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Adsorption Characteristics of Zinc (Zn^{2+}) from Aqueous Solution by Natural Bentonite and Kaolin Clay Minerals: A Comparative Study

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ABSTRACT

Clay minerals are one of the potential good adsorbent alternatives to activated carbon because of their large surface area and high cation exchange capacity. In this work the adsorptive properties of natural bentonite and kaolin clay minerals in the removal of zinc (Zn^{2+}) from aqueous solution have been studied by laboratory batch adsorption kinetic and equilibrium experiments. The result shows that the amount of adsorption of zinc metal ion increases with initial metal ion concentration, contact time, but decreases with the amount of adsorbent and temperature of the system for both the adsorbents. Kinetic experiments clearly indicate that adsorption of zinc metal ion (Zn^{2+}) on bentonite and kaolin is a two-step process: a very rapid adsorption of zinc metal ion to the external surface is followed by possible slow decreasing intraparticle diffusion in the interior of the adsorbent. This has also been confirmed by an intraparticle diffusion model. The equilibrium adsorption results are fitted better with the Langmuir isotherm compared to the Freundlich model. The value of separation factor, R_L from Langmuir equation give an indication of favourable adsorption. Finally from thermodynamic studies, it has been found that the adsorption process is exothermic due to negative ΔH^0 accompanied by decrease in entropy change and Gibbs free energy change (ΔG^0). Overall bentonite is a better adsorbent than kaolin in the the removal of Zn^{2+} from its aqueous solution.

Keywords: Metal Ion Adsorption; Clay Minerals; Kinetics; Isotherms

1. Introduction

Heavy metal ion pollution is currently of great concern due to the increased awareness of the potentially hazardous effects of elevated levels of these materials in the environment [1,2]. There is an increasing and alarming challenge to researchers and environmental control agencies from the indiscriminate disposal of metals in the environment. The main sources of zinc in the environment are the manufacturing of brass and bronze alloys and galvanization [3,4]. It is also utilized in paints, rubber, plastics, cosmetics and pharmaceuticals [4]. Zinc is an essential element for life and acts as micronutrient when present in trace amounts [3]. The WHO recommended maximum acceptable concentration of zinc in drinking water as 5.0 mg/L [5]. Beyond the permissible limits, Zn^{2+} is toxic [6]. Precipitation, ion exchange, filtration, solvent extraction and membrane technology and adsorption on activated carbon are the conventional method for the removal of heavy metal ions from aqueous solutions and all of which may be ineffective or extremely expensive, when the metals are dissolved in large volumes of solution at relatively low concentration [3].

Adsorption on activated carbon is the conventional methods for the removal of heavy metal ions from aqueous solutions but its high cost limits its use [7]. Therefore, adsorption is used especially in the water treatment field and the investigation has to be made to determine inexpensive and good adsorbent. Clay minerals such as kaolin, bentonite are the most wide-spread minerals of the earth crust which are known to be good adsorbents/sorbents of various metal ions, inorganic anions and organic ligands [8]. These clay minerals are good adsorbent alternatives to activated carbon because of their large surface area, high cation exchange capacity, chemical and mechanical stability and layered structure Moreover, oxides and clay minerals are important tropical soil secondary minerals, responsible for the low mobility and bioavailability of heavy metals [9]. Although, there are reported results on the adsorption capacity of clay minerals towards heavy metal ions [2] but a systematic studies on zinc (Zn^{2+}) adsorption characteristics on kaolin, bentonite under various physicochemical parameters are limited and also very scare. Therefore a study was conducted in order to determine the influence of initial metal

ion concentration, adsorbent dosages and temperature changes on adsorption characteristics of natural bentonite and kaolin. It is also essential to understand the mechanism and kinetics of adsorption, because the studies of adsorption kinetics and mechanism are ultimately a prerequisite for designing an adsorption column [3]. Another reason for this study is the importance of adsorption on solid surfaces in many industrial applications in order to improve efficiency and economy. The kinetic adsorption results have been analysed using both pseudo-first-order and pseudo-second-order kinetics models. The mechanism of the adsorption process has been explained based on intra-particle diffusion model. The isotherm equilibrium results are better fitted with Langmuir model. Finally thermodynamic parameters are determined at three different temperatures and it has been found that the adsorption process is exothermic due to negative ΔH^0 accompanied by decrease in entropy change and Gibbs free energy change (ΔG^0).

2. Materials and Methods

2.1. Chemicals

All chemicals used were of analytical grade. Stock standard solution of Zn^{2+} has been prepared by dissolving the appropriate amount of its nitrate salt in deionised water, acidified with small amount of nitric acid. This stock solution was then diluting to specified concentrations. Kaolin BET surface area of 15.72 m^2/g, mean particle size of 17.94 μm) was obtained from Chem-Supply pty Ltd, Perth WA. Bentonite (BET surface area of 238.47 m^2/g and mean particle size of 7.49 μm) was obtained from Bronson & Jacobs Pty Ltd Australia. All plastic sample bottles and glassware were cleaned, then rinsed with deionised water and dried at 60°C in a temperature controlled oven. All measurements were conducted at the room temperature (28 ± 2, ℃). The concentration of Zn^{2+} was measured using a double beam flame atomic absorption spectrophotometer. Sizes of particles were measured by Malvern Master Seizer, Ver 1.2, UK. The pH was measured by Orion pH meter.

2.2. Adsorption Procedure

Adsorption measurements were determined by batch experiments of known amount of the sample with 40 mL of aqueous Zn^{2+} solutions as per Aries & Sen [3] in a series of 60 ml plastic bottles. The mixture were shaken in a constant temperature orbital shaker at 120 rpm at 30 ℃ for a given time and then the suspensions were filtered through a What man glass micro filter and the filtrates were analyzed using flame atomic absorption spectrophotometer with an air-acetylene flame. The experiments were carried out by varying concentration of initial Zn^{2+} solution, contact time, amount of adsorbent and

temperature of the system. Adsorption mechanisms were studied according to predefined procedure with the Zn^{2+} concentration ranging from 1.0 to 40 mg /L. The Zn^{2+} concentration retained in the adsorbent phase was calculated according to Equation (1)

$$q_t = \frac{(C_0 - C_t)V}{m} \qquad (1)$$

where C_0 (mg/L) and C_t (mg/L) are the concentration in the solution at time t = 0 and at time t, V is the volume of solution (L) and m is the amount of adsorbent (g) added.

The kinetics of adsorption of Zn (II) was carried out at low and high initial metal ion concentration using the same adsorption procedure started above. The only difference was that samples were collected and analyzed at regular time intervals during the adsorption process.

The transient behavior of the Zn (II) adsorption process was analyzed using two adsorption kinetic models; pseudo first and pseudo-second-order rate models. The rate constant of adsorption was determined from the pseudo-first-order rate model [10] as

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \qquad (2)$$

where q_t and q_e represents the amount of metal ion adsorbed (mg/g) at any time t and at equilibrium time respectively and K_1 represents the adsorption first-order rate constant (min^{-1}). Plot of Log ($q_e - q_t$) versus t gives a straight line for pseudo first-order adsorption kinetics which allow computation of the rate constant K_1.

The pseudo-second-order model [3,10] based on equilibrium adsorption is expressed as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t \qquad (3)$$

A plot between t/q_t versus t gives the value of the constants K_2 (g/mg h) and also q_e (mg/g) can be calculated.

The Constant K_2 is used to calculate the initial sorption rate h, at t → 0, as follows

$$h = K_2 q_e^2 \qquad (4)$$

Thus the rate constant K_2, initial adsorption rate h and predicted q_e can be calculated from the plot of t/q versus time t using Equation (3).

According to Weber & Morris (1963) [11] the intraparticle diffusion model for most the uptake varies almost proportionately with $t^{1/2}$ rather than with the contact time and can be represented as follows:

$$q_t = K_{id} = t^{0.5} \qquad (5)$$

where q_t is the amount adsorbed at time t and $t^{0.5}$ is the square root of the time and K_{id} (mg/g.min$^{0.5}$) is the rate constant of intraparticle diffusion. When intra-particle diffusion plays a significant role in controlling the kinet-

ics of the adsorption processes, the plots of q_t vs. $t^{0.5}$ yield straight lines passing through the origin and the slope gives the rate constant K_{id}.

Thermodynamic parameters such as Gibb's free energy (ΔG^0), enthalpy change (ΔH^0) and change in entropy (ΔS^0) for the adsorption of zinc on aluminum oxide has been determined by using the following equations [2]:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{6}$$

$$\log\left(\frac{q_e}{C_e}\right) = \frac{\Delta S^0}{2.303\,R} + \frac{-\Delta H^0}{2.303\,RT} \tag{7}$$

where q_e is the amount of zinc adsorbed per unit mass of aluminium oxide (mg/g), C_e is equilibrium concentration (mg/L) and T is temperature in K. q_e/C_e is called the adsorption affinity. The above equation is for unit mass of adsorbent dose.

3. Results and Discussions

3.1. Characterization of Adsorbenst

The characterization of the structure and surface chemistry of the adsorbent is of considerable interest for the development of adsorption and separation processes. FT-IR spectroscopy of bentonite which is not shown here indicated the presence of hydroxyl, carboxyl and Si-O which are important sorption sites. The particle size distribution of bentonite which is not shown here for which mean particle size was 7.49 μm, whereas mean particle size of kaolin was 17.95 μm. XRD analysis also indicates that the main mineral of kaolin was kaolinite with trace impurities of quartz, whereas in bentonite four different mineral phases were present: mainly quartz (SiO_2) and muscovite.

3.2. Effect of Contact Time and Initial Metal Ion Concentration on Zn(II) Metal Ion Adsorption Kinetics

Figure 1 represents a plot of the amount of zinc metal ion adsorbed (mg/g) versus contact time for Zn-kaolin and Zn-bentonite system. **Figure 2** represents a plot of the amount of Zn (II) adsorbed at different initial metal ion concentration range for both the system. From these plots, it is found that the amount of adsorption *i.e.* mg of adsorbate per gram of adsorbent increases with increasing contact time at all initial metal ion concentrations and equilibrium is attained within 80 minutes for both the systems Further it was observed that the amount of metal ion uptake, q_t (mg/g) is increased with increase in initial metal ion concentration (**Figure 2**). The increase in adsorption is more pronounced for the Zn-bentonite system compared to the Zn-Kaolin system. These kinetic experiments clearly indicate that the adsorption of Zn (II) on clay surface is a two-step process: a rapid adsorption of
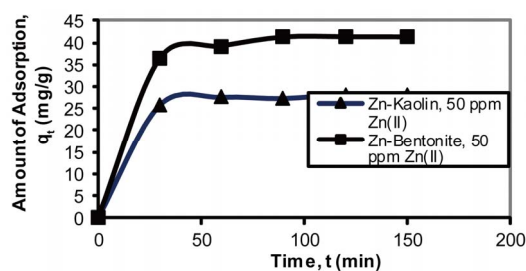

Figure 1. Effect of contact time on Zn (II) metal ion adsorption by kaolin and bentonite. Initial metal ion concentrations = 50 ppm, Initial solution pH = 6.65.
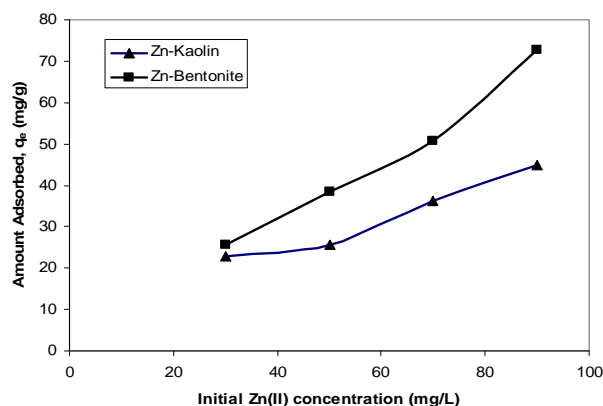

Figure 2. Effect of initial Zn (II) concentration on adsorption.

metal ions to the external surface is followed by possible slow intraparticle diffusion in the interior of the particles [10]. This has been confirmed by fitting experimental data with diffusion model which is presented latter section. This two-stage process is also due to presence of two different types of binding sites on the adsorbents. Moreover, the amount of Zn(II) ions adsorbed per unit mass of the biosorbent increases with the initial metal ion concentration (**Figure 2**) which might be due to the higher availability of Zn(II) ions in solution. Further a higher initial concentration provides increased driving force to overcome all mass transfer resistance of metal ions between the aqueous and solid phases resulting in higher probability of collision between Zn(II) ions and sorbents.

3.3. Effect of Adsorbent Dose on Zn(II) Adsorption Kinetics

The results of the kinetic experiments with varying adsorbent concentrations for which plots are not presented here. It has been found that the amount of Zn (II) adsorbed per unit mass of adsorbent decreases as the adsorbent mass increase for both systems. Several other investigators have also reported the same trend of adsorbent concentration effect on metal ion adsorption [3]. Although the number of adsorption sites per unit mass of

an adsorbent should remain constant, independent of the total adsorbent mass, increasing the adsorbent amount in a fixed volume reduces the number of available sites as the effective surface area is likely to decrease

3.4. Effect of Temperature on Zn(II) Adsorption Kinetics and Thermodynamics Study

To observe the effect of temperature on the adsorption capacity, experiments were carried out in three different temperatures of 30℃, 50℃ and 70℃ for a fixed initial metal ion concentration of 50 ppm for which plots are not presented here. It was found that with the increased in temperature, adsorption capacity decreased for both the systems. This is mainly because of decreased surface activity suggesting that adsorption between metal ion and clay minerals was an exothermic process. With increasing temperature, the attractive forces between the clay surfaces and metal ion are weakened and then sorption decreases. This may be due to a tendency for metal ion to excape from the solid phase of clay to the liquid phase with an increase in temperature of the solution. The values of Gibbs free energy (ΔG^0) have been calculated by knowing the value of the enthalpy of adsorption (ΔH^0) and the entropy of adsorption (ΔS^0) which are obtained from the slope and intercept of a plot of log (q_e/C_e) versus 1/T (not shown here).

All these thermodynamic parameters are presented in **Table 1**.

3.5. Zn(II) Adsorption Kinetic Models & Isotherm

In this study, the two most widely used kinetic models; pseudo-first-order and pseudo-second-order were employed which are described in earlier section. In the pseudo-first-order model, the rate constant k_1 and correlation coefficient, R^2, were determined by plotting log ($q_e - q_t$) against time, t for both systems (not presented) with very poor regression coefficient, R^2 with range of 0.15 to 0.74 for various physicochemical parameters. Moreover, the pseudo-first-order kinetic model predicts a much lower value of the equilibrium adsorption capacity than the experimental value for this system and hence it gives the inapplicability of this model. But the pseudo-second-

order kinetic model is fitted very well with very high regression coefficient (R^2) which is shown in **Table 2**. The pseudo-second-order rate constant, k_2, equilibrium sorption capacity, q_e and initial rate constant, h were calculated for these systems from the fitted model equations which are tabulated in **Table 2**. Higher correlation coefficients (R^2) with respect to fitted pseudo-first-order model suggest that adsorption of zinc metal ion on clay minerals follow Pseudo-second-order.

The most commonly used technique for identifying the mechanism involved in the sorption process is by fitting the experimental kinetic data with intraparticle diffusion plot (Equation (5)). It has been found that the adsorption plots (Which are not shown here) are not linear over the whole time range and can be separated into two-three linear regions which confirm the multi stages of adsorption.

The adsorption equilibrium data was fitted with Langmuir and Frenundlich isotherms within the metal ion concentration range of 30 - 90 ppm respectively. Linear regression was used to determine the most fitted isotherm. The Freundlich adsorption isotherm can be expressed as [10]

$$\ln q_e = \ln K_f + 1/n \, (\ln C_e) \tag{8}$$

where q_e is the amount of metal ion adsorbed atequili-

Table 1. Thermodynamic parameters for zinc adsorption at different temperatures.

System	Temperature (℃)	ΔG^0 (kJ·mol^{-1})	ΔH^0 (kJ·mol^{-1})	ΔS^0 (j·mol^{-1}·K^{-1})
Zn-Kaolin	30	2.18	−0.228	−0.0072
	50	2.10	−0.228	−0.0072
	70	2.24	−0.228	−0.0072
Zn-Bentonite	30	0.065	−0.268	−0.0011
	50	0.087	−0.268	−0.0011
	70	0.109	−0.268	−0.0011

Table 2. Pseudo-second-order kinetic parameters.

System	System parameters	k_2 (g/mg.min)	q_e (mg/g)	H (mg/g.min)	R^2
Zn-kaolin	Initial Zn(II) concentration				
	30.00 ppm	0.0143	25.4	9.25	0.999
	50.00 ppm	0.0250	28.4	20.0	0.999
	70.00 ppm	0.0071	37.3	9.80	0.998
	Kaolin dosages				
	0.01 g	0.0329	28.4	26.0	0.998
	0.02 g	0.0535	13.0	9.61	0.996
	0.03 g	0.0253	9.09	2.05	0.9
	Temperature				
	30℃	0.0358	27.5	27.7	0.999
	50℃	0.0271	24.9	16.2	0.999
	70℃	0.0066	21.3	2.88	0.9
Zn-bentonite	Initial Zn (II) concentration				
	30.00 ppm	0.0090	30.9	8.69	0.9
	50.00 ppm	0.010	41.6	18.3	0.995
	70.00 ppm	0.002	57.1	7.63	0.999
	Bentonite dosages				
	0.01 g	0.013	45.2	27.7	0.9
	0.02 g	0.440	19.4	166.62	0.9
	0.03 g	0.022	9.85	2.19	0.990
	Temperature				
	30℃	0.013	36.2	17.1	0.990
	50℃	0.0197	35.9	24.9	0.997
	70℃	0.0194	30.0	17.5	0.9

brium time, C_e is equilibrium concentration of nickel metal ion in solution. K_f and n are isotherm constants which indicates the capacity and the intensity of the adsorption respectively and can be calculated from the intercept and slope between ln q_e and lnC_e which are shown in **Table 3** for both the systems. The Freundlich plots are not shown here.

Also Langmuir isotherm equation was also fitted for both the system with this same metal ion concentration range. The linearized form of Langmuir can be written

$$C_e/q_e = (1/K_a q_m) + C_e/q_m \qquad (9)$$

The Langmuir constants, q_m (maximum adsorption capacity) and K_a (values for Langmuir-2) can be obtained from plots between C_e/q_e versus C_e which are shown in **Figure 3** & **Figure 4** respectively with fixed initial conditions. The maximum adsorption capacity of Zn (II), q_m and constant related to the binding energy of the sorption systems, K_a is calculated which are 56.49 mg/g and 0.0437 for Zn-kaolin and 62.5 mg/g and 0.0648 for Zn-bentonite respectively. Overall Langmuir isotherm model had higher regression coefficient (R^2) compared to the Freundlich isotherm model for both the systems.

A further analysis of the Langmuir equation can be

Table 3. Freundlich parameters obtained from Freundlich plots. Amount of iron oxide and also kaolin added = 8 mg; pH 4.5; Temperature = 28℃; Shaker speed = 120 rpm.

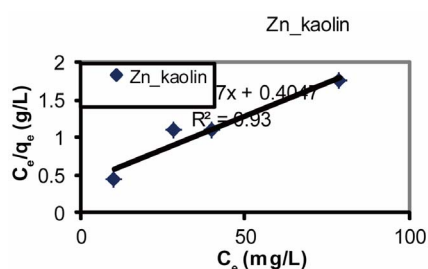| Adsorbent	Freundlich constants		
	K_F	n	R^2
Kaolin	9.58	2.92	0.874
Bentonite	7.69	1.75	0.994

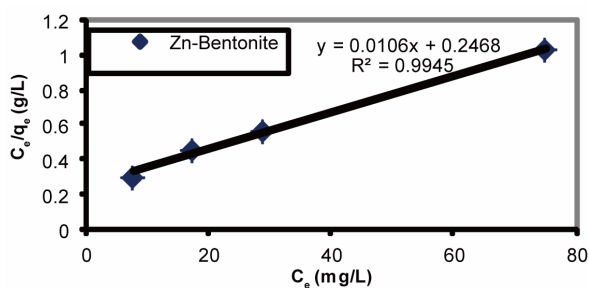**Figure 3. Langmuir plot Zn-Kaolin system.**

Figure 4. Langmuir plot for Zn-bentonite system.

made on the basis of a dimensionless equilibrium parameter, R_L, also known as the separation factor, given by (Sen & Gomez, 2011)

$$R_L = \frac{1}{1 + K_a\ C_0} \qquad (10)$$

where K_a is the Langmuir constant and C_0 is the initial metal ion concentration (mg/L). The separation factor, R_L has been calculated from Langmuir plot. It has been found that the calculated range of RL values from 0.432 to 0.202 for Zn-kaolin and 0.339 to 0.146 for Zn-bentonite system with the initial metal ion range of 30 to 90 ppm. These R_L values indicates favourable adsorption as it lie in the range $< 0 < R_L < 1$ [2]. The maximum Langmuir adsorption capacity of bentonite was more than kaolin.

4. Conclusions

The results obtained in this study demonstrated that kaolin and natural bentonite both can be used as an excellent natural adsorbent to remove Zn (II) from wastewaters with good efficiency and low cost. The amount of metal ion Zn (II) adsorption on both clay minerals was found to increase with increase in initial metal ion concentration and contact time but found to decreases with an increase in amount of adsorbent and temperature. The maximum adsorption capacity of bentonite was found to 62.5 mg/g with an initial Zn(II) concentration range of 30 to 90 ppm, whereas for kaolin it was 56.49 mg/g with the same metal ion concentration range. Kinetic experiments clearly indicated that sorption of Zn (II) on both kaolin and bentonite is a two steps process: a rapid adsorption of metal ion to the external surface followed by intraparticle diffusion into the interior of adsorbent which has also been confirmed by intraparticle diffusion model. Overall the kinetic studies revealed that adsorption process followed the pseudo-second-order kinetics model. The Langmuir isotherm model was applicable for both systems. The constant value, R_L (low separation factor) in Langmuir isotherms indicated that there was favourable adsorption for both systems. Finally thermodynamic parameters were determined at three different temperatures.

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