

Zn(II) removal using natural bentonite: Thermodynamics and kinetic studies

O.A. ALDAYEL¹, N.M. ALANDIS², W.K. MEKHEMER²,
J.A. HEFNE¹ and S. AL-RADDADI¹

¹King Abdulaziz City for Science & Technology, P.O. Box 6086 Riyadh - 11442 (Saudi Arabia)

²King Saud University, P.O. Box 11495, Riyadh - 11452 (Saudi Arabia)

(Received: April 10, 2008; Accepted: June 16, 2008)

ABSTRACT

This paper describes the adsorption of Zn(II) from aqueous solutions by commercial natural bentonite (NB). The contact time, pH of the solution, metal ion concentration, Temperature, adsorbent doses, bentonite treatment (calcinations of NB at 700°C and washing by deionized water to remove the excess salt from bentonite surface) on the adsorption process were examined. The washed and calcined bentonite samples were labeled by WB and CB respectively. The adsorption process follows pseudo-second-order reaction kinetics. The Langmuir and Freundlich models were used to describe the adsorption equilibrium of zinc on NB and the adsorption followed the Langmuir isotherm. The Langmuir and Freundlich constants for adsorption of zinc on NB were determined. This work discusses the thermodynamic parameters of the adsorption (the Gibbs free energy, entropy, and enthalpy). Our results demonstrate that the adsorption process was spontaneous and endothermic under natural conditions. The results show that adsorption behavior of NB was strongly depending on the pH. The optimum pH for adsorption was found to be 6.0. Also the adsorption capacity of NB for Zn (II) increases with increased bentonite dose. The adsorbed amount of Zn (II) on WB was increased by 100% compared NB and CB. The results generally showed that bentonite could be considered as a potential adsorbent for Zn(II) removal from aqueous solutions especially WB.

Key words: Heavy metals; adsorption; isotherms; natural bentonite; kinetics; thermodynamics ; heat treatment; desorption.

INTRODUCTION

Main industries containing heavy metals in discharged waters are mining, metal coating and battery production¹. Zn(II) is among the most common heavy metal in these wastewaters. Zn(II) being in the list of priority pollutants proposed by Environmental Protection Agency (EPA) gives rise to serious poisoning cases. The main symptoms of zinc poisoning are dehydration, electrolyte imbalance, stomachache, nausea, dizziness and in coordination in muscles². Therefore, the removal of excess heavy metal ions from wastewater is essential to protect human and environmental health. As a result, the removal of toxic heavy metal ions from sewage and from industrial and mining effluents has been widely studied in recent years.

Although there are many adsorbents used in adsorption methods, active carbon is the most common one used in wastewater treatment all over the world³. However, its high cost causes restrictions in use⁴. For this reason, many studies have been carried out in order to find out effective and low cost adsorbents⁵⁻¹⁵. Natural clay is evaluated as an appropriate adsorbent due its low cost and high removal efficiency. Their sorption capabilities come from their high surface area and exchange capacities. The negative charge on the structure of clay minerals gives the capability to attract metal ions⁴.

Montmorillonite and kaolinite were used for removal of lead and cadmium¹⁶. It was determined that adsorption capacity of lead and cadmium is greater on montmorillonite (Pb: 0.68, Cd: 0.72 mg/

g) than on kaolinite (Pb:0.12, Cd:0.32 mg/g). In another study, removal efficiency of 52.91 mg/g was obtained for zinc removal using bentonite, another type of clay¹⁷.

The adsorption of Zn(II) ions on montmorillonite was also evaluated¹⁸. Since the ionic potential of zinc is higher than cadmium, its hold is stronger on montmorillonite than cadmium. Chantawong *et al.*, studied adsorption of lead on clay consisting mainly kaolin and illite¹⁹. In the study, it is confirmed that the adsorption efficiency increases with increase in pH. Nevertheless, presence of co-ions such as Cd^{2+} , Cr^{6+} , Cu^{2+} , Ni^{2+} and Zn^{2+} reduces the lead uptake from aqueous solutions due to the fact that the co-ions bind strongly with organic matter present in clay to form a complex.

Bentonite, consisting of clay, silt and sand, was also used in zinc removal¹⁷. The sorption process usually follows the Langmuir isotherm. In another study, it was reported that adsorption capacities of 20 mg of Pb^{2+} /g were achieved by bentonite at pH 3.4^{20,21}.

Besides providing high removal efficiency in heavy metal removal from waste streams, clay is an appropriate adsorbent with its low cost. Among the main factors of choosing adsorbent in wastewater treatment, the cost and the availability come after the efficiency. Clay is a natural substance widely available and abundant in Saudi Arabia. In this study, natural commercial bentonite was used for removing zinc from aqueous solutions. In order to determine the reaction of heavy metals with

natural commercial bentonite, experimental results were applied to Langmuir, and Freundlich adsorption isotherms. Adsorption kinetics was applied in order to determine adsorption mechanism and adsorption characteristic constants.

MATERIAL AND METHODS

Instrumentation

Elemental concentration analyzed using a Perkin- Elmer Optima 5300 DV ICP optical emission spectrometer coupled with peristaltic pump and AS-93 plus auto sampler unit.

Chemicals

Zinc nitrate $\text{Zn}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Extra pure Merck) was used in adsorption experiments. PH adjustments were carried on using 0.1N hydrochloric acid (HCl) and 0.1N sodium hydroxide (NaOH). All Zn (II) solutions were prepared with ultra-pure water (specific resistivity of 18 MW. cm) obtained from an E-pure (Barnstead, USA) purifier system. Super purity nitric acid (*SpA*, 68%) purchased from ROMIL Ltd., UK was used for sample preparation. Single element ICP Standard solutions from MV Laboratories INC. (USA) were used for system calibrations.

Adsorbent

NB was characterized by X-ray diffraction (XRD) and chemical analysis. The chemical composition of the tested samples was as follows (wt %) SiO_2 40.43, Al_2O_3 15.87, CaO 2.80, K_2O 0.14, Na_2O 2.02, Fe_2O_3 10.86, MgO 3.32.

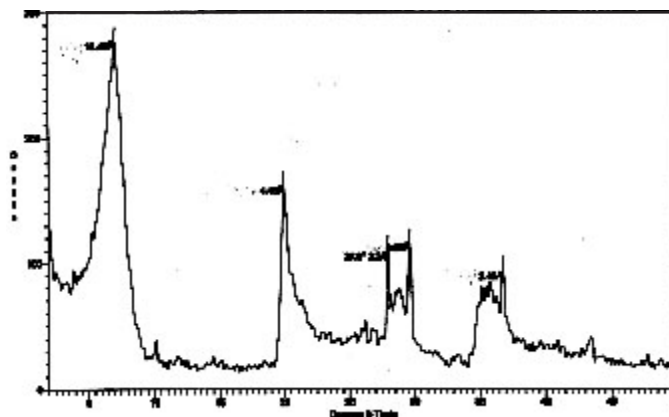


Fig. 1: The XRD patterns of the NB

Comparative XRD patterns of the natural commercial bentonite clay are shown in Fig. 1. The XRD patterns of this clay indicate that the dominant component is montmorillonite (68.74 %). The remaining components are feldspar (15.72%) and Calcite (15.723%).

Characterization of adsorbent

Commercial natural bentonite, grey in color, particles size ranged between 0.25- 0.0375 mm, was used. Bentonite sample was divided into three parts: first part used in the adsorption studies as received and labeled by NB; the second part was washed with distilled water several times to remove any dust and other water-soluble impurities. The washed sample was dried in an electric oven at 150–200 °C for several hours before use in the adsorption studies. The washed sample labeled by WB, and the third part was calcined in an oven at 700°C for 12 h. The hot sample was cooled down to room temperature over silica gel then ground and passed through sieves. The calcinations bentonite was labeled by CB and stored in sealed polyethene bags. (The particles size of WB and CB such as the particles of the received bentonite , NB, ranged between 0.25- 0.0375 mm). The specific surface area of NB was determined by applying the BET (Brunauer, Emmet, Teller) equation. The resulted surface area of NB, $S_{\text{NCB}} = 45.9 \text{ m}^2 \text{ g}^{-1}$ this values are lower than those expected for montmorillonites²², but it may be due to the lack of treatment. In fact, Bourg and Goldberg²³⁻²⁴ have measured, for a montmorillonite without pretreatment, specific surface areas of $18.6 \text{ m}^2 \text{ g}^{-1}$: it is possible that N_2 molecules can not penetrate easily the interlayer regions between the layer sheets, involving an underestimation of specific surface areas²⁵⁻²⁶.

EXPERIMENTAL

Adsorption of copper and zinc with NB was carried out in a batch reactor. 2000 mg/L of Zinc stock solution was prepared by dissolving 7.6 g of $\text{Zn}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in 1 L distilled water. Standard zinc solutions ranging between 40 and 2000 mg/L were prepared by diluting the stock solutions. The volume of the samples was determined to be 50 mL. The NB content is 0.5g. pH adjustments were carried out using 0.1N HCl and 0.1N NaOH. 200 rpm

stirring rate and 25 °C temperature were applied in the shaker. Samples with clay content were taken from the shaker after 24 h and the clay was separated by centrifugation. The concentration of zinc remained in the solution was analyzed using a Perkin- Elmer Optima 5300 DV ICP optical emission spectrometer coupled with peristaltic pump and AS-93 plus auto sampler unit.. In this study, the effects of several factors such as pH, concentration of solution, clay dosage, temperature, heat and washing treatment and contact time on zinc removal efficiency were examined. Equilibrium isotherms for zinc were obtained by performing batch adsorption studies. The adsorbed heavy metal amount (q_e) per unit absorbent mass was calculated as follows:

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

where C_o is the initial heavy metal concentration, C_e is the concentration of heavy metal at equilibrium (mg/L), m is the clay mass (mg) and V is the solution volume (L). Calculations were made by using these data and adsorption curves were obtained.

Effect of initial pH

The effect of pH on the sorption was studied by adjusting the pH in the range of 2–10. In these experiments, the NB loading was kept at 10 g/l of solution containing 100 mg/l each of $\text{Zn}(\text{II})$ at 25°C. The contact time (t) was kept as 2 h, since equilibrium was found to have been attained in 2 h contact time. Also the pH of NB suspension was measured before and after $\text{Zn}(\text{II})$ adsorption.

Kinetic studies

Kinetic studies for zinc were performed by using $\text{Zn}(\text{II})$ concentrations of 200 mg/L. Optimum conditions were used during these experiments. Temperature was 25°C and clay mass was 0.5 g.

Effect of temperature

The effect of temperature on adsorption isotherms was conducted under isothermal conditions at 20, 40, and 60 °C by maintaining the mixtures in a water circulation shaker bath whose temperature varied within ± 0.5 °C. The experimental procedures employed for studying the effect of

temperature on the adsorption isotherm of Zn(II) on NB were the same as those described in the above section. In order to assume maintaining thermal equilibrium, the bottles were first put into the temperature controlled shaker bath for about 1 h prior to the experiment.

Desorption studies

For batch desorption experiments, a series of 250 ml Erlenmeyer flasks containing 50 ml of deionized water was contacted with Zn-loaded NB (0.5 g) at 25 ± 1 °C. The mixtures were agitated at 150 rpm for 5 h in the orbital shaker. Thereafter, the mixture was centrifuged and the supernatant was analyzed for metal ions released into the water.

RESULTS AND DISCUSSION

Effect of pH

In order to investigate the effect of pH on zinc adsorption with NB, metal solutions of 100 mL in volume and 500 mg/L in concentration were used at pH ranging from 2 to 12. In the experiments, clay content was kept constant (0.5 g) and agitation time was determined to be 2 h at 200 rpm. The results are shown in Fig. 2. As can be seen from figure, adsorption capacity of NB increased when the initial pH of the solution was gradually increased from 2 to 6. After pH 6 a plateau was attained and the adsorption of Zn(II) by NB suddenly increased to 48 mg/g in the ranges of pH 8-12. These results are in agreement with other studies performed with montmorillonite²⁷⁻²⁹. The mechanisms that influence the adsorption characteristics of bentonites can be given by dissolution, ion exchange/adsorption, and precipitation²⁷⁻²⁸. From Fig. 2, the lowest Zn (II)

sorption rates were obtained at pH 2. This could be due to the increase in competition for adsorption sites by H^+ and dissolution of Al^{3+} ions from the aluminosilicate layers²⁹. Altin *et al.*²⁷ revealed that the removal efficiency of Pb^{2+} by montmorillonite decreased at low pH values (pH 2–4). The similar results were obtained by other researchers for some heavy metals such as Zn, Cd, Cu, Ni and Cr at pH 3²⁹.

The basic mechanism that governs the adsorption characteristics of bentonites at pH ranging between 2 and 6 is adsorption and ion exchange. At these pH levels, exchangeable cations present at the exchangeable sites, i.e. Na^+ , K^+ , Ca^{2+} and Mg^{2+} are exchanged for Zn^{2+} cations in the aqueous solutions. Sharp increase was observed for NB at high pH level (i.e. pH 8), which was due to the formation of zinc hydroxyl species. Depending on the pH and metal concentration, zinc may form complexes with OH^- , for example, $Zn(OH)_2$, $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$, at higher pHs and as a result, zinc hydroxyl species may participate in the adsorption and precipitate onto the bentonite structure¹⁷. Previous studies showed a similar behavior for other heavy metals^{30,31}.

Measuring the final pHs of the NB suspension before and after Zn(II) can give good information for revealing the above comments. Fig. 3. shows the final pH values at the end of the experiments.. As can be seen from this figure, increase in the final suspension pH after silver adsorption may be attributed to the replacement of alkaline and alkaline earth metals (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) located in the exchange sites of commercial

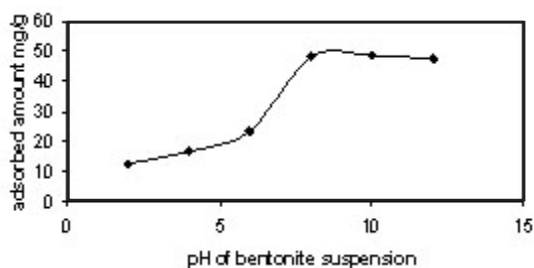


Fig. 2: Effect of pH on the removal of Zn (II) by NB, Initial metal concentrations 500 mg/L, clay dosage 1 g/100 mL, contact time 2 h

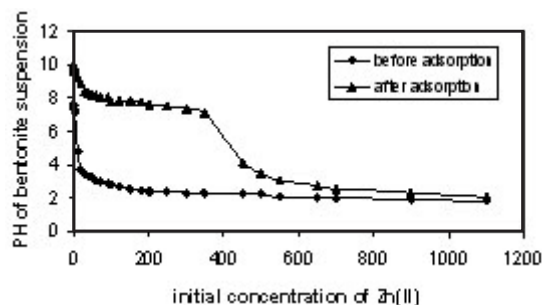


Fig. 3: pH of NCB suspension before and after Zn(II) adsorption on NB

bentonite (untreated) (NB) with silver ions existed in the solutions. Furthermore, carbonate, presented in the commercial bentonite (untreated, NB) structure, may also be dissolved.

Effect of clay dosage

In experimental studies carried on in order to determine the optimum clay dosage, solutions with an initial metal concentration of 500 and 1000 mg/L were used at natural pH values. During the contact time of 2 h, the amount of NB added to the solutions varied between 0.1 and 5 g. The results are shown in Fig. 4.

Increasing the mass of NB slightly increased the percentage adsorption of Zn(II) (Fig. 4). This is an expected result because as the amount of NB increases, the number of adsorbent sites increases; therefore, these particles attach more ions to their surfaces³²⁻³⁴. But the decrease in adsorbed amount with increasing the mass of NB (Fig. 5) can be attributed to the fact that some of the adsorption sites remain unsaturated during adsorption process; Nasseem and Tahir^{20, 21} reported

similar findings for Pb(II) removal from aqueous/acidic solutions by using bentonite as an adsorbent. After 3g addition of NB, the removal efficiency stays constant at 100% for two concentrations of Zn (II) solutions tested (500 and 1000mg/L). It also confirms the same observations by other investigators³⁴⁻³⁶.

Also it was observed, as Zn(II) concentrations increased, the adsorption % decreased. It is likely that a given mass of adsorbent material has a finite number of adsorption sites, and that as metal concentrations increase, these sites become saturated. That is, there is some metal concentration that produces the maximum adsorption for a given adsorbent mass, and thereafter, adding more metal cannot increase adsorption because no more sites are available: all are occupied. Another cause may have been a progressive decrease in the proportion of covalent interactions and an increase in the proportion of electrostatic interactions at sites with a lower affinity for heavy metals as the initial heavy metal concentrations increased.

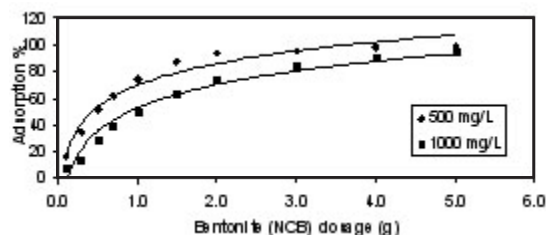


Fig. 4: Effect of clay dosage on the adsorption % of Zn(II) by NB. Initial metal concentrations 500 and 1000 mg/L, contact time 2 h.

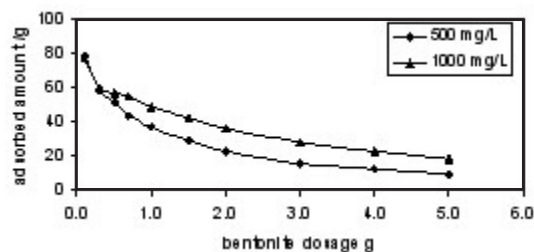


Fig. 5: Adsorbed amount of Zn(II) as function of NB. Initial metal concentrations 500 and 1000 mg/L, contact time 2 h.

Effect of agitation time

The agitation time was also evaluated as one of the most important factors affecting the adsorption efficiency. The effect of time on removal efficiency was analyzed. At the study carried out in a batch system, samples were taken at different time periods varying between 5 and 180 min, and the remaining concentrations were analyzed by the spectrophotometer. The optimum time for zinc removal was determined at 5 min (Fig. 6). As a result of the experimental studies, it is seen that high

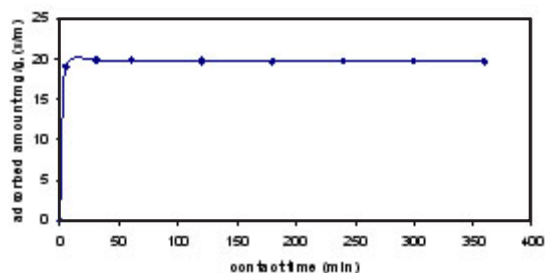


Fig. 6: Effect of contact time on Zn (II) adsorption onto NB Zn (II) concentration 200 mg/L, 25°C and NB dose = 10 g /L

efficiency for zinc adsorption can be obtained at short time periods.

The kinetic curves in Fig 7 (a, b). can be described by suitable kinetic models. The first kinetic model used is the Lagergren first-order model that was also used for the analysis of adsorption kinetics³⁷:

$$\frac{dq_M}{dt} = k_1(q_e - q_M) \quad \dots(2)$$

where k_1 is the rate constant of the pseudo first-order kinetic model; q_e is the metal concentration in the resin phase at equilibrium. Assuming k_1 and q_e are constant, Eq.(2) can then be integrated into a linear form with which the rate constant k_1 can be easily obtained from the slope and the intercept, respectively:

$$\ln(q_e - q_e) = \ln q_e - k_1 t$$

Another empirical equation, the pseudo second-order kinetic model that was also used to describe the adsorption phenomena³⁸⁻³⁹, is:

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

$$h = K_2 q_e^2 \quad \dots(4)$$

where K_1 is the rate constant of pseudo-first-order adsorption (min^{-1}), K_2 (g/mg min) the rate constant of pseudo-second-order adsorption, h the initial adsorption rate (mg/g min) and q_e and q_t are the amount of adsorbed Zn(II) on NB (mg/g) at

equilibrium and at time t , respectively. Since the pseudo first-order and second-order models are widely used in adsorption and ion-exchange processes, we use these empirical models to fit our experimental data. It is seen that the curves in the plots of $\ln(q_e - q_t)$ against time, are linear. First order reaction kinetics for zinc adsorption onto NB is shown in Fig. 7 (a). Pseudo-second-order kinetic was also applied for the experimental data of each metal. The curves in the plot of t/q_t against t are linear and k_2 rate constants can be calculated from the slope of these curves (Fig. 7 b). The parameters of the pseudo first-order and pseudo second-order models are summarized in Table 1. The first order was used to check the adsorption data of Zn(II) on NB but the correlation coefficient was not high ($R=0.85$) However, pseudo-second order kinetic model was successfully applied with very high correlation coefficient ($R=1$) for explaining kinetic data of an adsorption processes⁴⁰. The adsorption of Zn(II) on NB could be pseudo-second order process rather than first order.

Adsorption of Zn on NB

The adsorption of Zn(II) onto NB as a function of temperature was studied at initial Zn (II) concentration from 40 to 2000 mg/l while keeping all other parameters constant. The results are shown in Fig 8. This figure shows that the adsorption capacities of Zn(II) from aqueous solutions by NB increased with increasing temperature. This result occurs because of increasing kinetic energy of the sorbent particles, which increases the frequency of collisions between the adsorbent and metal ions and thus enhances adsorption of metals on the surface of the NB.

Isotherm models

The sorption data have been subjected to

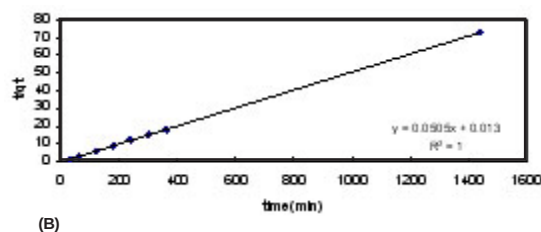
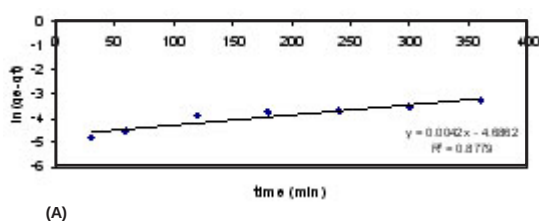


Fig. 7: Pseudo-first-order (a) and Pseudo-second-order (b) adsorption kinetics of Zn(II) on NB surface

different sorption isotherms, namely, Langmuir and Freundlich. The equilibrium data for Zn (II) over the concentration range from 40 to 2000 mg/l at have been correlated with the Langmuir isotherm.

$$\frac{C_e}{q_e} = \frac{1}{q_m K} + \frac{1}{q_m} C_e \quad \dots(5)$$

where q_e is the equilibrium Zn concentration on adsorbent (mol g^{-1}), q_m the maximum amount of adsorption (mol g^{-1}), K the affinity constant (L mol^{-1}) and C_e is the solution concentration at equilibrium (mol L^{-1}). From a plot of C_e/q_e versus C_e , q_m and K can be determined from its slope and intercept. Maximum amount of adsorption (q_m) represents monolayer coverage of sorbent with NB and K represents enthalpy of sorption and should vary with temperature. Linear plot is obtained when C_e/q_e is plotted against C_e over the entire concentration range of Zn(II) investigated (Fig. 9). The Langmuir model effectively described the sorption data with all R^2 values >0.95 , according to the q_m (mg/g) parameter. Sorption of ZN on NB is produced following the sequence $333\text{K} > 313\text{K} > 293\text{K}$. The Langmuir model

parameter and the statistical fits of the sorption data to this equation are given in Table 2. The Langmuir model effectively described the sorption data with R^2 value > 0.95

The Freundlich sorption isotherm, one of the most widely used mathematical descriptions, usually fits the experimental data over a wide range of concentrations. This isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. The Freundlich adsorption isotherms were also applied to the removal of Zn(II) on NB (Fig.10)

$$\ln x/m = \ln K + 1/n \ln C_e, \quad \dots(6)$$

where C_e is the equilibrium concentration in mg/l and x/m shows that the adsorption seems to follow the Freundlich isotherm model as well as the Langmuir isotherm. The constants K and n were calculated for each cation (Table 3), K is a parameter related to the temperature and n is a characteristic constant for the adsorption system under study. Values of n between 2 and 10 show good adsorption

Table 1: Parameters for adsorption of Zn(II) onto NB derived from the pseudo-first- and second-order kinetic models.

Pseudo-first-order			pseudo-second-order			
q_e (mg/g)	K_1 (min^{-1})	R^2	q_e (mg/g)	K_2 (g/mg.min)	h (mg/g min)	R^2
9.22×10^{-3}	0.0042	0.877	19.8	0.196	76.8	1

Table 2: Characteristic parameters and determination coefficient of the experimental data according to the Langmuir equation

Temperature (K)	q_m (mg/L)	K (L/mg)	K (L/mol)
293	27	0.019	1242
313	30.4	0.026	1700
333	46.2	0.032	2092

Table 3: Freundlich adsorption equations and constants ($\ln k$ and n) for metal cations on NB at various temperature

Temperature (K)	$\ln k$	N	R^2
293	1.7	4.1	0.85
313	1.8	4.1	0.88
333	2.1	4.2	0.83

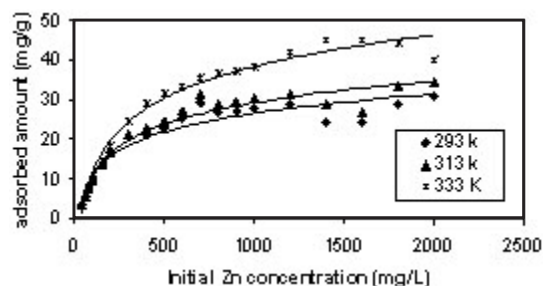


Fig. 8: Adsorbed amount of Zn(II) on NB as a function of temperature, 293 K, 313K and 333K

Adsorption thermodynamics

The changes in Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) for the adsorption process were obtained using the following equations³⁷

$$\Delta G = -RT \ln k \quad \dots(12)$$

$$\ln k = \Delta S / R - \Delta H / RT \quad \dots(13)$$

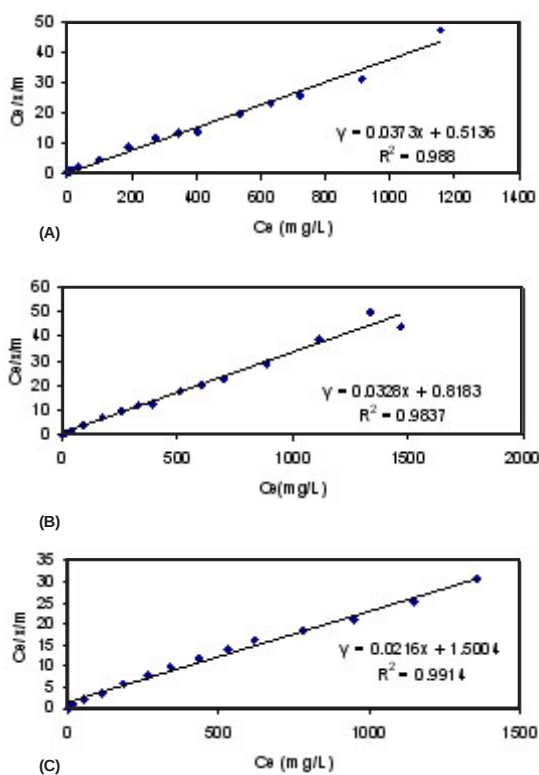


Fig. 9: Langmuir plots for Zn(II) adsorption onto NB at 293K (a), 313K (b) and 333K (c)

Effect of bentonite treatment

Fig. 12 shows the maximum adsorbed amount of Zn(II) ions on natural bentonite (NB), washed bentonite (WB) and calcined bentonite (CB) at initial Zn (II) concentrations 500 and 1000 mg/L. The adsorbed amount of Zn (II) on WB was higher than NB and CB. This result may be due to removal of dissolved and excess salts located in the exchange sites of commercial bentonite (untreated) (NB) upon washing. Therefore, the exchange sites on bentonite surfaces increased and consequently become available for more adsorption of Zn(II) ions from solution. Also in this figure, it was observed that the adsorption capacity of CB was very lowered compared to NB. This result due to the heat treatment of NB leads to dehydration and dehydroxylation of the bentonite, cation exchange capacity and surface area decreased and consequently the adsorption capacity decreased⁴⁰⁻⁴².

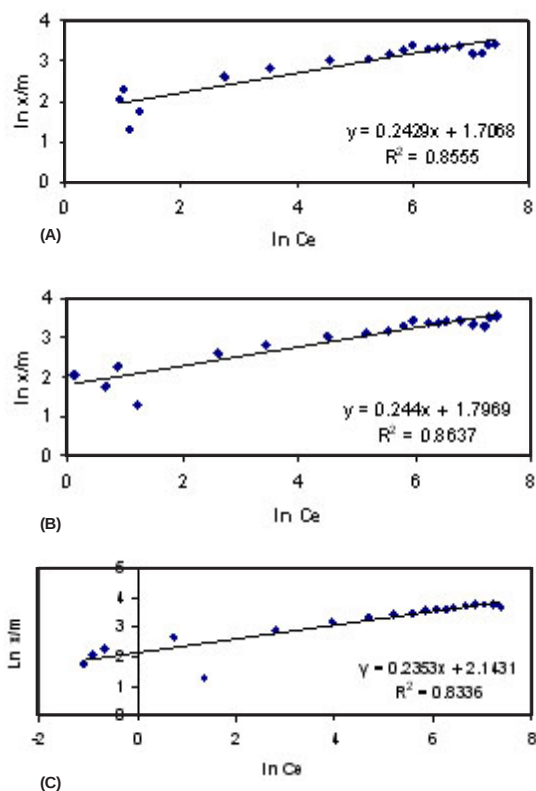


Fig. 10: Freundlich plots for Zn(II) adsorption onto NB at 293(a), 313 (b) and 333 K (c)

Table 4: Thermodynamic constants for the adsorption of Zn(II) on NB at various temperatures

Temperature K	Ln k	ΔG , kJ/mol	ΔH , kJ/mol	ΔS , kJ/mol.k	R, kJ/mol.k
293	7.12	-17.35	5.6	0.096	8.314×10^{-3}
313	7.43	-19.33			
333	7.64	-21.15			

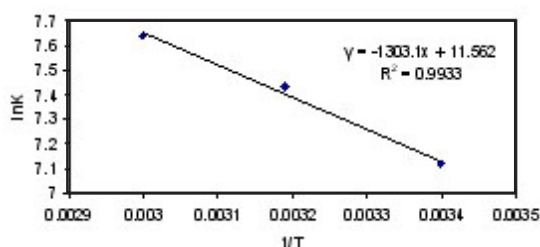


Fig. 11: Plot of the Langmuir isotherm constant (ln k) vs. temperature (1/T). The thermodynamic parameters in Table 4 are determined from this graph.

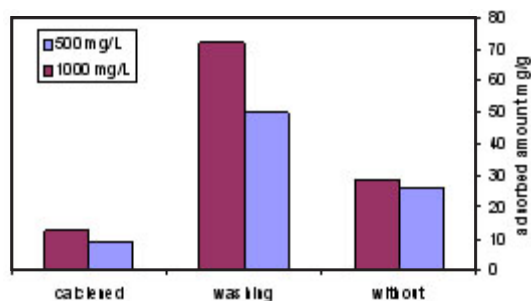


Fig. 12: Maximum adsorbed amount of Zn(II) ions on natural bentonite (NB), washed bentonite (WB) and calcined bentonite (CB) at initial Zn (II) concentrations 500 and 1000 mg/L

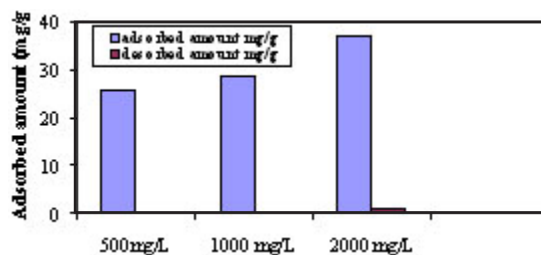


Fig. 13: Adsorbed and desorbed amount of Zn (II) from NB surfaces

Desorption

In metal ion removal process, it is important to study the desorption of the adsorbed metal ions under suitable conditions. In the desorption studies deionized water was used as desorption agent. The NB samples loaded with different adsorbed amount of Zn(II) ions (initial cobalt concentration = 500, 1000 and 2000 mg/L) were placed in 50 ml deionized water and the amount of Zinc ions desorbed within 1h measured. Fig. 13 shows the data of the adsorbed and desorbed amount Zn (II) ions. The data show that there is about 0.16, 0.362 and 0.778 mg of Zn (II) ions desorbed from NB surface loaded by 25.7, 28 and 37 mg Zn(II) /g NB.

CONCLUSIONS

The adsorption characteristics of natural bentonite (NB) was determined for Zn(II) at different conditions. The obtained results can be summarized:

1. pH is a significant factor in adsorption processes since it causes electrostatic changes in the solutions. The optimum pH values for Zn(II) removals is determined as 6.
2. Maximum removal efficiencies were succeeded within 10 min
3. The empirical values are evaluated according to the Langmuir, Freundlich that are generally used to describe the adsorption processes
4. Zn(II) adsorption from aqueous solutions using NB is well described with the second order reaction kinetic
5. Isotherm analysis of the data showed that the adsorption pattern for cobalt on bentonite followed the Langmuir isotherm.
6. The adsorption process is endothermic in nature and increases with increasing

temperature.

7. Washing of natural bentonite provides a simple possibility to modify the adsorption properties of bentonite.

The commercial natural bentonite (untreated, NB) demonstrated a good capacity of zinc removal. The kinetics of zinc adsorption by NB was fast, reaching 95% of the total adsorption capacity in five minutes. The adsorption process is a function of the adsorbent concentration, pH, metal ion concentration and adsorbent doses.

NB possesses adsorption capacity of 30.8, 34.6 and 40.2 mg/g at 293, 313 and 333 K respectively confirming that the adsorption process is endothermic in nature and increases with increasing temperature. The experimental data gave good fit with Langmuir isotherm and the adsorption coefficients agreed well with the conditions of favorable adsorption. Kinetic studies indicated that the adsorption tends to follow pseudo-second order kinetics. Washing of natural bentonite provides a simple possibility to modify the adsorption properties of bentonite.

REFERENCES

1. Cheremisinoff, P.N., Handbook of Water and Wastewater Treatment Technology, Marcel Dekker Inc., New York (1995).
2. Jain C.K., Singhal D.C. and Sharma M.K., Adsorption of zinc on bed sediment of river Hindon: adsorption models and kinetics, *J. Hazard. Mater. B* **114**: 231-239 (2004).
3. Veli S., and Öztürk, T., Kinetic modeling of adsorption of reactive azo dye on powdered activated carbon and pumice, *Fresenius Environ. Bull.* **14**: 212-218 (2005).
4. Babel S., and Kurniawan, T.A., Low-cost adsorbents for heavy metal uptake from contaminated water, *J. Hazard. Mater.* **9**: 219-243 (2003).
5. Lai C.L., and Lin S.H., Electrocoagulation of chemical mechanical polishing (CMP) wastewater from semiconductor fabrication, *Chem. Eng. J.* **95**: 205-211 (2003).
6. Özdemir C., Karatas M., Dursun S., Argun M.E., and Dogan S., Effect of MnSO_4 on the chromium removal from leather industry wastewater, *Environ. Technol.* **26**: 397-400 (2005).
7. Cardoso V.A., de Souza, A.G., Sartoratto P.P.C., and Nunes L.M., The ionic exchange process of cobalt, nickel and copper(II) in alkaline and acid-layered titanates, *Colloid Surf. A: Physicochem. Eng. Asp.* **248**: 145-149 (2004).
8. Axtell N.R., Sternberg S.P.K. and Claussen K., Lead and nickel removal using *Microspora* and *Lemna minor*, *Bioresour. Technol.* **89**: 41-48 (2003).
9. Argun M.E., Dursun S., Gur K., Özdemir C., Karatas M., and S. Dogan S., Nickel adsorption on the modified pine tree materials, *Environ. Technol.* **26**: 479-488 (2005).
10. Argun M.E., Dursun S., Gür K., Özdemir C., Karatas M., Heavy metal adsorption by oak sawdust: thermodynamics and kinetics, *J. Hazard. Mater.* **141**: 77-85 (2007).
11. Chuah, T.G., Jumasiah A., Azni, I., Katayon S., and Thomas Choong S.Y., Rice husk as a potentially low-cost biosorbent for heavy metal and dye removal: an overview, *Desalination* **175**: 305-316 (2005).
12. Márquez, G.E., Ribeiro M.J.P., Ventura J.M., and J.A. Labrincha J.A., Removal of nickel from aqueous solutions by clay-based beds, *Ceram. Int.* **30**: 111-119 (2004).
13. Erdem, E., Karapinar N., and Donat R., The removal of heavy metal cations by natural zeolites, *J. Colloid Interf. Sci.* **280**: 309-314 (2004).
14. Ho, Y.S., Wase D.A.J. and Forster C.F., Batch nickel removal from aqueous solution by sphagnum moss peat, *Water Res.* **29**: 1327-1332 (1995).
15. Li Q., Wu S., G. Liu G., Liao X., Deng X., Sun, D., Hu Y., and Huang Y., Simultaneous biosorption of cadmium (II) and lead (II) ions by pretreated biomass of *Phanerochaete chrysosporium*, *Sep. Purif. Technol.* **34**: 135-142 (2004).
16. Srivastava, S.K., Tygai R., and Pal N., Studies on the removal of some toxic metal-

- ions. 2. Removal of lead and cadmium by montmorillonite and kaolinite, *Environ. Technol. Lett.* **10**: 275-282 (1989).
17. Mellah A., and Chegrouche, S., The removal of zinc from aqueous solution by natural bentonite, *Water Res.* **31**: 621–629 (1997).
18. Undaybeytia T., Morillo E., and Maqueda C., Adsorption of Cd and Zn on montmorillonite in the presence of a cationic pesticide, *Clays Clay Miner.* **31**: 485-490 (1996).
19. Chantawong, V., Harvey N., and Bashkin V.N., Comparison of heavy metal adsorptions by Thai kaolin and ball clay, *Asian J. Energy Environ.* **1**: 33-48 (2001).
20. Naseem R., and Tahir, S.S., Removal of Pb(II) from aqueous/acidic solutions by using bentonite as an adsorbent, *Water Res.* **35**: 3982-3986 (2001).
21. Naseem R., and Tahir S.S., Removal of Fe(II) from the wastewater of galvanized pipe manufacturing industry by adsorption onto bentonite clay, *J. Environ. Manage.* **73**: 285-292 (2004).
22. Hillel, D. *Environmental Soil Physics* Academic Press, New York (1998).
23. Bourg A., Modélisation du comportement des métaux traces à l'interface solide-liquide dans les systèmes aquatiques. Thèse de doctorat, Bordeaux I, France, (1983).
24. Goldberg S., Su C., and Forster H.S., . In: E.A. Jenne Editor, *Adsorption of Metals by Geomedia* Academic Press, New York (1998).
25. Sparks D., *Environmental Soil Chemistry* Academic Press, New York (1995).
26. Dékány I. and Nagy L.G., Immersional wetting and adsorption displacement on hydrophilic/hydrophobic surfaces, *J. Coll. Interface Sci.* **147**: 119-128 (1991).
27. Altin O., Ozbelge O.H., and Dogu T., Effect of pH, flow rate and concentration on the sorption of Pb and Cd on montmorillonite. I. Experimental, *J. Chem. Tech. Biotechnol.* **74**: 1131–1138 (1999).
28. Saha U.M., Iwasaki K., and Sakurai K., Desorption behavior of Cd, Zn and Pb sorbed on hydroxylaluminum- and hydroxylaluminosilicate-montmorillonite complexes, *Clays Clay Miner.* **51**(5): 481-492 (2003).
29. Alvarez-Ayuso E., and Garcia-Sanchez A., Removal of heavy metals from waste waters by natural and Na-exchanged bentonites, *Clays Clay Miner.* **51**(5): 475–480 (2003).
30. F. Barbier, G. Duc, M. Petit-Ramel, Adsorption of lead and cadmium ions from aqueous solution to the montmorillonite/water interface, *Colloids Surfaces A: Physicochem. Eng. Aspects* **166**(1-3): 153-159 (2000).
31. Bradl H.B., Adsorption of heavy metal ions on soils and soils constituents, *J. Colloid Interface Sci.* **277**: 1–18 (2004).
32. Yu L.J., Shukla S.S., Dorris K.L., Shukla A. and Margrave J.L., Adsorption of chromium from aqueous solutions by maple sawdust *Journal of Hazardous Materials B.* **100**: 53-63 (2003).
33. Dakiky M., Khamis M., Manassra A., and Mer'eb M.,_Selective adsorption of chromium(VI) in industrial wastewater using low-cost abundantly available adsorbents, *Advances in Environmental Research* **6**: 533–540 (2002).
34. Arslan G., and Pehlivan E., Batch removal of chromium (VI) from aqueous solution by Turkish brown coals, *Bioresource Technology*, **98**: 2836-2845 (2007)
35. Potgieter J.H., Potgieter-Vermaak S.S., and Kalibantonga P.D., Heavy metals removal from solution by palygorskite clay *Minerals Engineering*, **19**: 463-470 (2006).
36. Shukla S.S., Yu L.J., Dorris K.L., A. Shukla A., and Margrave J.L., Adsorption of chromium from aqueous solutions by maple sawdust, *Journal of Hazardous Materials* **100**(1–3): 53–63 (2003).
37. D. Mohan D., and K.P. Singh K.P., Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse: an agricultural waste, *Water Res.* **36**: 2304–2318 (2002).
38. Sharma, A. and Bhattacharyya, K.G. (), *Azadirachta indica* (Neem) leaf powder as a biosorbent for removal of Cd(II) from aqueous medium. *Journal of Hazardous Materials*, **125**: 102-112 (2005).

39. Gulnaz O., Saygideger S., and E. Kusvuran E, Study of Cu (II) biosorption by dried activated sludge: effect of physico-chemical environment and kinetics study, *J. Hazard. Mater.* **120**: 193-200 (2005).
40. Ho Y.S., and McKay G., The kinetics of sorption of divalent metal ions onto sphagnum moss peat, *Water Res.* **34**(3): 735–742 (2000).
41. Ho S.Y., Removal of copper ions from aqueous solution by tree fern, *Water Res.* **37**: 2323–2330 (2003).
42. Bujdak J. and Komadel P., Interaction of methylene blue with reduced charge montmorillonite, *J. Phys. Chem. B* **101**: 9065–9068 (1997).
43. Suraj G., Iyer C. S. P. and Lalithambika M., Adsorption of cadmium and copper by modified kaolinites, *Appl Clay Sci.*, **13**: 293-306 (1998).
44. Alkan, M., Celikcapa, S., Demirbas O. and Dogan M., Removal of reactive blue 221 and acid blue 62 anionic dyes from aqueous solution by sepiolite, *Dyes Pigments* **65**: 251–259 (2005).