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Research Article

Kinetics and Thermodynamics study of Zinc Ions Adsorption onto the modified Nanobentonite

Shahab. A. Nasseri[#,!] *, Ali .I. Yagubov[#], Abdolali. A. Alemi[!] And Ali. N. Nuriev[#]

[#]Institute of Catalyze and Inorganic Chemistry named after academician M. F. Nagiyev of Azerbaijan National Academy of Sciences, Baku, Azerbaijan
[!]Department of Inorganic Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran

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Abstract

Heavy metal pollutants are known as the most serious toxic sources. Therefore, removal of heavy metal contaminations has become the global concern. Adsorption has recognized as an appropriate method for water treatment. In this study, adsorption of zinc ions onto the Na- and Ca- forms of heat-treated nanobentonite were considered by using model solutions in static-batch mode. The modified adsorbents were characterized by emission electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDX). Experiments were investigated with certain characteristics such as adsorption efficiency, thermodynamics and initial concentrations (C_0) in static batch conditions. The thermodynamic parameters such as $\Delta S°$, $\Delta H°$ and $\Delta G°$ were examined in various temperature (20-60°C) The results admit strongly the adsorption process was endothermic and spontaneous.

Keywords: *Modified nanobentonite, Adsorption, Heavy metal ions, Thermodynamic*

1. Introduction

Nowadays, industrial activities such as electroplating, fabrication of batteries, pharmaceutical industry and mining cause lots of environmental ruin. Heavy metal ions existence in nature have both natural and human source side effects also it can be harmful for health (D. Xu *et al*,2008;D.C.K. Ko, *et al*,2005). Natural and treated waters are contaminated with several heavy metals. Heavy metal ions are non-degradable, therefore, existence of this kinds of pollutant could be lead to the major concern (N.A. Badawy *et al*,2009; A. Demirbas,2008). Different techniques have been applied to eliminate the toxic metal ions from aqueous solutions, include precipitation, coagulation,flotation, sedimentation, adsorption, membrane processes, electrochemical techniques, ion exchange, biological processes and chemical reactions (J.P.Chen *et al*,2001; H .Cheng *et al*,2012). The adsorption process is one of the best methods for the removal of trace concentrations of metal ions from wastewater. Many mechanisms have been studied for metal ion adsorption, such as cation-exchange(N.A.Badawy *et al*,2009), surface complexion (P. Chen *et al*,2001), surface-induced precipitation (A.H. Schneider *et al*,2001), surface co-precipitation(A. Demirbas *et al*,2008), colloid formation at surface and diffusion into particle microproes(H .Cheng *et al*,2012). During the adsorption process a thick film correspond with forming one or several diameters of metal ions. Absorbed molecules could be localized or movable. It means that they are either hold in definite lattice areas and easily change their location. Particles of dissolved substances get to the pores of sorbent grain by diffusion through the pore on its outer surface. For example the presence of metal ions such as copper, zinc, cadmium, lead, mercury, iron and nickel depicts adversarial effects when metal ions exist massively in a solution (A. Demirbas *et al*,2008). Also Zinc is a kind of ions used vastly in various industrial applications such as dry battery, electroplating industry, insecticides, foundry, metallurgy, pigments and explosive manufacturing. The high amount of zinc could be actuated to depression, lethargy and enhanced thirst and neurologic symptoms such as seizures and ataxia. Applying adsorption process to zinc elimination known such an effective method and also it could be economic by using of authentic low-cost adsorbent like bentonite (H. Zhang *et al*,2001).

Bentonite is natural and polysillicate mineral clay. Bentonite possess high cation exchange rate and lots of host position of adsorbing ions which tend to considered this clay as an acceptable candidate to metal ion adsorption (D.Xu *et al*,2008; A.L.Iskander *et al*,2011). Its structure can be explained as a framework of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedron linked to each other's corners by sharing atoms. More negative charges and cation exchange capacity can be achieved

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*Corresponding author: **Shahab. A. Nasseri** by the substitution of Si in tetrahedral sites. Bentonite is a 2:1 mineral clay with layer arrangement that included one and two silica sheets. Meanwhile, Layers are kept together with Vander Waals forces, so water molecules can easily penetrate between layers, also cations balance the deficiencies. Furthermore, Bentonite has intermediate characteristics for Zinc adsorption. Zinc ion adsorption is a critical issue in soil properties that can be affected by various parameters such as pH and surface area (A.L. Iskander *et al*,2011).

Although a lot of studies have been focused on Zn (II) removal by bentonite, there is still potential research space for improving Zn (II) adsorption performance of bentonite due to the relatively low adsorption capacity of natural bentonite. Therefore, investigation on Zn (II) removal by using modified bentonite could be helpful. For this purpose, Na-bentonite and Ca-bentonite were used. Na-bentonite has the ability to absorb large amounts of water and form viscous, thixotropic suspensions but Ca-bentonite has lower water adsorption, swelling capabilities and the inability to stay suspended in water (M.Ç.Karakaya *et al*,20011). Due to lower water adsorption of Ca-bentonite, containing moisture in saturated state is much lower than Na-bentonite (I.Dananaj *et al*,2005).

The objective of the present work is to investigate the adsorption potential of Na- and Ca- forms of heat-treated nanobentonite in the removal of Zn (II) ions. Generalized rate constants, thermodynamic parameters such as ΔH°, ΔS° and ΔG° of adsorption of zinc ions were calculated. Also the equilibrium and kinetics adsorption of Zn (II) ion onto the modified nanobentonite has been investigated.

2. Experimental

2.1 Materials

Analytical grade of zinc chloride ($ZnCl_2$), purchased from Merck Co., was used as adsorbate in adsorption studies. Bentonite was obtained from Dash-Salahli deposit of Azerbaijan. The characteristics demonstrate as Table 1. In all experiments, pH adjustments were done by using 0.1N hydrochloric acid (HCl) and 0.1N sodium hydroxide (NaOH).

Table 1 Bentonite characteristics

Characters	value
Density	2.22 g/cm^3
SiO_2:Al_2O_3 ratio	5.7:2.1
Exchange cations, meq/100g sorbents (Na^+(K^+))	49.80
Exchange cations, meq/100g sorbents (Ca^{2+}(Mg^{2+}))	43.20
Total capacity meq/100g sorbents	93.00

2.2 Adsorbent preparation

The farmer bentonite purification is carried out as the first step of bentonite preparation with specified volume of HCl solution. Second step is calcination at 600°C for 2h and the latter prepared bentonite was mixed in ball mill (MM400 RETSCH) for 10 hours due to gain bentonite particles in equal size.

2.3 Characterization

Heat-treated form of Na-bentonite and Ca-bentonite were characterized by Scanning Electron Microscope ((SEM) TESCAN MIRA 3) and Energy dispersive X-ray spectroscopy analysis (EDS). Meanwhile, Initial concentration and equilibrium concentration of zinc ions were determined by using UV-vis spectrophotometer (SF-26) and atomic-adsorption, Perkin-Elmer 180.

2.4 Adsorption kinetics and thermodynamics experiments

Experiments were carried out under static conditions on modified bentonite samples. Certain amounts of the sorbent were put in a thermostatic glass bottle which was contained 100 ml zinc chloride solution with a specified concentration. Sorbent solution was mixed with a blade glass mixer in an appropriate rate of stirring which all the particles could be weighted in a solution. According to the experimental results boundary of 7.80±0.05 was identified as the best pH for zinc ions adsorption onto the bentonite (H. Zhang *et al*.2011). Consequently, Kinetics and thermodynamics studies were examined at 20-60°C on different initial concentrations for considering zinc adsorption onto the Na- and Ca- forms of heat-treated nanobentonite ($2/58\times10^{-5}$– $8/37\times10^{-4}$ mol/L) from model solutions at pH 7.80±0.05. Adsorption efficiency was investigated at different temperatures (293.2, 298.16, 303.1, 323.2, 333.1 K) and identified pH (7.80±0.05).

3. Results and discussions

3.1 Theoretical calculation

In order to study the kinetics of ions adsorption, Johnson-Mehl-Avrami-Erofeev-Kolmogorov equation was considered as a base of calculations by using Sakovich ratio (J. Farjas *et al*,2006; A.Khawam *et al*,2006). Although, this was developed by Avrami later in 1930, other workers were at the same time developing the equal relationships and so the model is now referred to as the Johnson-Mehl-Avrami-Erofeev-Kolmogorov or JMAEK model. The JMAEK equation is expressed by equation (1) (V.M. Gorbachev,1978):

$$\alpha = 1 - \exp(-(Kt)^n) \tag{1}$$

where α is reached fraction, n is the Avrami exponent, K is the temperature-dependent rate constant. Generalized rate of adsorption (K) was calculated by Sakovich ratio as follow (N.A.Badawy *et al*,2009):

$$K = n \cdot k^{\frac{1}{n}} \tag{2}$$

where k is the constant rate of adsorption process and n is a constant which depends on condition of experiment and mechanism of interaction between adsorbed ions onto the sorbent ($0< n \leq 1$).

Temperature dependences of ions adsorption rate onto the bentonite as an adsorbent in adsorption process are well described by the following equation (3):

$$\ln K = \frac{C-d}{T} \tag{3}$$

where, K is known as a constant rate of adsorption (c^{-1}), T is absolute temperature (K); C and d are constants. Adsorption studies of heavy metal ions have been conducted to calculate the distribution coefficient (K_d), which is regarded as a standard parameter in the assessment of the physicochemical behavior of metal ions between solid and liquid phases. It is calculated as equation (4) (A.Moreale *et al*,1979):

$$K_d = \frac{C_{init} - C_{P,\infty}}{C_{P,\infty}} \times \frac{V}{m} \tag{4}$$

where V (L) is the volume of solution and m (g) is the weight of adsorbent. C_{init} and $C_{p,\infty}$ (mg/L) are initial concentration and equilibrium concentration at different temperatures. M (g) is amount of adsorbent. The separation factor describes the selectivity of adsorption of two metal ions.

Following equation obtains distribution coefficients of metal ions at equilibrium:

$$\ln K_d = a + b \times \ln C_{P,\infty} \tag{5}$$

where K_d (ml/g) is distribution coefficient of metal ions at equilibrium condition in the system; a and b are constants which relate to the pH value and initial temperature of solution, respectively. These parameters were calculated by using least squares method. Which are presented in Table 3.

Thermodynamic parameters are calculated by using the following equation (S.A. Khan *et al*,1995):

$$\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{6}$$

Enthalpy (ΔH°), entropy (ΔS°) and temperature (T) in Kelvin are the most important parameter in thermodynamic studies. Additionally, R is recognized gas constant ($8.314*10^{-3}$ Kj/(K mol)). The values of enthalpy (ΔH°) and entropy (ΔS°) obtained from the slope and intercept of ln$K$ vs. $1/T$, which are calculated by a curve-fitting program.

Change in free energy (ΔG°) of specific adsorption is determined from the well-known equations represented below (M.J.Angove *et al*,1997):

$$\Delta G^o = -RT \ln K_d \tag{7}$$

$$\Delta G^o = \Delta H^o - T\,\Delta S^o \tag{8}$$

where K_d is distribution coefficient constant, T is absolute temperature, R the universal gas constant ($8.314*10^{-3}$ Kj/(K mol)). According to the value of Gibbs energy in various rang of temperature it would be considered the adsorption process is spontaneous or not. When ΔG^o values be negative due to increase temperature, process is also identified as a spontaneous process. On the other hand, positive values would be demonstrated opponent mechanism.

According to explore the general regularities in the adsorption of zinc ions onto the adsorbents, the constant parameters such as *"a"* and *"b"* which represent initial solution and temperature were investigated. As equation 9 represents adsorption of zinc ions in system with Na- and Ca- forms of bentonite is determined as following:

$$\ln K_d = \frac{13.49 - 0.25\ln C_{p,\infty} - 13361 - 98.1\ln C_{p,\infty}}{T} \tag{9}$$

However, coefficient distribution could be calculated by equation (10):

$$\ln K_d = \frac{4.71 - 1.80\ln C_{init.} - (1229 - 303\ln C_{init.})}{T} \tag{10}$$

3.2. Characterization of bentonite

3.2.1 SEM

SEM images shows the morphology of Na- and Ca- forms of heat-treated nanobentonite which have been presented in Fig.1 a and b, respectively. It can be observed that nanobentonite samples include various phases and particles size distribution about less than 200 nm.

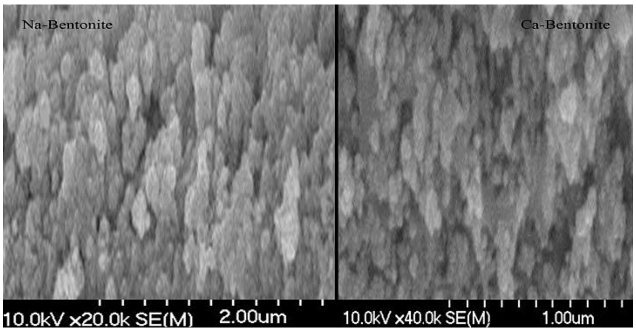

Fig. 1 SEM images of Na- (a) and Ca- (b) forms of heat-treated Nanobentonite

3.2.2. EDS

Fig.2 demonstrates the spectrum of Na-form of heat-treated nanobentonite which attained by EDS. Spectrum shows traces of aluminum (Al), silicon (Si), carbon (C), oxygen (O) and sodium ions which caused to be known this clay is Na-form of bentonite. Meanwhile, mineral aluminum silicate has a majority element content of Aluminum (Al), Silicon (Si). This is confirmed by EDS results.

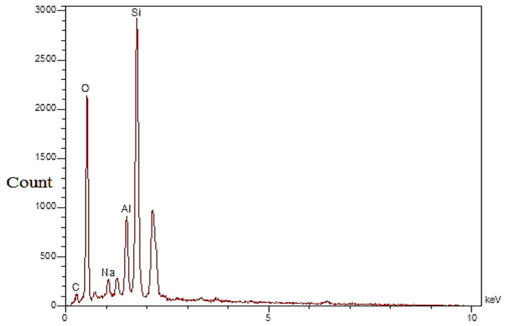

Fig. 2 EDS spectrum of Na-form of heat-treated nanobentonite

3.3 Kinetics studies

Fig.3 shows lnK_d versus ln$C_{P,\infty}$ for determining zinc ions adsorption onto the modified forms of Na-bentonite and Ca-bentonite at different concentration of adsorbate. The results illustrate that when contaminant concentration are reduced; consequently, distribution of ions were increased onto the surface of sorbent. It means that low ion concentration has depicted higher removal. By analogy, Na-Bentonite possesses higher efficiency because of having advanced distribution coefficient in various concentrations.

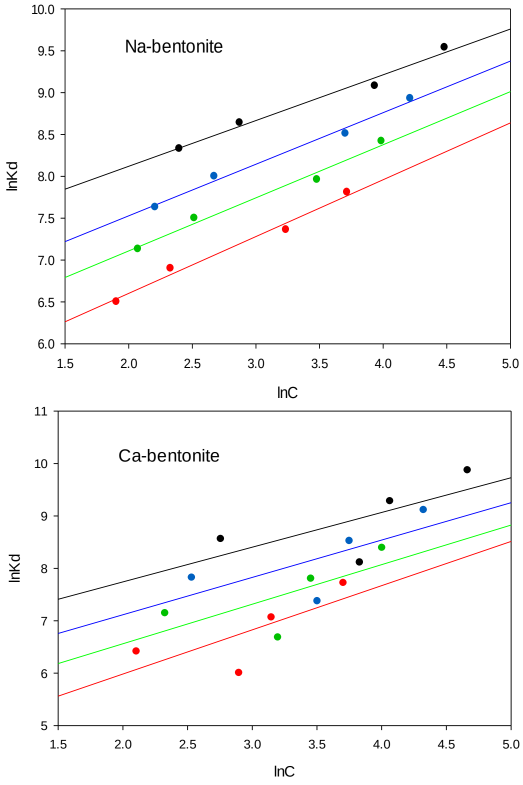

Fig.3 ln$C_{P,\infty}$ vs. lnK_d adsorption zinc ions onto two absorbents at different concentrations (mol/L): 2.58×10^{-5} (black), 7.54×10^{-5}(blue), 1.77×10^{-4} (green) and 8.37×10^{-4} (red)

According to the Table 2 values of "a" and "b" have been calculated by regression method. Experiment demonstrations that the temperature rises, affects values irregularly.

Table 2 The constants of initial solution and temperature at four different temperatures

Sorbents	*T*, K	*a*	*B*
Na-bentonite	293.2	-0.59±0.10	2.26±0.92
	303.1	-0.60±0.10	2.46±0.93
	323.2	-0.55±0.06	3.20±0.66
	333.1	-0.54±0.05	3.70±0.47
Ca-bentonite	293.2	-0/58±0.09	2.24±0.92
	303.1	-0.56±0.07	2.42±0.92
	323.2	-0.54±0.07	3.30±0.67
	333.1	-0.55±0.51	2.26±0.51

3.4. Thermodynamic studies

Entropy and enthalpy values were calculated by using temperature dependences of equilibrium distribution coefficient. It is very common to quote thermodynamic parameters for a standardized set of environmental parameters, or standard conditions which are typically temperature of 298K and a pressure of either 1atm or 101/3kPa so some of the experiments were done at 298/16 K. Table 3 illustrates the values of Gibbs energy, constant parameters which depends on entropy and enthalpy at different temperatures and initial concentrations. According to the calculated ΔG^o values for zinc ions adsorption onto the Na-bentonite and Ca-bentonite adsorbent, the process is considered as a nonspontaneous reaction.

Table 3 Thermodynamic Values of Na-bentonite and Ca-bentonite for adsorption of zinc ions

Sorbent	**C $^*_{\text{init}}$ (mol/L)**	**Constants**		**ΔG° kJ/mol**
		D	**C**	
Na-bentonite	2.58×10^{-5}	-4.01	1287.03	20.04
	7.54×10^{-5}	-7.56	173.97	20.25
	1.77×10^{-4}	-10.25	716.85	19.53
	8.37×10^{-4}	-6.86	392.01	20.31
Ca-bentonite	2.58×10^{-5}	-7.19	414.20	21.31
	7.54×10^{-5}	-7.22	239.78	19.95
	1.77×10^{-4}	-10.02	588.61	19.96
	8.37×10^{-4}	-7.84	174.86	20.87

$C^*_{\text{init.}}$ - Initial concentration of zinc ions in solution

Enthalpy is known as a thermodynamic potential. It is a state function and an extensive quantity. The total enthalpy (H) of a system cannot be measured directly; therefore, differential values of first and last enthalpies (ΔH°) is recognized as an useful quantity than its absolute value. The change in enthalpy is positive in endothermic reactions and negative in heat-releasing exothermic processes (V. Wylen *et al*,1985). It could be understood from Table 4 that the positive values of ΔH° indicate the endothermic behavior of the adsorption and suggest a large proportion of heat is consumed to transfer Zn (II) ions from aqueous into the solid phase. The transition metal ions must give up a larger share of their hydration water before they could enter the smaller cavities (D.Xu *et al*,2008). The results illustrate that uptake of these metal ions is favored with increasing temperatures, since a higher temperature activates the metal ions for enhancing adsorption at the coordinating sites of the minerals. Also, it is mentioned that cations move faster with increasing temperature (B. Owolabi *et al*,2010).

In addition, Entropy is an extensive thermodynamic parameter that is known as criterion for adsorption system as the aspect of thermodynamic behavior. The experiments illustrate that changes in entropy was positive; therefore, it was considered the entropy grows during the adsorption process (H.S.J.Tsao *et al*,1992). Entropy values could be seen in Table 4. The results show entropy decline slightly by increasing the initial concentration. In addition, the positive values of ΔS° demonstrate that Zn (II) ions are less hydrated in the bentonite layers than in the aqueous solution. Also, the positive values of ΔS indicates that disorientation increased in the system. As a result, the distribution of rotational and translational energy among the small number of molecules will rise by increasing adsorption (E.I. Unuabonah *et al*,2007; J. A.Hefne *et al*.2008).

Table 4 Thermodynamics values of zinc ions adsorption onto the heat treated bentonite

Sorbents	C $^{*}_{init.}$, mol/L	ΔH°, kJ.mol^{-1}	ΔS°, J mol·grad.$^{-1}$	ΔG°, kJ.mol^{-1}
Na-bentonite	2.58×10^{-5}	23.72	147.69	-20.30
	7.54×10^{-5}	23.29	143.37	-19.41
	1.77×10^{-4}	25.03	144.70	-18.26
	8.37×10^{-4}	25.67	104.20	-15.42
Ca-bentonite	2.58×10^{-5}	39.31	197.41	-19.51
	7.54×10^{-5}	39.43	193.89	-18.42
	1.77×10^{-4}	31.57	166.01	-17.81
	8.37×10^{-4}	21.86	125.72	-15.58

By combining entropy, temperature and enthalpy thermodynamic behavior of adsorption system is investigated. On the one hand, the negative value of ΔG° indicates the spontaneous reaction and on the other hand positive value of ΔG° demonstrates a non-spontaneous reaction. Consequently, the calculated ΔG° show the adsorption of zinc ions onto the heat treated Na- bentonite and Ca-bentonite was a spontaneous process and the increase of ΔG° values with increase of temperature indicates the desirable adsorption process at higher temperatures (J. He *et al*, 2010; R.Huang *et al*,2011).

Fig.4 illustrates the value of lnK_d against temperature of zinc ions adsorption onto the Na- and Ca-nanobentonite for various concentration of zinc ions. It can be seen from the results that ln K_d value of Na-bentonite decreased by reducing the temperature, but, by contrast ln K_d value of Ca-bentonite increased due to temperature growth.

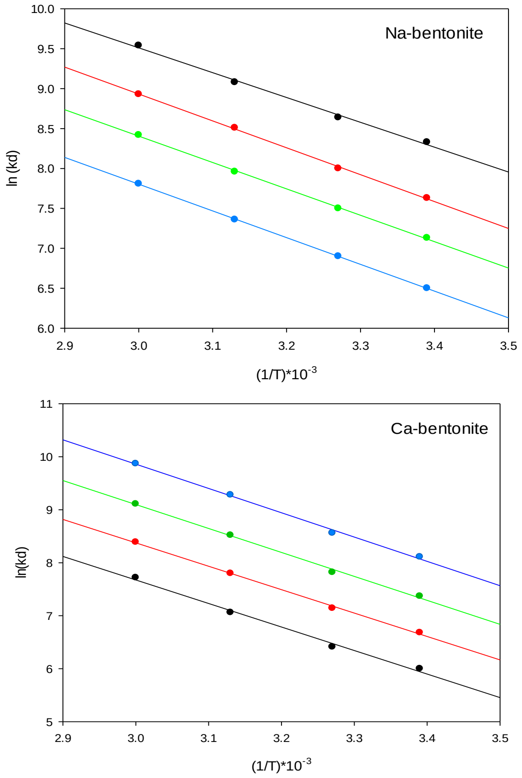

Fig. 4 Temperature dependences of equilibrium distribution of zinc ions adsorption onto the two sorbents. Zinc ions concentration of (mol/L): 2.58×10^{-5} (blue), 7.54×10^{-5}(green), 1.77×10^{-4} (red) and 8.37×10^{-4} (black) (mol/L)

Conclusion

In this study, kinetics and thermodynamics were investigated for the adsorption of zinc ions by using bentonite adsorbents. Bentonite adsorbents are categorized as Na- and Ca- forms. The amount of ion adsorbed onto the bentonite substrate were demonstrated equal capacity of zinc adsorption approximately. It was found that kinetic and thermodynamic parameters for both sorbents on adsorption of zinc ions differ slightly from each other. The main reason for the variation between two kinds of bentonite can be associated with acceptor sites. Meanwhile, the mono-cation forms play an important role.

The negative values of ΔG° indicates the zinc ion adsorption as a spontaneous process; the positive values of **ΔH°** demonstrates an endothermic adsorption. In addition, positive value of ΔS° shows that randomness will increase at the solid-solution interface during the process of adsorption. To sum of briefly, heat treated Na-bentonite and Ca-bentonite are known as suitable adsorbents in high temperature condition.

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