Q_e - Q_t)^2 \tag{2}$$

The linear form of eqn. 2 can be written as follow eqn. 3

$$\frac{t}{Q_t} = \frac{1}{kQ_e^2} + \frac{t}{Q_e} \tag{3}$$

where Q_t(mg g^{-1}) is the adsorption capacity of Cr(VI) adsorbed by the baritite clay at time *t*, Q_e(mg g^{-1}) is the equilibrium adsorption capacity and k (g mg^{-1} min^{-1}) is the rate constant of pseudo-second-order model.

The initial sorption rate h (mg g^{-1} min^{-1}) was obtained according to eqn. 3, as t/Q_t approaches zero.

$$h = kQ_e^{\,2} \tag{4}$$

The amount Cr(IV) adsorbed data *vs.* time were shown in Fig. 1. According to the eqn. 3, the linear relation t/Q_t-t of experimental data were also shown in Fig. 2.

According to the adsorption kinetics experiments data shown in Figs. 1 and 2, the parameters values of the eqn. 3 and 4, such as the pseudo-second-order rate constant k (g mg^{-1} min^{-1}), the initial sorption rate h (mg g^{-1} min^{-1}) and the equilibrium adsorption capacity Q_e (mg g^{-1}) can obtained by linear regression. The results were shown in Table-2.

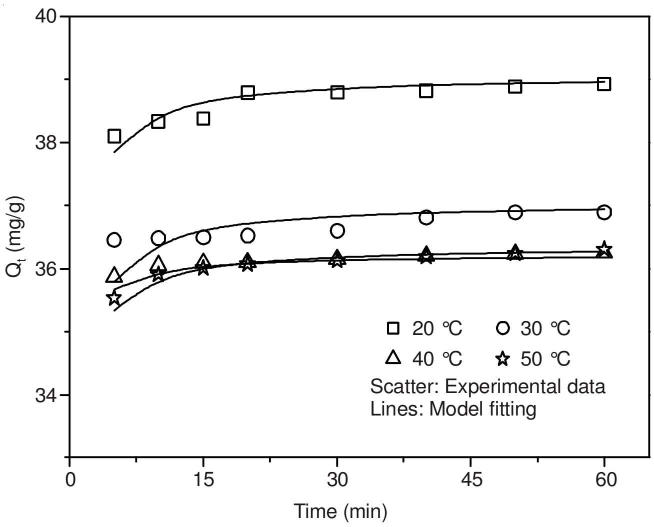

Fig. 1. Adsorption kinetics of Cr(VI) by baritite clay at different temperatures

TABLE-2
PARAMETERS OF THE ADSORPTION KINETICS
AT VARIOUS TEMPERATURE

Temperature (K)	Q_e (mg g^{-1})	k (g mg^{-1} min^{-1})	h (mg g^{-1} min^{-1})
293.15	39.08	0.1596	243.7
303.15	37.37	0.1523	212.6
313.15	36.18	0.3470	454.2
323.15	36.65	0.1967	240.3

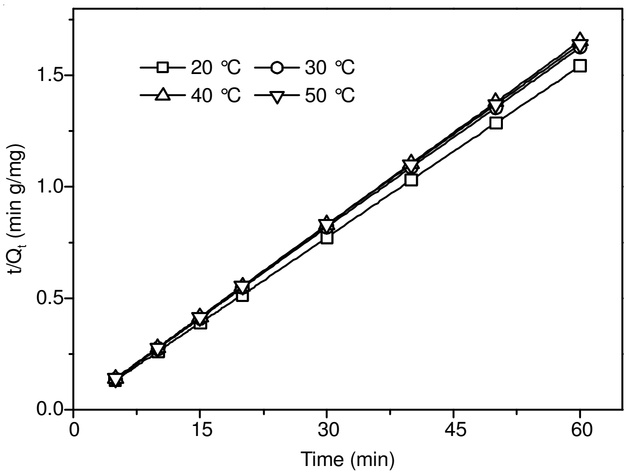

Fig. 2. Linear relation eqn. 3 describing the adsorption of Cr(VI)

As the initial sorption rate h is very fast (more than 200). It was shown that the linear correlation coefficient R^2 at different temperature was about 1. It indicated that the chemical reaction rather than physico-sorption is the main rate-controlling step throughout most of the adsorption process[13].

The amount of Cr(VI) uptake, Q_e (mg g^{-1}) was found to decrease from 39.08 to 36.65 mg g^{-1} when temperature increased from 20 to 50 °C. This indicates that temperature has only a little effect on Cr(VI) adsorbed by baritite clay. The adsorption of Cr(VI) onto baritite clay was investigated in terms of the kinetics of adsorption mechanism by using pseudo-second-order. Table-1 showed that the increase in temperatures in the range of 20 to 40 °C resulted in the increase of the rate constant, k, from 0.1596 to 0.3470 g/mg min^{-1}. However, when the temperature increased to 50 °C, the rate constant (k) decreased to 0.1967 g/mg min^{-1}. In addition, the initial sorption rate (h) also increased from 243.7 to 454.2 mg/g min^{-1} and the initial sorption rate (h) decreased to 240.3 mg g^{-1} min^{-1} when it was 50 °C. The results of the rate constant (k) and initial sorption rate (h) indicated that it's adverse for Cr(VI) adsorbed at higher or lower temperature in the range of 20 to 50 °C. Increase in temperature causes increase in the mobility of the ions. If temperature is further increased, the kinetic energies of chromium ions become higher than the potential attractive forces between active sites and ions[14]. The results described above may be explained as a result of this phenomenon.

Thermodynamics of Cr(VI) adsorption: When the adsorption equilibrium of the Cr(VI) on the baritite clay is established, the adsorbed Cr(VI) is in equilibrium with the residual Cr(VI) concentration[15,16]. The values of equilibrium constant (K_d) of the adsorption process at different temperatures could be calculated from eqn. 5.

$$v-\frac{Q_e m}{C_e V} \qquad (5)$$

Which Q_e (mg g^{-1}) is the equilibrium adsorption capacity, C_e (mg L^{-1}) is the Cr(IV) concentration remaining in solution at equilibrium, m (g) is the mass of the adsorbent and V (L) is the volume of solution.

The standard Gibbs free energy (ΔG°) of the adsorption process could be calculated from eqn. 6

$$\Delta G^\circ = -RT \ln K_d \qquad (6)$$

where R (8.3145 J mol^{-1} K^{-1}) is the ideal gas constant and T (K) is the temperature.

According to the van't Hoff equation eqn. 7, The values of entropy (ΔS°) and enthalpy (ΔH°) changes of the adsorption process can also by calculated by plotting of ln K_d *versus* 1/T.

$$\ln K_d = \frac{\Delta S^\circ}{R} - \left(\frac{\Delta H^\circ}{R}\right)\frac{1}{T} \qquad (7)$$

The plots of ln K_d *versus* 1/T were shown in Fig. 3. The linear data fitting was satisfactory with of the linear relation coefficient R^2 = 0.9528. The calculated values of ΔH° and ΔS° of the adsorption of Cr(VI) on the Baritite clay and the experimental K_d data were all listed in Table-3.

TABLE-3
THERMODYNAMIC PARAMETERS FOR
THE ADSORPTION OF Cr(VI) ON THE BARITITE CLAY

Temperature (K)	K_d	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})
293.15	3.579	-3.109	-9.653	-22.57
303.15	2.959	-2.735		
313.15	2.618	-2.507		
323.15	2.484	-2.446		

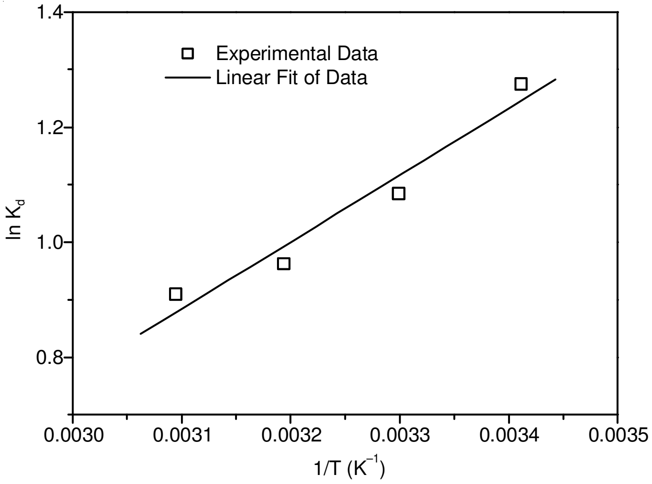

Fig. 3. Plot of ln K_d *versus* 1/T for the adsorption of Cr(VI) on the baritite clay

As it was shown in Table-3, the negative value of enthalpy change (ΔH°) -9.653 kJ mol^{-1} indicated that the adsorption of Cr(VI) was exothermic process with chemical reactions. The negative entropy change (ΔS°) values -22.57 J mol^{-1} K^{-1} revealed that the orderliness of the adsorbed system was higher than the solution phased before adsorption. The Gibbs free energy ΔG°, listed in Table-3, as calculated for adsorption of Cr(VI) on baritite clay were -3.109, -2.735, -2.507 and -2.446 kJ mol^{-1} when the temperature was set at 293.15, 303.15, 313.15 and 323.15 K. It suggested that the adsorption process of Cr(VI) on the baritite clay was feasible and spontaneous thermodynamical. Furthermore, the Gibbs energy increase with increasing temperature suggested that the adsorption of Cr(VI) on the baritite clay was less favorable at higher temperatures.

Mechanism of Cr(VI) adsorption on baritite clay: The main ingredient of baritite clay is barium sulfate $BaSO_4$, which can form in dissolvable dichromates from the aqueous solution of Cr(VI). Then the in dissolvable chromates such as $BaCr_2O_7$

and $Ba(HCr_2O_7)_2$ adsorbed on the clay with $Cr_2O_7^{2-}$ and $HCr_2O_7^-$ to remove Cr(VI). The process of adsorption on the baritite clay surface sites are formulated as following expressions:

$$BaSO_4 + Cr_2O_7^{2-} \leftrightarrow BaCr_2O_7 + SO_4^{2-} \quad (8)$$

$$BaSO_4 + 2HCr_2O_7^- \leftrightarrow Ba(HCr_2O_7)_2 + SO_4^{2-} \quad (9)$$

The formation of $BaCr_2O_7$ and Ba $(HCr_2O_7)_2$ complexes can explain the higher adsorption capacity of baritite for Cr(VI).

Conclusion

The results obtained from baritite clay used for removal of Cr(VI) from aqueous solution demonstrated that baritite clay is a feasible alternative for the chemical and physical adsorption of Cr(VI). In addition, the adsorption of Cr(VI) by baritite clay followed the linearity of the plots of the pseudo-second-order model well. Furthermore, The negative value of enthalpy change, ΔH° and Gibbs free energy change, ΔG°, indicated that the adsorption of Cr(VI) on baritite clay was a feasible, spontaneous thermodynamically and exothermic process. Thus, baritite clay is a meaningful material used to remove heavy mental like Cr(VI), it makes sense to research further.

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