*Full Length Research Paper*

# Kinetic and thermodynamic study of the adsorption of Pb (II) from aqueous solution to the natural and treated bentonite

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**Lead (Pb) is one of the major environmental pollutants. Adsorption appears to be the most widely used for the removal of heavy metals. The aim of this work is to investigate the adsorption potential of commercial natural bentonite (NB) in the removal of Pb (II) ions from aqueous solution. The effect of different variables, such as, concentration of Pb, mass of NB, pH, time, NB washing and heat treatment and temperature was investigated. The bentonite sample under the heat and washed treatment are labeled as CB and WB respectively. The adsorption experiments were carried out using batch process. The equilibrium time for Pb (II) adsorption on NB was 5 min, the processes conforming to second order kinetics. NB had a much higher adsorption capacity for Pb (II) with the Langmuir monolayer capacity (qm) of 107, 110 and 120 mg g– 1 at 293, 313 and 333 K respectively compared to others adsorbents. Thermodynamic parameters such as ΔH°, ΔS° and ΔG° were calculated. The adsorption process was found to be endothermic and spontaneous. The enthalpy change for Pb (II) by NB adsorption has been estimated as 33 kJ mol–1, indicating that the adsorption of Pb (II) by NB corresponds to a physical reaction. The adsorption capacity of washed bentonite WB was very high compared to NB and CB**

**Key word:** Adsorption, clay minerals, bentonite, lead, wastewater treatment

## INTRODUCTION

Lead (Pb) is one of the major environmental pollutants. It is mainly discharged from exhaust gases of automobile to environment (Sekar et al., 2004). Moreover, it diffuses to the water and environment through effluents from lead smelters, battery manufacturers, paper and pulp Industries and ammunition industries (Sekar et al., 2004). Major lead pollution has been through in the manufacture of storage batteries, painting pigments, ammunition, solder, plumbing fixtures, automobiles, cable coverings, radioactivity shields, caulking and bearings (Ake et al., 2001; Tunali et al., 2006). Lead ions concentrations approach $200 - 500$ mg $dm^{-3}$ in the industrial wastewaters. This value is very high in relation to the water quality standards and it should be reduced to a range of $0.1 - 0.05$ mg $dm^{-3}$ (Kapoor et al., 1999; Lo et al., 1999).

Several methods have evolved over the years on the removal of these metal ions present in industrial wastewaters and soils such as chemical precipitations, conventional coagulation, reverse osmosis, ion exchange and adsorption on activated carbon (Patterson, 1999). Out of these methods, adsorption appears to be the most widely used for the removal of heavy metals (Adebowale et al., 2006; Baghel et al., 2006; Adebowale et al., 2008). The use of various adsorbents such as kaolinite (Srivastava et al., 1989; Orumwense et al., 1996, Chantawong et al., 2001; Gupta et al., 2005), illite (Echeverría et al., 2005), bentonite (Naseem et al., 2001; Donat et al., 2005), montmorillonite (Srivastava et al., 1989, Gupta et al., 2005; Barbier et al., 2000), zeolite (Zamzow et al., 1990; Ouki et al., 1993) and sepiolite (Brigatti et al., 2000; Bektas et al., 2004) have been reported the removal of heavy metal ions from aqueous solutions. Adsorption have been used to remove Pb (II) ions from aqueous solutions by adsorption. The chemical and pore struc-

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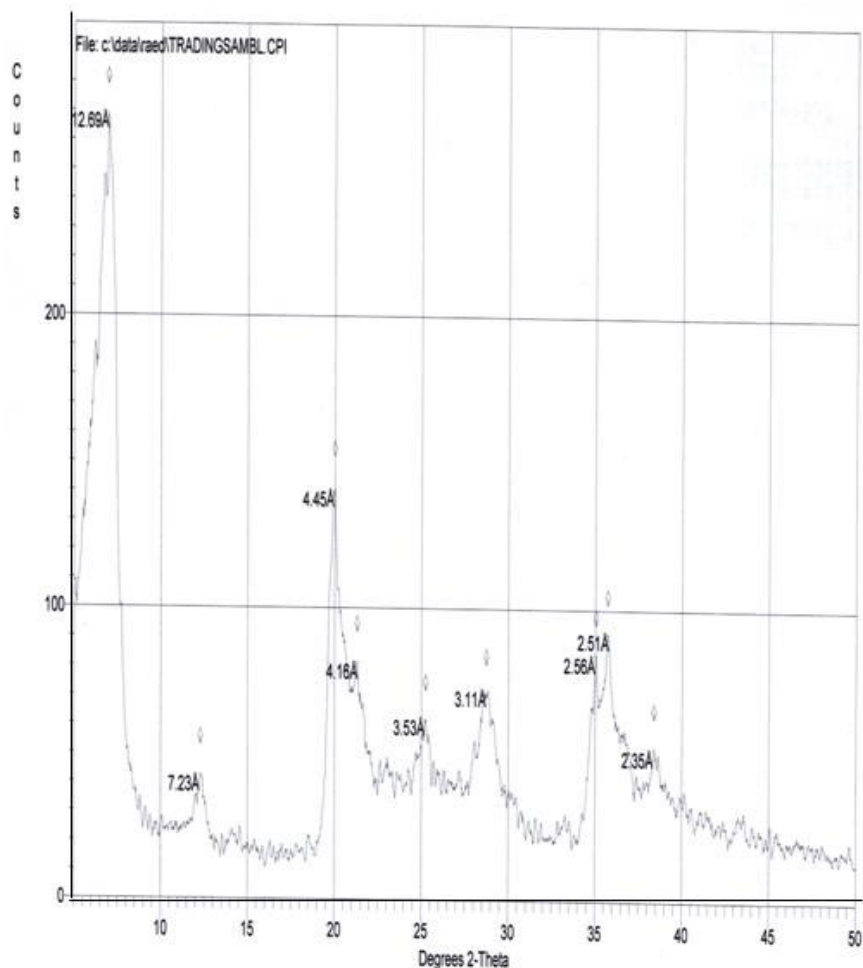*Corresponding author. E-mail: nandis@KSU.EDU.SA

**Figure 1**. The XRD patterns of the NB.

tures of clays usually determine their adsorption ability (Juang et al., 2002). Bentonite, which is predominantly montmorillonite clay, is used a wide range of applications such as clarification of edible and mineral oils, paints, cosmetics and pharmaceuticals industries (Banat et al., 2000).

The objective of the present work is to investigate the adsorption potential of commercial natural bentonite (NB) in the removal of Pb (II) ions from aqueous solution. The effects of pH, mass of bentonite, contact time, bentonite treatment (washing and calcinations) and temperature on the adsorption capacity of NB were studied. The Langmuir and Freundlich isotherm models were used to describe equilibrium data. The adsorption mechanisms of Pb (II) ions onto NB were also evaluated in terms of thermodynamics and kinetics.

## MATERIALS AND METHODS

### Material

Lead nitrate Pb(NO3)$_2$ used in adsorption experiments in Extra pure grade and was purchased through Merck. pH adjustments were carried on using 0.1N hydrochloric acid (HCl) and 0.1N sodium hydroxide (NaOH). All Pb (II) solutions were prepared with ultra-pure water specified resistivity of 18 MW. ΩCm obtained from an E-pure purifier of Barnstead, USA system. A single element ICP standard solutions from MV Laboratories INC USA were used for system calibrations.

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

Comparative X-ray powder diffraction (XRD) patterns of NB are shown in Figure 1. It was proved by X-ray analysis on this clay that the dominant component is bentonite (64.9%), kaolinite (10.6%), Geothite (9.5%), Hematite (9.4%) and Boehmite (5.6%).

Natural bentonite used in this study was grey in color of particles size ranging 0.25- 0.0375 mm. Bentonite sample was divided into three parts. The 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 (WB) was dried in an electric oven at 150 – 200 °C for several hours before use in the adsorption studies. 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 polythene bags. The particles size of WB and CB were between 0.25 -0.0375 mm.
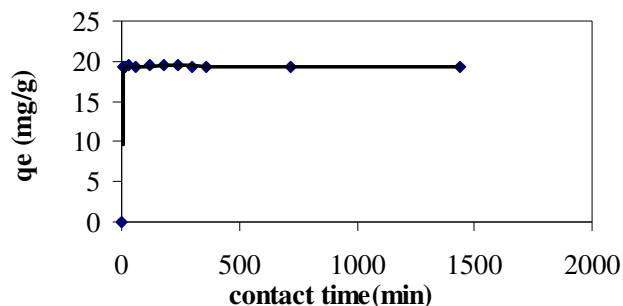
**Figure 2**. Effect of contact time on Pb (II) adsorption onto NB (Pb (II) concentration 200 mg/L, 25°C and NB dose = 10 g /L.

The specific surface area of NB was determined by applying the Brunauer, Emmet, Teller (BET) equation. The resulted surface area of NB ($S_{NB}$) was 45.9 $m^2$ $g^{-1}$. While our result showed to be less than those expected for bentonite (Hillel 1998), it is in agreement with other pervious studies (Bourg et al., 2007; Goldberg 2002). This result may be due to the lack of bentonite treatment, $N_2$ molecules can not penetrate easily between the interlayer sheets of bentonite, involving an underestimation of specific surface areas (Sparks, 1995) and (Dékány and Nagy, 1991).

### Methods

#### Batch adsorption procedure

Adsorption experiments were carried out at the desired pH value, contact time, temperature, Pb(II) concentrations and NB mass level using the necessary adsorbents in a 250 mL conical flask containing 50 mL of Pb (II) solution. Initial solutions with different concentration of Pb(II) was prepared by proper dilution from stock 2000 mg/L Pb(II) standards. The NB suspension was shaken for 2 h with a rotary shaker at a speed of 150 rpm. After being centrifuged, Pb(II) concentration was analyzed by Perkin- Elmer Optima 5300 DV ICP optical emission spectrometer coupled with peristaltic pump and AS-93 plus auto sampler unit. All experiments were carried out in duplicate. The adsorption % of Pb (II) was calculated as follows:

Adsorption % = [($C_i$ – $C_f$) / ($C_i$) ]x 100          (1)

Where $C_i$ and $C_f$ are the initial and final metal ion concentrations, respectively.

#### Kinetic studies

The kinetic experiments were conducted in batch mode on NB. The experimental details were as follows: 0.5 g NB was added to 50 mL Pb(II) solution. The corresponding Pb (II) concentration was 200 mg/L. The suspension was shaken for a period between 5 and 360 min with a rotary shaker at a speed of 150 rpm. After the mixture being centrifuged, Pb (II) was analyzed by a Perkin- Elmer Optima 5300 DV ICP optical emission spectrometer. All experiments were carried out in duplicate.

#### Effect of pH

The influence of pH in the range of 2 - 8 was studied in lead ions concentration of 500 mg/L, stirring speed at 162 rpm for 1 h, NB

dose of  0.5 g, temp. at 298 K. The pH of lead solution was adjusted after adding the adsorbent. The pH of the solution was adjusted by using a dilute NaOH and HCl solutions. Also the pH of NB suspension measured before and after Pb (II) adsorption.

#### Effect of NB mass

The adsorption percent of Pb (II) on NB was studied at different NB mass [0.1 – 5.0 g /50 ml Pb (II) solution] at Pb (II) concentrations (500 and 1000 mg/l), keeping stirring speed 162 rpm, temperature (298 K) and contact time (1 h) constant.

#### Effect of temperature

The influence of temperature on adsorption behavior of Pb (II) onto NB was determined at 293, 303 and 313 K. The samples was prepared by mixing 0.5 g of NB with 50 ml of solution of Pb (II) concentration ranging from 40 to 2000 mg/L. The mixture was shaken for 1 h and centrifuged; Pb (II) was analyzed by a Perkin-Elmer Optima 5300 DV ICP optical emission spectrometer. All experiments were carried out in duplicate.

## RESULTS AND DISCUSSION

### Adsorption kinetics

Figure 2 shows the effect of contact time on the adsorption of Pb (II) on NB. Adsorption increased rapidly with time and the equilibrium is reached within 5 min. The result indicates that equilibrium is reached very rapidly compared with observations by Potgieter et al. (2006) and Sari et al. (2007). The difference might imply that the adsorption sites on the NB are very well exposed and the adsorption mechanisms are very easy.

In order to clarify the adsorption kinetics of Pb (II) ions onto NB, Lagergren's pseudo-first-order and pseudo-second-order kinetic models were applied to the experimental data.

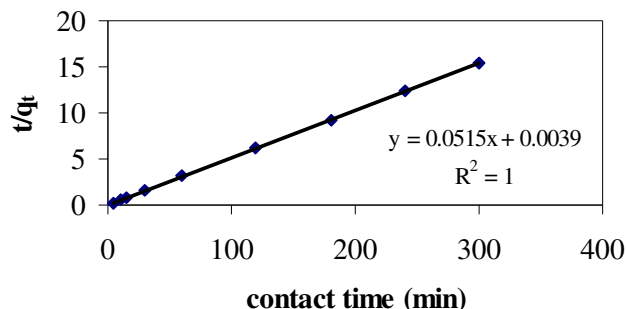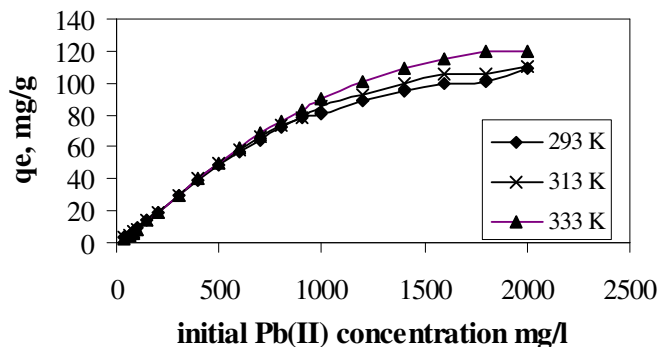The linearized form of the pseudo-first-order rate equation by Lagergren is given as:

Ln ($q_e$-$q_t$) = ln $q_e$ – $k_1$t          (2)

Where $q_t$ and $q_e$ (mg/g) are the amounts of the metal ions adsorbed at equilibrium (mg/g) and t (min), respectively, and $k_1$ is the rate constant of the equation ($min^{-1}$). The adsorption rate constants ($k_1$) can be determined experi-mentally by plotting of $ln(q_e – q_t)$ versus t. The plots of $ln(q_e – q_t)$ versus t for the Lagergren-first-order model (was not shown here) does not fit a pseudo-first-order kinetic model and  the $R^2$ value for this model is very low (0.045) for the Pb(II) adsorption by NB . The similar results were found for the adsorption of same metal ions on various adsorbents by several authors (Gündogan et al., 2004; King et al., 2006). Expe-rimental data were also applied to the pseudo-second-order kinetic model which is given in the following form (Wen et al., 2006; Ho et al., 1999)

t/$q_t$ = 1/($k_2$$q_e^2$) + (1/$q_e$) t          (3)

**Table 1.** Parameters for adsorption of Pb (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) | $R^2$ |
| 0.72 | -0.0005 | 0.019 | 19.4 | 0.68 | 1.5 | 0.9998 |



**Figure 3.** Pseudo-second-order adsorption kinetics of Pb (II) on NB surface.



**Figure 4.** Adsorption isotherms of Pb (II) onto NB adsorbent at different temperatures.

Where $k_2$ (g/mg min) is the rate constant of the second-order equation, $q_t$ (mg/g) the amount of adsorption time t (min) and $q_e$ is the amount of adsorption equilibrium (mg/g).

This model is more likely to predict the kinetic behaviour of adsorption with chemical sorption being the rate-controlling step (Wen et al., 2006; Ho et al., 1999). The linear plots of $t/q_t$ versus t for the pseudo-second-order model for the adsorption of Pb (II) ions onto NB at 25°C are shown in Figure 3. The rate constants ($k_2$), correlation coefficients of the plots together with the $q_e$ value is given in Table 1. It is clear from these results that the $R^2$ value equal 1. These results suggest that the adsorption of Pb (II) ions onto NB follows well the pseudo-second-order kinetics. The similar results were reported for the adsorption of Pb (II) on different adsorbents which have similar chemical structure with that of NB (King et al., 2006; Tunali, et al., 2006; Liu et al 2006).

## Adsorption isotherm

Figure 4 shows the adsorption amount of Pb (II) adsorption by NB adsorbent at various temperatures (293, 313 and 333 K). It was observed with increasing the temperature the adsorbed amount of Pb (II) on NB surfaces increased. This change occurs because of increasing kinetic energy of the of the Pb ions, which increases the frequency of collisions between the adsorbent and metal ions and thus enhances adsorption of metals on the surface of the sorbent.

All batch experimental data were fitted to the isotherm models of the well-known Langmuir and Freundlich using the method of least squares and an optimization algorithm. These models are represented mathematically as follows: The Langmuir equation is given by Eq.(4): (Chiron et al., 2003).

$$C_e/q_e = 1/(q_m k) + 1/(q_m) C_e \qquad (4)$$

Where $q_e$ is the equilibrium copper 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.
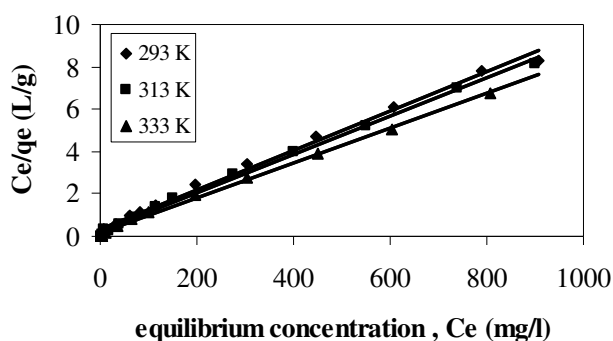
## Freundlich isotherm

The adsorption effects of lead ions on NB surface were interpreted with the Freundlich adsorption model, which depends on a heterogeneous surface with a continuous 1970). The Freundlich isotherm model show the relationship between the amount of Pb (II) adsorbed by the NB adsorbent ($q_e$, mg g$^{-1}$) and the equilibrium concentration of Pb (II) ($C_e$, mg l$^{-1}$) in solution. The Freundlich adsorption model can be expressed by the following equation:

$$q_e = K_F (C_e)^{1/n} \qquad (5)$$

Where $K_F$ and n are Freundlich adsorption isotherm constants, being indicative of the extent of the adsorption and the degree of non-linearity between solution concentration and adsorption, respectively; $q_e$ is the amount of chromium adsorbed per unit weight of distribution of adsorption sites (Li et al., 2005; Smith adsorbent; $C_e$ the equilibrium concentration (mol L$^{-1}$). By the logarithmic linearization of Eq. (5), the two parameters of the Freundlich equation, $K_F$ and 1/n could be estimated from the intercept and the slope of the straight line, respectively:

**Table 2.** Parameters of Langmuir and Freundlich adsorption isotherm models for Pb(II) on NB adsorbent at different temperature.

| T(K) | Langmuir | | | | Frendlich | | |
|---|---|---|---|---|---|---|---|
| | $q_m$ ( mg/g) | $K_L$(l/mg) | $K_L$ (l/mol) | $R^2$ | $K_f$ | n | $R^2$ |
| 293 | 107 | 0.0301 | 6261 | 0.994 | 4.5 | 0.28 | 0.83 |
| 313 | 110 | 0.0422 | 8777 | 0.996 | 30 | 5.2 | 0.73 |
| 333 | 120 | 0.059 | 12272 | 0.997 | 36.2 | 5.46 | 0.65 |



**Figure 5.** Linearized  Langmuir  isotherm models for Pb (II) adsorption by the NB adsorbent at (a) 293 K, (b) 313 K and 333 K (adsorbent dosage, 10 g/L and shaking time, 2 h.

The adsorption isotherms for Pb (II) removal were studied using initial concentrations of metal ions between 40 and 2000 mg $l^{-1}$ at NB mass of 10 g/L ml at 293 , 313 and 333 K. Adsorption isotherms can be expressed in terms of the Langmuir and Freundlich models. The Langmuir model fitted better with the experimental data (Figure 5) rather than the Freundulich mode l (not presented here). The values of correlation coefficient (R), $K_L$, $K_F$ and n obtained from both models were presented in Table 2.

A value of 107, 110, and 120 mg/g had been obtained as the adsorption capacity of NB for lead from batch studies at 298, 313 and 333 K. A comparison of the maximum Pb (II) adsorption capacity, $q_m$, of NB especially at 293, 313 and 333 K with those of other low-cost adsorbents reported in the literature is given in Table 3. The adsorption capacity of NB is very high when compared with other clay minerals as shown in Table 3.

## Adsorption thermodynamics

The thermodynamic parameters of the adsorption, i.e. the standard enthalpy $\Delta H°$, Gibbs free energy $\Delta G°$ and entropy $\Delta S°$ were calculated using the following equations:

$$\Delta G = - RT \ln K_L \qquad (6)$$
$$\ln KL = \Delta S/R - \Delta HT \qquad (7)$$
$$\Delta G = \Delta H - T\Delta S \qquad (8)$$

Where R is the ideal gas constant (kJ $mol^{-1}$ $K^{-1}$), $K_L$ = $k_{ads}/k_d$ is the Langmuir constant and T is the tem-

perature (K). $\Delta H°$ and $\Delta S°$ values can be obtained from the slope and intercept respectively of Van't Hoff plots of ln $K_L$(from the Langmuir isotherm) versus 1/T (Mohan et al., 2002; Anirudhan and Radhakrishna, 2007). The results of these thermodynamic calculations are shown in Figure 6 and Table 4. The negative value for the Gibbs free energy for Pb (II) adsorption shows that the adsorption process is spontaneous and that the degree of spontaneity of the reaction increases with increasing temperature. The overall adsorption process seems to be endothermic ($\Delta H = 13.88$  kJ $mol^{-1}$). Although not very high, these values of $\Delta H$ can be interpreted on the basis of considerably strong interaction between lead ions and NB surface. This result also supports the suggestion that the adsorption capacity of NB for Pb (II) increases with increasing temperature. One possible explanation of positive $\Delta H$ is that the Pb ions are well solvated. In order for the Pb ions to be adsorbed, they have to lose part of their hydration sheath. This dehydration process of the ions requires energy. This energy of dehydration super-sedes the exothermicity of the ions getting attached to the surface. We can say that the removal of water from the ions is essentially an endothermic process and it appears that endothermicity of desolvation process exceeds that of the heat of adsorption to a considerable extent. The values of free energy change $\Delta G°$ are negative as expected for a spontaneous adsorption process (Naseem et al., 2001)

Table 4 also shows that the $\Delta S$ value was positive. This occurs as a result of redistribution of energy between the adsorbate and the adsorbent. Before adsorption occurs, the heavy metal ions near the surface of the adsorbent will be more ordered than in the subsequent adsorbed state and the ratio of free heavy metal ions to ions inte-racting with the adsorbent will be higher than in the adsorbed state. As a result, the distribution of rotational and translational energy among a small number of mole-cules will increase with increasing adsorption by produc-ing a positive value of $\Delta S$ and randomness will increase at the solid–solution interface during the process of adsorption. Adsorption is thus likely to occur sponta-neously at normal and high temperatures because $\Delta H > 0$ and $\Delta S > 0$.
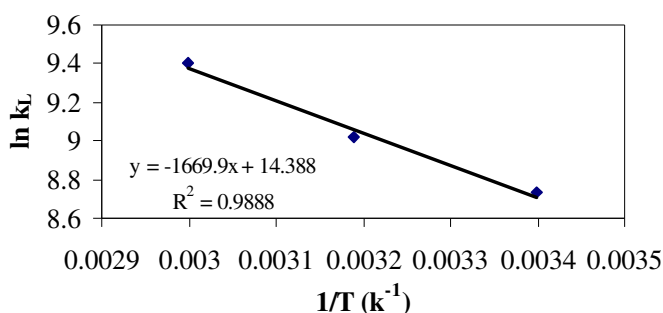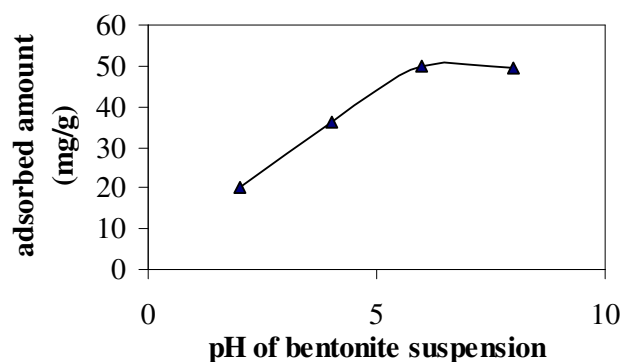
## Effect of pH

pH is one of the most important parameters while assess-ing the adsorption capacity of an adsorbent for metal ions

**Table 3.** Comparison of adsorption capacity of NB with different adsorbent materials.

| Adsorbent | Adsorption capacity ,$q_m$ (mg/g) | References |
|---|---|---|
| Turkish clay (Celtek) | 18.0 | Sari et al., 2007 |
| Expanded perlite (EP) | 13.39 | Sari et al., 2007 |
| Montmorillonite | 31.05 | Gupta et al., 2005 |
| Natural bentonite | 20 | Naseem and Tahir, 2001 |
| Natural Jordanian clay | 66.24 | Al-Degs et al., 2006 |
| Illite | 4.29 | Chantawong et al., 2001 |
| Poly(hydroxyl) zirconium modified montmorillonite | 31.44 | Gupta et al., 2005 |
| 293 k | 107 | This study |
| 313 k | 110 | |
| 333 k | 120 | |

**Table 4.** Thermodynamic constants for the adsorption of Pb(II) on commercial natural bentonite (untreated ) (NB) at various temperatures.

| T (K) | Ln $K_L$ | $\Delta G$ (k/mol$^{-1}$) | $\Delta H$(kJmol$^{-1}$) | $\Delta S$(kJmol$^{-1}$K$^{-1}$) |
|---|---|---|---|---|
| 293 | 8.73 | -21.3 | | |
| 313 | 9.02 | -23.4 | 13.8 | 0.12 |
| 313 | 9.4 | -26 | | |



**Figure 6.** Plot of the Langmuir isotherm constant (ln $K_L$) vs. temperature (1/T). The thermodynamic parameters in Table 4 are determined from this graph.



**Figure 7.** Effect of pH on Pb (II) removal by NB at initial Pb (II) concentrations 500 mg/L, NB dose = 10 g/L.

sequestering from aqueous solution. The pH of the system controls the adsorption capacity due to its influence on the surface properties of the adsorbent and ionic forms of the lead ions in solutions. In the present work, adsorption of Pb(II) on the NB was studied over the pH range of 2 – 8 at a constant clay amount of 10 g/L. Initial Pb(II) concentration was 200 mg/L. Figure 7 shows the effect of pH on the adsorption of Pb(II) ions onto NB from aqueous solutions. Removal of the Pb (II) ions increases slightly with increasing pH up to pH = 6, then remains constant. This is because the pH $_{(PZC)}$ value of the NB suspension is about 4, As the surface of NB is more protonated at pH lower than pH$_{PZC}$, it is less able to retain Pb(II) (Neubauer et al., 2000; Abollino et al., 2003;

Kadirvelu et al., 2000). In such a system H$^+$ com-petes with lead ions, resulting in active sites becoming protonated to the virtual exclusion of metal binding on the bentonite surface (Barbier et al., 2000). This means that at higher H$^+$ concentrations, the bentonite surface becomes more positively charged thus reducing the attracttion between surface and metal cations. As the pH increases (above pH$_{PZC)}$, more negatively charged surface becomes available thus facilitating greater metal uptake (Vassilis et al., 2007). At higher pH values than 6, metal precipitation appeared and adsorbent was deteriorated with accumulation of metal ions (Liu et al., 2006; Sari et al., 2007; King et al., 2006; Demirbas et al., 2005).
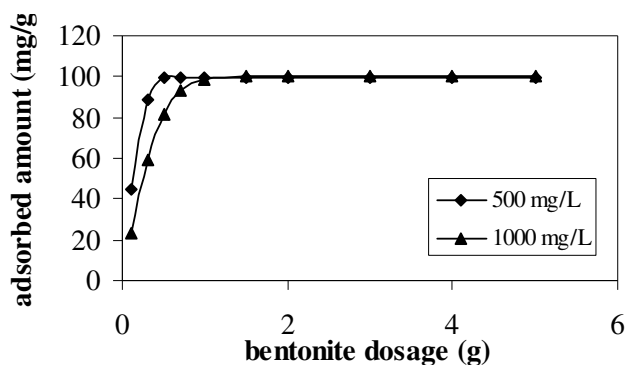
**Figure 8.** Effect of bentonite (NB) doses on adsorption % of Pb (II) at different Pb (II) concentration (500 and 1000 mg/L) and at 25°C.
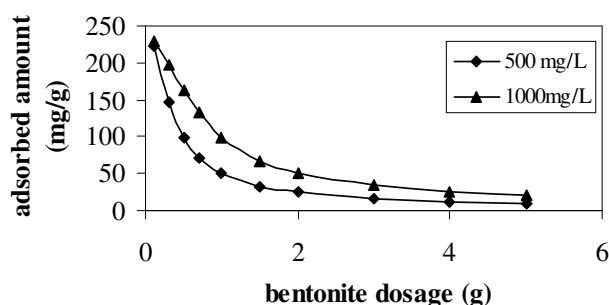


**Figure 9.** Effect of bentonite (NB) dose on the adsorbed amount of Pb (II) at different Pb (II) concentration (500 and 1000 mg/L) and at 25°C

Therefore, pH 6 was selected to be the optimum pH for further studies.

## Influence of NB mass

Adsorption % of Pb (II) on NB was studied at different bentonite (NB) mass [0.1, 0.3, 0.5, 0.7, 1, 2, 3, and 5 g/50 ml, respectively] keeping initial lead concentration (500 and 1000 mg/l), temperature (25 °C) and contact time (1 h) constant. The results showed that with increase in the NB mass, adsorption % of Pb (II) was increased and the maximum removal was observed with NB doses (Figure 8). Increase in the adsorption percentage with NB mass may be due to the increase in adsorbent surface area and availability of more adsorption sites (Garg et al., 2004). But unit adsorption (adsorbed amount, mg/g) of Pb(II) was decreased with increase in adsorbent dosage (Figure 9).This result attributed to the metal ions can easily access the adsorption sites when the adsorbent amount is small. With increasing NB content, the corresponding increase in adsorption per unit mass is less because the metal ions find it difficult to approach the adsorption sites due to overcrowding of clay mineral particles termed as a kind of solid concentration effect. In addition higher adsorbent amount
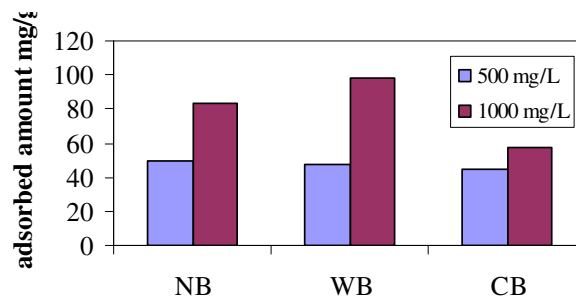


**Figure 10.** The adsorbed amount of Pb (II) on NB, calcined bentonite at 700°C (CB) and washed bentonite (WB) at initial concentration, 500 and 1000 mg/L.

creates particle aggregation, resulting in a decrease in the total surface area and an increase in diffusional path length both of which contribute to decrease in amount adsorbed per unit mass (Shukla et al., 2002).

## Effect of bentonite treatment

Figure 10 shows the maximum adsorbed amount of Pb (II) ions on natural bentonite (NB), washed bentonite (WB) and calcined bentonite (CB) at initial Pb (II) concentrations 500 and 1000 mg/L. The adsorbed amount of Pb (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 Pb 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 clay that leads to dehydration and dehydroxylation of the bentonite, cation exchange capacity and surface area decreased and consequently the adsorption capacity decreased (Bujdak et al., 1997; Suraj et al., 1998; Alkan et al., 2005).

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