Adsorption Thermodynamics of Cobalt Ions onto Attapulgite

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Abstract

The effect of temperature on the equilibrium adsorption of cobalt ions from aqueous solution using Attapulgite was investigated. A trial-and-error non-linear method was used to obtain Langmuir parameters. Thermodynamic parameters, such as $\Delta G°$, $\Delta H°$, and $\Delta S°$ were calculated using adsorption equilibrium constant obtained from the Langmuir isotherm. Results suggested that the cobalt ions adsorption on Attapulgite was a spontaneous and endothermic process.

1. Introduction

Adsorption has been recognized as an effective method for the removal of pollutants from water [1,2]. The adsorption of cobalt ions onto a solid phase has long been investigated using inorganic adsorbents such as hydrous ferric oxide [3], activated carbon [4], hydrous stannic oxide [5], porous-glass [6], TiO_2 [7], magnetite [8], γ-Al_2O_3 [9], kaolinite [10], sepiolite [11], clay [12], sepiolite [13], and hydroxyapatite [14]. 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 to retard contaminant migration [17]. Numerous studies have been presented on the adsorption of heavy metals from aqueous solutions by Attapulgite [18,19].

The study of adsorption isotherms in water treatment is significant as it provides valuable insights into the application of design. An isotherm describes the relationship between the quantity adsorbed and that remaining in the solution at a fixed temperature at equilibrium. Adsorption thermodynamic parameters can be obtained from adsorption equilibrium constants with temperatures [20,21].

In the present study, Attapulgite was used as an adsorbent for the removal of cobalt ions from aqueous solutions. The adsorption isotherm was studied at different temperatures. The thermodynamics of the adsorption process were also evaluated with the adsorption equilibrium constant obtained from the Langmuir isotherm.

2. Method and Materials

The granular attapulgite samples were of 200 mesh size with a purity of 80%, obtained from the Longwang Hill in Xuyi, in the Jiangsu Province of China. Elements were analyzed in the form of oxide percentage in Table 1. Analytical grade reagents were used in all cases. A stock cobalt solution was prepared in distilled water using analytical grade $Co(CH_3COO)_2$. All working solutions were prepared by diluting the stock solution with distilled water.

A volume of 50 ml of cobalt solution with a concentration in the range 30 - 135 mg/dm^3 was placed in a 125-ml conical flask. An accurately weighed Attapulgite sample of 0.20 g was added to the solution. A series of such conical flasks were then shaken at a constant speed of 80 rpm in a shaking water bath with temperatures 10, 15, 25, 35, and 40°C, respectively. After shaking the flasks for 16 h, the Attapulgite was separated by filtration through a membrane filter (0.45 mm).

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The filtrate was analyzed for the remaining cobalt ion concentration by an inductively coupled plasma atomic emission spectrophotometer (ICP-AES).

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

The amount of cobalt ion adsorbed onto Attapulgite was calculated by using the following expression:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where q_e was the equilibrium adsorption capacity of cobalt adsorbed on unit mass of Attapulgite (mg/g); C_0 and C_e were the initial cobalt concentration (mg/dm^3) and cobalt concentration (mg/dm^3) at equilibrium, respectively; V was the volume of the cobalt solution (dm^3); and m was the weight of Attapulgite (g).

3. Results and Discussion

In order to investigate the adsorption thermodynamics of cobalt ions onto Attapulgite, the Langmuir isotherm was studied. The Langmuir adsorption isotherm is perhaps the best known of all isotherms describing adsorption [22]. The theoretical Langmuir isotherm is often used to describe adsorption of a solute from a liquid solution as [22,23]

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

where q_e is the equilibrium adsorption capacity, (mg/g), C_e is the equilibrium liquid phase concentration, (mg/dm^3), q_m is the maximum adsorption capacity, (mg/g), and K_a is adsorption equilibrium constant, (dm^3/mg).

It has been presented that the non-linear method is a better way to obtain the isotherm parameters [24]. A trial-and-error procedure, which is applicable to computer operation, was used to compare the best fit of the three isotherms using an optimization routine to maximize the coefficient of determination r^2, between the experimental data and isotherms in the *solver* add-in with Microsoft's spreadsheet, Microsoft Excel [21,25]. The coefficient of determination r^2 was

$$r^2 = \frac{\sum(q_m - \overline{q_e})^2}{\sum(q_m - \overline{q_e})^2 + \sum(q_m - q_e)^2} \quad (3)$$

where q_m was the equilibrium capacity obtained from the isotherm model, q_e was the equilibrium capacity obtained from experiment, and $\overline{q_e}$ was the average of q_e.

Figure 1 shows the theoretical non-liner Langmuir isotherm with the experimental data for adsorption of cobalt ions on Attapulgite at different temperatures. The adsorption capacity of cobalt ions increases with temperature, which is typical for the adsorption of most metal ions from aqueous solution. When the system is in a state of equilibrium, the distribution of cobalt ions between the Attapulgite and the cobalt solution is of fundamental importance in determining the Langmuir maximum adsorption capacity of Attapulgite for the cobalt ions from the isotherm. The Langmuir isotherm constants are shown in Table 2. The Langmuir maximum adsorption capacity, q_m, and the adsorption constant, K_a, were found to increase from 6.76 to 9.39 mg/g and 0.155 to 0.568 dm^3/mg for an increase in the solution temperatures from 283 to 313 K, respectively. The increase in K_a values with temperature indicates a higher heat of adsorption with increasing temperature. It might be that stronger bonds are formed at higher temperatures supporting the fact that adsorption is endothermic.
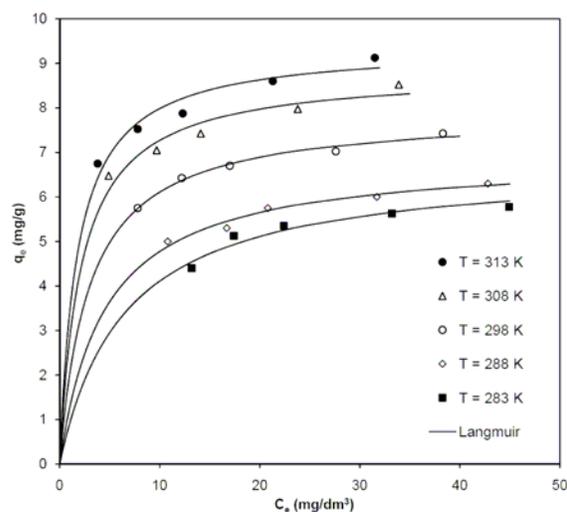

Figure 1. Langmuir isotherms of cobalt ions adsorbed onto Attapulgite in different temperatures

The plateau on each isotherm corresponds to monolayer coverage of the surface by the cobalt ions. This value is the ultimate adsorptive capacity at high concentrations and can be used to estimate the specific surface area of Attapulgite using the following equation (results are shown in Table 2).

$$S = \frac{q_m \cdot N \cdot A}{M} \quad (4)$$

where S is the specific surface area, m^2/g Attapulgite; q_m is monolayer adsorption capacity, mg cobalt per g Attapulgite; N is Avogadro number, 6.02×10^{23}; A is the cross sectional area of cobalt ion, 1.72×10^{-20} m^2 (Co^{2+} radius is 0.74×10^{-10} m); M is molecular weight of cobalt, 58.9 g/mol. Therefore, the specific surface areas can be calculated for various temperature values and are shown in Table 2.

Table 2. Langmuir isotherm parameters obtained using the non-linear method for the adsorption of cobalt ions onto Attapulgite at various temperatures.

T (K)	r^2	q_m (mg/g)	K_a (dm^3/mg)	$\Delta G°$ (kJ/mol)	S (m^2/g)
283	0.933	0.115	9.13	-5.20	1.19
288	0.963	0.117	13.1	-6.16	1.22
298	0.984	0.134	20.0	-7.42	1.39
308	0.918	0.150	27.5	-8.49	1.55
313	0.928	0.159	33.5	-9.14	1.65

The effect of isotherm shape can be used to predict whether an adsorption system is "favorable" or "unfavorable." According to Hall et al. [26], 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:

$$K_R = \frac{1}{1 + K_a C_0} \quad (5)$$

where K_R is a dimensionless separation factor, C_0 is initial cobalt concentration (mg/dm^3), and K_a is adsorption equilibrium constant (dm^3/mg). This parameter indicates the shape of the isotherm 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

The values of K_R for different temperatures are given in Figure 2. The K_R values indicate that adsorption is more favorable for the higher initial cobalt ion concentrations and solution temperatures than for the lower ones.
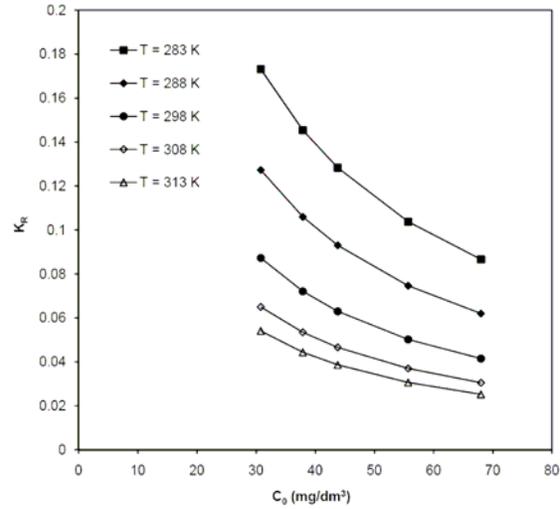

Figure 2. Plot of K_R against initial cobalt concentration in different temperatures.

Thermodynamic Studies
Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. The Gibbs free energy change, $\Delta G°$, is an indication of the spontaneity of a chemical reaction and therefore is an important criterion for spontaneity. Both energy and entropy factors must be considered in order to determine the Gibbs free energy of the process. Reactions occur spontaneously at a given temperature if $\Delta G°$ is a negative quantity. The free energy of an adsorption, considering the adsorption equilibrium constant K_a is given by the following equation:

$$\Delta G^o = -RT \ln K_a \quad (6)$$

where $\Delta G°$ is the standard free energy change, J/mol; R is the universal gas constant, 8.314 J/mol K; and T is absolute temperature, K. Considering the relationship between $\Delta G°$ and K_a, change in equilibrium constant with temperature can be obtained in the differential form as follows [20,27]:

$$\frac{d \ln K_a}{dT} = \frac{\Delta H^o}{RT^2} \quad (7)$$

After integration, the integrated form of Eq. (7) becomes:

$$\ln K_a = -\frac{\Delta H^o}{RT} + Y \quad (8)$$

where Y is a constant. Eq. (8) can be rearranged to obtain

$$- RT \ln K_a = \Delta H^o - TRY \qquad (9)$$

Let

$$\Delta S^o = RY \qquad (10)$$

Substituting Eqs. (9) and (10), $\Delta G°$, can be represented as follows:

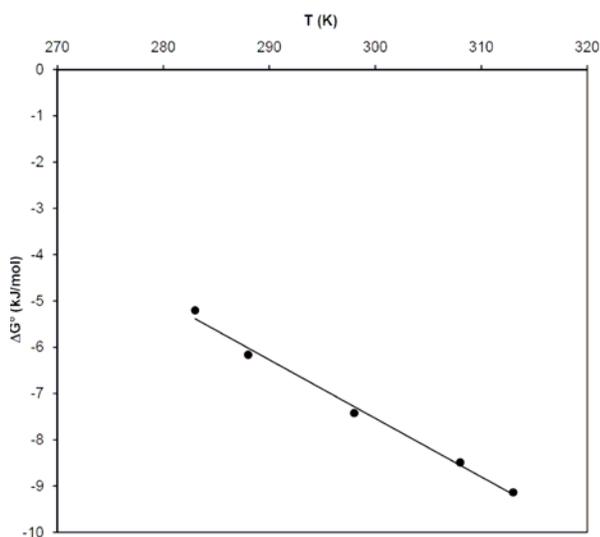$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (11)$$

Figure 3. Plot of Gibbs free energy change, $\Delta G°$, versus temperatures, T

The adsorption equilibrium constant, K_a, obtained from the non-linear method was analyzed using Eqs. (2) and (11). A plot of $\Delta G°$ versus temperature, T, will be linear and the values of $\Delta H°$ and $\Delta S°$ are determined from the slope and intercept of the plot (Figure 2). The parameter $\Delta G°$ for the adsorption process using the K_a from the Langmuir isotherm is shown in Table 2. The values of $\Delta G°$ calculated using the K_a were negative for the adsorption of cobalt ions onto Attapulgite at all temperatures. The negative values confirm the feasibility of the process and the spontaneous nature of the adsorption. The values of $\Delta G°$ were found to decrease -5.20 to -9.14 kJ/mol using the equilibrium constant, K_a. The decrease in the negative value of $\Delta G°$ with an increase in temperature indicates that the adsorption process of cobalt ions on Attapulgite becomes more favorable at higher temperatures [28]. The values of $\Delta H°$ and $\Delta S°$ calculated from the plot of $\Delta G°$ versus T were given as 30.4 kJ/mol and 127 J/mol K, respectively. The value of $\Delta H°$ was positive, indicating that the adsorption process was endothermic. The positive

value of $\Delta S°$ reflects the affinity of the Attapulgite for the cobalt ions and suggests some structural changes in adsorbate and adsorbent [29]. In addition, the positive value of $\Delta S°$ shows the increasing randomness at the solid/liquid interface during the sorption of copper ions on tree fern. Spontaneous and endothermic adsorption have also been reported for the system of basic dyes on tree fern [30], wheat shell [31], Mansonia wood sawdust [32], and Bentonite [33], as well as cobalt and europium ions on cerium tungstate powder [34].

4. Conclusion

Attapulgite is able to adsorb cobalt ions from aqueous solutions. The removal of cobalt ions using Attapulgite was a function of temperature. The adsorption capacity increased with increasing temperature. The Langmuir isotherm had a high coefficient of determination with experimental data. The thermodynamic parameter, $\Delta G°$, could be calculated from the adsorption equilibrium constant obtained from the Langmuir isotherm. The value of $\Delta H°$ and $\Delta S°$ could be also obtained from the slope and intercept of the relationship between $\Delta G°$ and reaction temperature. The negative values of $\Delta G°$ indicate the spontaneous nature of adsorption with a high preference of cobalt ions onto Attapulgite. The value of $\Delta H°$ was positive, which indicated that the adsorption reaction was endothermic. The positive value of $\Delta S°$ shows that increasing randomness at the solid/liquid interface during the adsorption of cobalt ions on Attapulgite.

5. References

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