

## Pb (II) ADSORPTION FROM AQUEOUS SOLUTION USING MODIFIED SODIUM MONTMORILLONITE CLAY: EQUILIBRIUM AND KINETIC STUDY

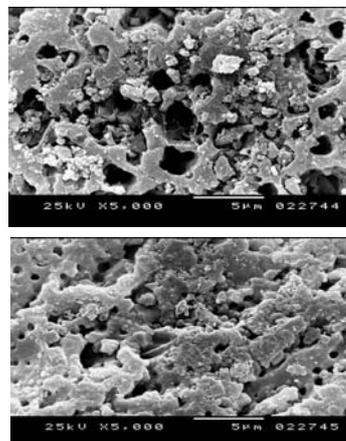
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The lead removal from waste water was examined by using a batch-type method. The ability of modified sodium montmorillonite to remove lead ions from aqueous solution has been studied. Sodium montmorillonite clay was prostrated with HCl and HNO<sub>3</sub> to improve the adsorption capacity for lead ions. During the adsorption process, the effect of various parameters, such as pH, adsorption time, clay dosage, and temperature on removal process has been investigated.

Experimental results showed that the adsorption of Pb (II) onto pretreated sodium montmorillonite is optimum in the pH 6. Residual lead ion concentration reached equilibrium in a short duration of 30 min. Additionally, a pseudo-second order rate model was adopted to describe the kinetics of adsorption. The thermodynamic parameters of the adsorption were calculated. The adsorption process was spontaneous and endothermic under investigated conditions.



### INTRODUCTION

Heavy metal ion pollution is currently of great concern due to the increased awareness of the potentially hazardous effect of elevated levels of these materials in the environment. Presently, the researchers and environmental control agencies are facing an increasing and alarming challenge as regards the several pollution of the water and soil resources through the indiscriminate disposal of metals in the environment.<sup>1</sup> Industrial waste often contains considerable amounts of metal ions that endanger public health and are hazardous for living organisms when they exceed the specific limits, as they cannot be biodegraded.<sup>2,3</sup>

Production and consumption of lead are increasing world wide. According to International

Lead and Zinc Study Group (2010) excessive amounts of lead reaching up to 8.757 million tonnes were used and consumed worldwide. The major industrial sources of lead released into the environment are battery manufacturing, acid metal plating and finishing ammunition, tetraethyl lead manufacturing, ceramic and glass industries printing, painting, dyeing, and other industries. Contamination could occur also when water flows through lead-containing pipes, though the use of lead for water piping is forbidden. On the other hand, it could enter the food chain through drinking and crop irrigation, which is considered to be a widespread problem. Lead is non-biodegradable and tends to bio-accumulate in the cells of the living things. Lead has been recognized for its negative effect on the environments where it

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accumulates in living systems. Lead poisoning in human causes severe damage to the kidney, nervous system, reproductive system, liver and brain. According to our environmental protection agency, the maximum contaminant level is 0.015 mg/L and the maximum contaminant level goal is zero.<sup>4-8</sup> A number of technologies for the removal of metal ions from aqueous solutions have been developed over the years. Most of these studies considered the adsorption characteristics of bentonite for some toxic elements. It has been well documented that bentonite is an efficient adsorbent for copper, zinc and cadmium,<sup>9-11</sup> and there are many studies that have reported using clays, mainly montmorillonite to show their effectiveness for the removal of metal ions such as zinc, lead and aluminum<sup>12,13</sup> from aqueous solution. However, systematic studies on lead adsorption characteristics on bentonite under various physicochemical parameters are limited and also are very scarce.

Besides providing high removal efficiency in heavy metal removal from waste streams, clay is an appropriate adsorbent with low cost. Montmorillonite, which has a high capacity for cations, is used as barrier material for the final repositories of hazardous waste.

Several researchers<sup>8, 14-21</sup> have studied the adsorption of different cations by montmorillonite clay. They found that the binding force was essentially electrostatic and that under ordinary conditions the adsorbed ions were hydrated as they were in solution.

The aim of the present work is to investigate the ability of sodium montmorillonite clay to remove lead ions from aqueous solution. Batch adsorption experiments will be applied. The effect of various parameters on the adsorption process such as the effects of pH, sodium montmorillonite dose, temperature and contact time will be investigated.

## EXPERIMENTAL

### Materials

The montmorillonite clay sample was Colony, Wyoming bentonite from Ward's Natural Science Establishment, New York. The unit cell formula is  $\text{Na}_{0.68}(\text{Al}_{3.32})\text{Mg}_{0.68}(\text{Si}_8\text{O}_{20})$

$(\text{OH})_4$ . The montmorillonite clay sample was saturated with  $\text{Na}^+$  using five washes of 1mol NaCl and centrifugation. It was then washed to be free of salt<sup>9</sup> (until  $\text{Cl}^-$  could not be detected in the leachate).

The clay was oven-dried at 70°C for 72h, ground, and stored in airtight vials. The moisture contents were determined on the sample at 300°C and the dry weights were calculated not to contain any adsorbed or cavity water but only the crystal lattice water.<sup>21</sup> The moisture content was found to be 11.7% on a dry basis.

### Adsorbent

#### X-ray powder diffraction (XRD)

XRD was used to characterize the sodium montmorillonite. Comparative XRD patterns of the natural sodium montmorillonite clay are shown in Fig. 1, which indicates that the dominant component is montmorillonite (68.74%). The remaining components are K-feldspar (15.72%) and Calcite (15.723%).

#### Specific surface area

The specific surface area of sodium montmorillonite was determined by applying the BET (Brunauer, Emmet and Teller) equation ( $770.7 \text{ m}^2\text{g}^{-1}$ ). The resulted surface area of natural montmorillonite is higher than those expected for commercial natural bentonite (untreated) (NB),  $S_{\text{NB}}=45.9 \text{ m}^2 \cdot \text{g}^{-1}$ . Several authors<sup>22, 23</sup> measured specific surface areas, for a montmorillonite without pretreatment, specific surface areas were 23.9 and 18.6  $\text{m}^2 \cdot \text{g}^{-1}$ . It is possible that  $\text{N}_2$  molecules can penetrate easily the interlayer regions between the layer sheets, involving an underestimation of the specific surface areas.<sup>24, 25</sup>

### General procedure

The adsorption of Pb (II) was studied by a batch technique. Stock and test solutions of Pb (II) were prepared by dissolving  $\text{Pb}(\text{NO}_3)_2$  in 1 litre deionized water. Standard lead solutions ranging between 50 and 100 mg/L were prepared by diluting the stock solutions. 0.6 gm of Na montmorillonite was mixed with 50 ml of lead solution with different concentrations (50-100 mg/L) in the shaker (160 rpm stirring rate) and 25°C temperature. The concentration of the remaining lead in the solution after shaking 1h was analyzed by using a Prodigy High Dispersion ICP Teledyne Leemanabs. pH was adjusted using 0.1M HCL and 0.1M NaOH solution. Fresh dilution was used for each experiment.

### Calculation

The adsorption capacity of Pb (II) ions adsorbed per gram adsorbed (mg/g) was calculated using the equation (1):

$$q_e = (C_0 - C_e) \cdot V/m \quad (1)$$

The amount of adsorbed Pb (II) was calculated from the difference of the lead concentration in aqueous solution before and after adsorption. The adsorption percentage of Pb (II) ions were calculated by the difference of initial and final concentration using the equation expressed as follows:

$$R\% = [(C_0 - C_e) / (C_0)] \times 100 \quad (2)$$

where  $q_e$  is the equilibrium concentration of Pb(II) on the adsorbent (mg/g).  $C_0$  the initial concentration of the Pb (II) solution (mg/L),  $C_e$  the equilibrium concentration of the Pb (II) solution (mg/L),  $m$  the mass of adsorbent (g),  $V$  the volume of Pb (II) solution, or the retention of Pb (II) in % of the added amount.

## RESULTS AND DISCUSSION

Various parameters for an effective removal of Pb (II) from aqueous solutions by using sodium montmorillonite adsorbent were studied.

### Effect of pH of the solution

The pH of the aqueous solution is an important controlling parameter in the adsorption process. In the present study, adsorption of Pb (II) cation on natural sodium montmorillonite adsorbents was studied over the pH range of 4-8.<sup>26</sup>

Experiments were carried out using Pb (II) ion concentrations (50 and 100 mg/L), keeping all other parameters are constant (stirring speed = 160 rpm, contact time 1 hour, adsorbent amounts (0.6g) at temperature  $298 \pm 0.2$  K) at different pH values. The results obtained revealed that the value of  $q_e$  increases by increasing the pH value and reaches a plateau at a pH value of 6.0.

Both the extent of absorption and the amount adsorbed showed a positive change. The influence of the pH values on concentration demonstrates that the cation strongly exchanges, by decreasing the acidity of the solution.

The surface charge of montmorillonite is a strong function of the pH. In this work the point of zero charge of montmorillonite at pH 4. Therefore, at low pH, the exchange sites on the montmorillonite particle become positive, the lead cations compete with the  $H^+$  ions in the solution for the active sites consequently lower adsorption.<sup>27</sup> At higher pH value, the surface of the sodium montmorillonite has a higher negative charge which results in a higher attraction of Pb (II) cation. At low pH values, for a strong acidic medium, the high hydrogen ion concentration at the interface (the hydrogen ions are more specifically adsorbed than Pb ions) repels the positively charged metal ions

electrostatically and prevents their approach to the morillonite clay.

For a strong acidic medium, the concentration of  $H_3O^+$  ions is out numbers Pb (II) ions in the adsorptive solution, and it is expected that at low pH, the adsorptive sites will be covered with  $H_3O^+$  ions preventing Pb (II) ions from adsorption. With increasing pH, surface sites become free for adsorption of various Pb – species such as Pb (II) and Pb (OH)<sup>+</sup>.

Therefore, the number of available hydrogen ions is high at low pH values and lead cations must compete with them to fulfill all adsorption sites on the inorganic surface. The active sites on the adsorbent surface are weakly acidic in nature and with the increase in the pH, they are gradually deprotonated, favoring Pb (II) uptake. A similar adsorption mechanism has been reported before.<sup>28, 29</sup> At higher pH (7-11), there are several species with different charges – this includes  $Pb(OH)^+$ ,  $Pb(OH)_2$  – and thus the removal of Pb is possibly accomplished by simultaneous precipitation of  $Pb(OH)_2$  and sorption of  $Pb(OH)^+$ .

### Effect of clay dosage

The adsorption efficiency of Pb (II) on sodium montmorillonite was studied at different adsorbent doses [0.1, 0.2, 0.4, 0.6, 0.8, 1 and 1.5 g, respectively] at initial lead concentrations (50 and 100 mg/L), temperature (25°C) and contact time (1 h) constant. Fig. 2 shows that with the increase in the adsorbent dose, the adsorption percentage of Pb(II) increased and the maximum removal was observed for an absorbed dose of 0.6 g. However, this result was expected since as the dose of adsorbent increases, the number of adsorbent sites increases. These amounts attach more ions to their surface. When clay dosage was increased to more than 0.6 g, the removal of lead was maintained constant, so 0.6 g of clay were enough for the quantitative removal of lead from the waste water. Similar results were reported where many types of materials were used as adsorbents.<sup>20, 30</sup>

On the other hand, unit adsorption (adsorbed amount, mg/g) decreased with increasing the adsorbent dosage (Fig. 3). This may be due to overlapping of adsorption sites as a result of the overcrowding of adsorbent particles.<sup>31</sup>

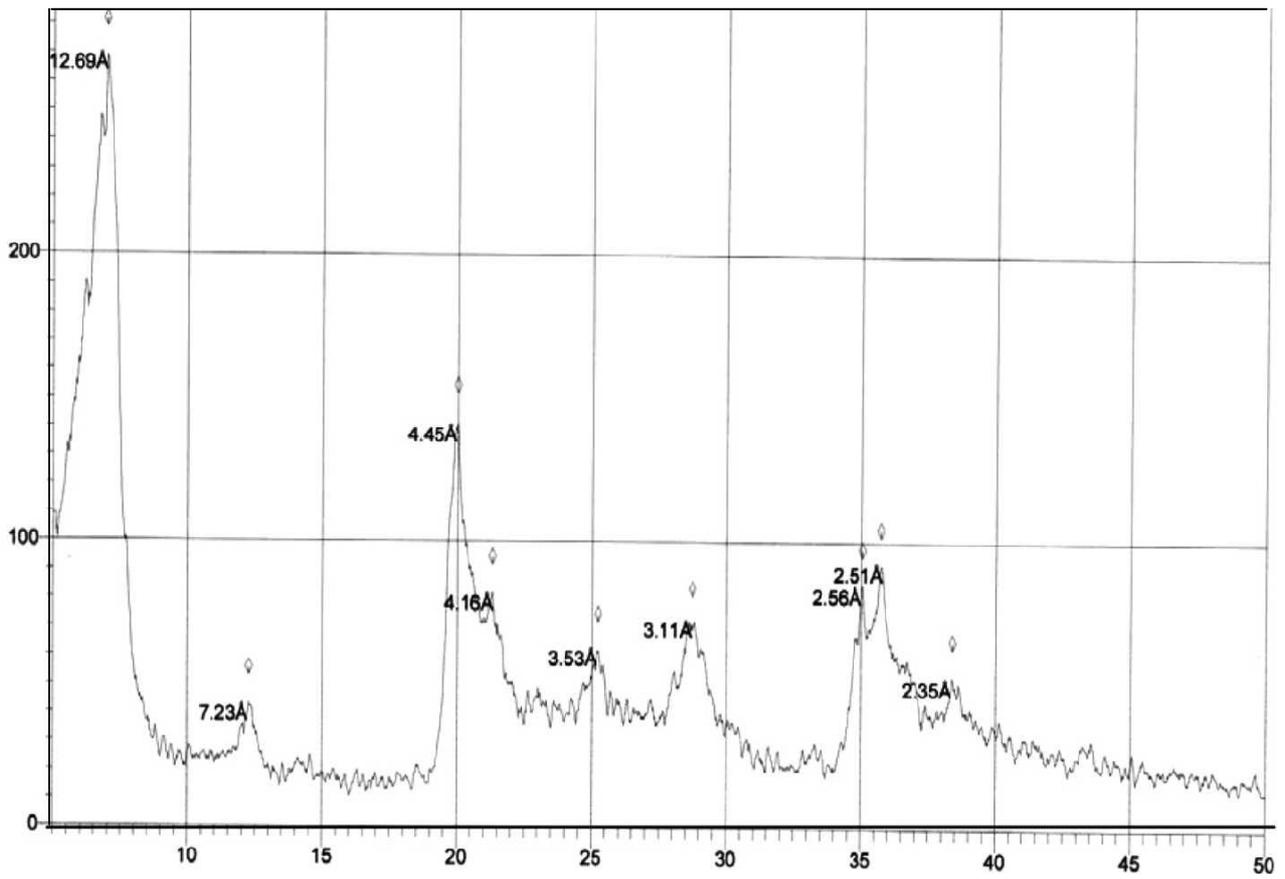


Fig. 1 – The XRD patterns of the sodium montmorillonite.

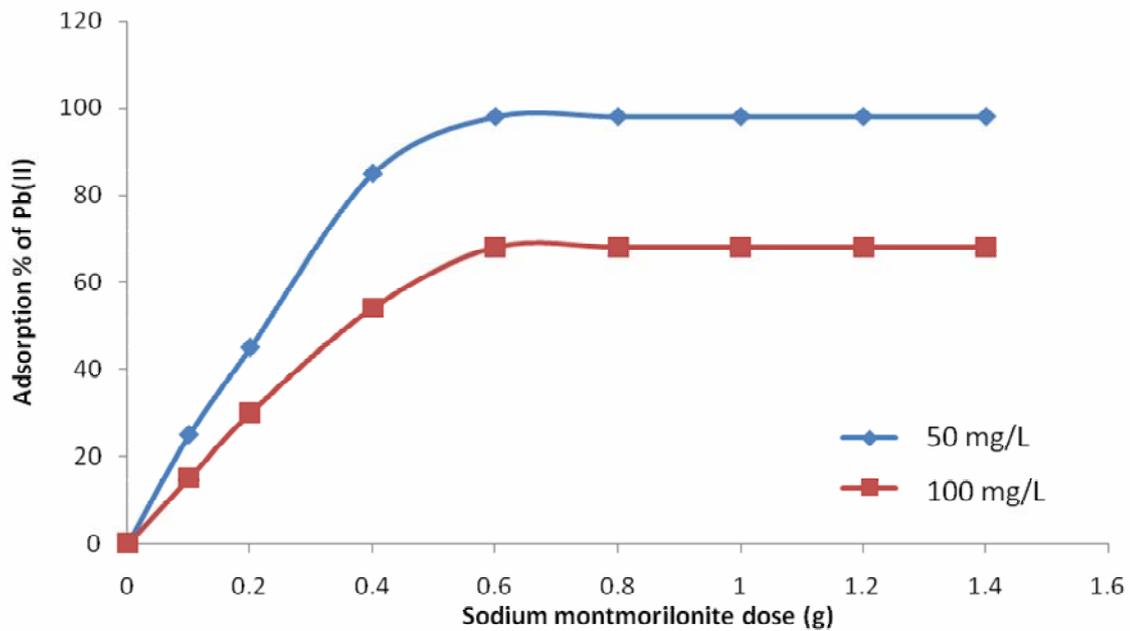


Fig. 2 – The effect of sodium montmorillonite dose on adsorption % of Pb(II) at different lead concentrations (50 and 100 mg/L) and constant temperature (25 °C).

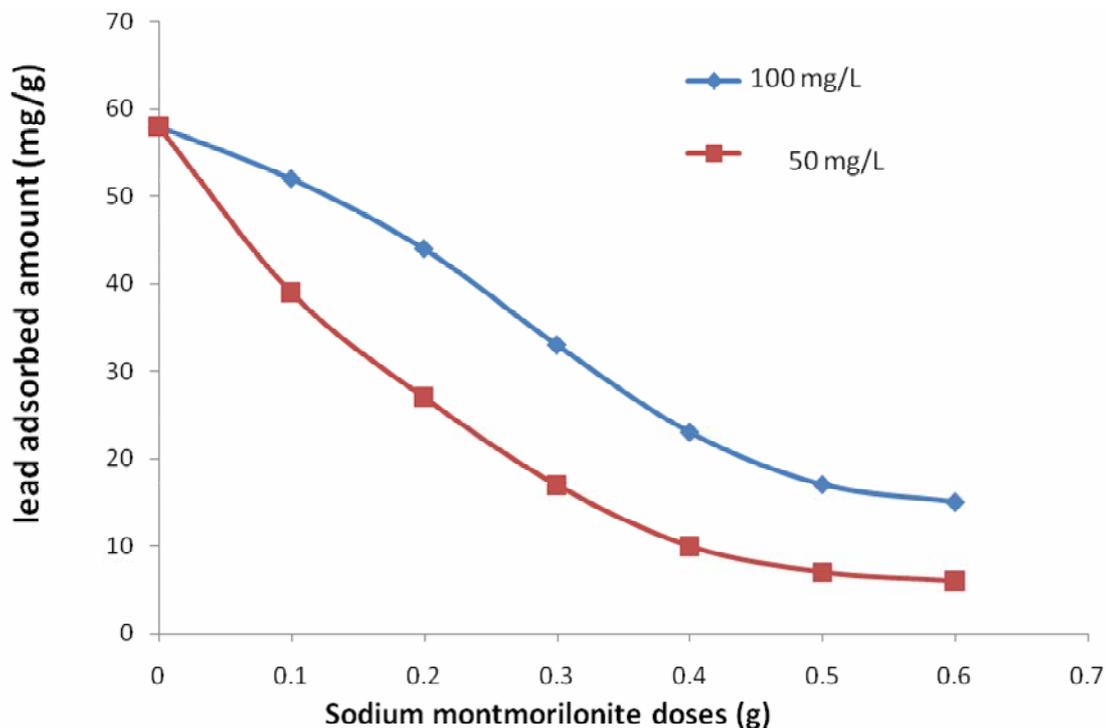


Fig. 3 – The effect of different lead concentrations on adsorption % of Pb(II) at sodium montmorillonite at 25 °C.

#### Effect of contact time

Fig. 4 shows that the removal of Pb (II) increases rapidly with time. Then it becomes relatively slower, continues at a relatively lower rate and reaches its maximum within about 30 min. Initially the removal of Pb (II) is rapid, but it slows down in later stages. This result might be attributed to initially large number of vacant surface sites available for absorption, having high free energy of

adsorption. After some time, the remaining vacant surface sites have lower free energy of adsorption and it is difficult to be occupied due to the competitions between the Pb (II) ions and the ions in the bulk solution.<sup>32</sup> The sorption equilibrium was reached quickly. The short time needed for adsorption to reach equilibrium could be attributed to high adsorption efficiency of clay.

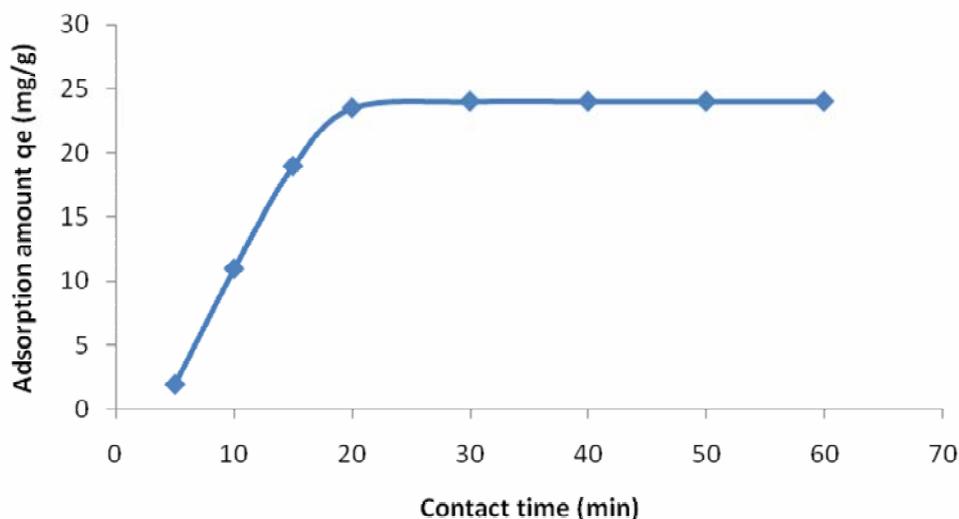


Fig. 4 – The effect of contact time on the % removal of Pb(II) at sodium montmorillonite at 25 °C.

### Kinetic modeling

In order to investigate the mechanism of adsorption, particularly the potential rate-determining step, the transient behavior of lead metal ions adsorption process was analyzed using the pseudo first order and pseudo-second order. As per Lagergren pseudo first order model, plot of  $\ln (q_e - q_t)$  versus  $t$  gives a straight line which allows computation of the rate constant  $k_1$  where  $q_t$  and  $q_e$  represent the amount of Pb(II) metal ion adsorbed (mg/g) at any time  $t$  and at equilibrium time, respectively. plot of  $\ln (q_e - q_t)$  versus  $t$  gives a straight line as with very poor linear regression coefficient ( $R^2$ ) of 0.66 to 0.87 more over pseudo first order model predicts a much lower value of the equilibrium adsorption capacity ( $q_e$ ) than the experimental value which is not shown here and hence it gives the inapplicability of this model. The adsorption data were then analyzed using the pseudo-second order kinetic model.

The pseudo-second order kinetic model based on equilibrium adsorption is expressed as:<sup>33</sup>

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

where ( $g, mg^{-1}min^{-1}$ ) is the rate constant of the second-order equation,  $q_t$  ( $mg g^{-1}$ ) the amount of adsorption time  $t$  (min) and  $q_e$  is the amount of adsorption equilibrium ( $mg g^{-1}$ ). A plot between  $t / q_t$  versus  $t$  gives the value of the constant  $k_2$  and  $q_e$  can be calculated. The pseudo-second order plot. High linear regression coefficient ( $R^2$ ) suggests that the lead ion adsorption experiment follows the pseudo-second order kinetics. This indicates that the absorption rate of Pb (II) depends on the concentration of ions on the sodium montmorillonite surface.<sup>34, 35</sup>

### Adsorption isotherm

An adsorption isotherm is a good tool for understanding the nature of surface. However, a correct selection of adsorption equation for different concentration ranges reveals a true picture of the surface. At low coverage, Henry and Freundlich models explain the adsorption process, whereas the Langmuir model describes the monolayer coverage at high concentration. The

equilibrium data for metal cation over the concentration range from 40-1000 mg/L and the temperature range of 298–328K have been correlated with the Langmuir isotherm. The basic assumption of the Langmuir model, the amount of  $Pb^{2+}$  adsorbed can be expressed by:

$$C_e/q_e = 1/(q_m k_L) + (1/q_m)C_e \quad (4)$$

where  $q_e$  is the equilibrium Pb (II) concentration on adsorbent ( $mg g^{-1}$ ),  $q_m$  is the maximum amount of adsorption ( $mg g^{-1}$ ),  $k_L$  is the affinity constant or Langmuir adsorption constant ( $L mg^{-1}$ ) and  $C_e$  is the solution concentration at equilibrium ( $mg L^{-1}$ ). Fig. 5 shows the relationship between the adsorbed amounts of Pb (II) per unit of mass of sodium montmorillonite and the equilibrium of Pb (II) concentration in the temperature range of 298–328K. It is clear that, when the temperature increased, the adsorbed amount decreased, suggesting the sorption process was an energy dependent mechanism.<sup>36, 37</sup>

In this study, the adsorption results were analyzed in terms of Freundlich and Langmuir isotherms. Fig. 5 shows that the adsorption capacities of Pb (II) from aqueous solutions by sodium montmorillonite increased with increasing temperature. This result occurs because of increasing the frequency of collisions between the adsorbent and metal ions, which enhances the adsorption of metals on the surface of the sodium montmorillonite.

From a plot of  $C_e/q_e$  versus  $C_e$ ,  $q_m$  and  $k_L$  can be determined from its slope and intercept (see Table 1).

The data in Table 1 present the results, along with associated correlation coefficients ( $R_2$ ). The data in Table 1 reveal that the Langmuir model yields a better fit than the Freundlich model, according to the correlation coefficients.

### Thermodynamics of adsorption

The thermodynamic parameters for the adsorption of Pb(II) are shown in Table 2. The plot used to obtain data for the various thermodynamic parameters is shown in Fig. 6.

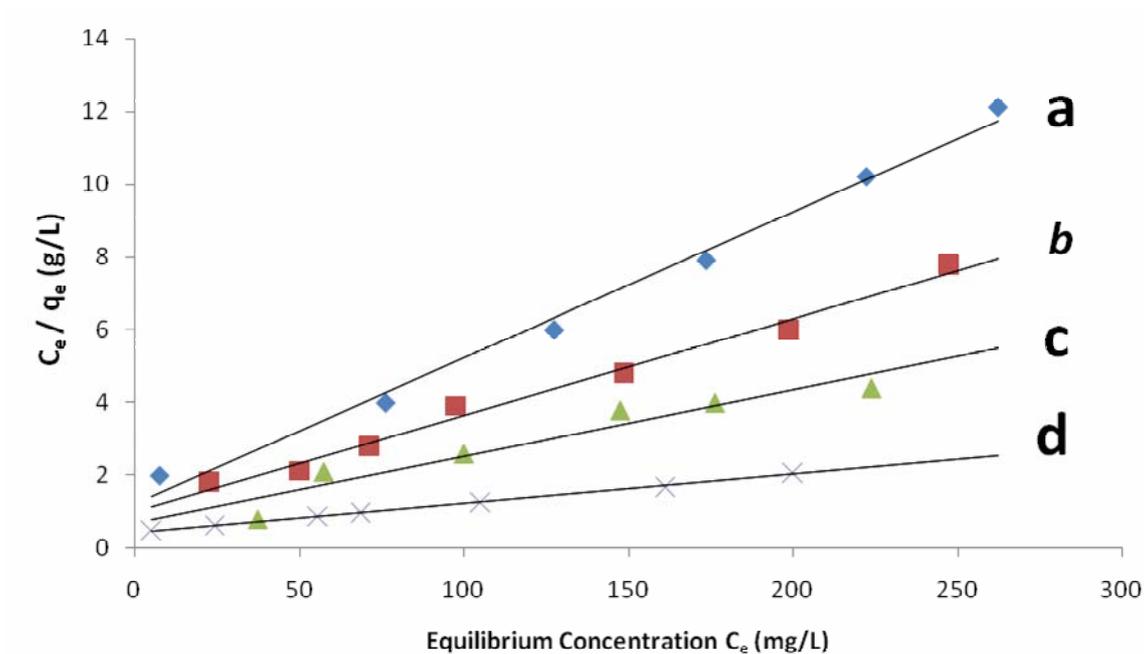


Fig. 5 – The relationship between the adsorbed amounts of Pb (II) per unit mass of sodium montmorillonite and the equilibrium of Pb (II) concentration in the temperature range of 298–328K.

Table 1

Parameters of Langmuir adsorption isotherm models for Pb (II) on modified sodium montmorillonite at different temperatures

Temperature (K)	$q_m$ (mg/g)	$k_L$ (L/mg)	$R^2$
298	79.37	0.0126	0.991
308	109.89	0.0228	0.987
318	125	0.04	0.915
328	142.9	0.0567	0.998

Table 2

Thermodynamic constants for the adsorption of Pb (II) on modified sodium montmorillonite at various temperatures

Temperature (K)	$\Delta G^\circ$ (kJ mol <sup>-1</sup> )	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )
298	-19.22	22.5	140
308	-20.62		
318	-22.02		
328	-23.42		

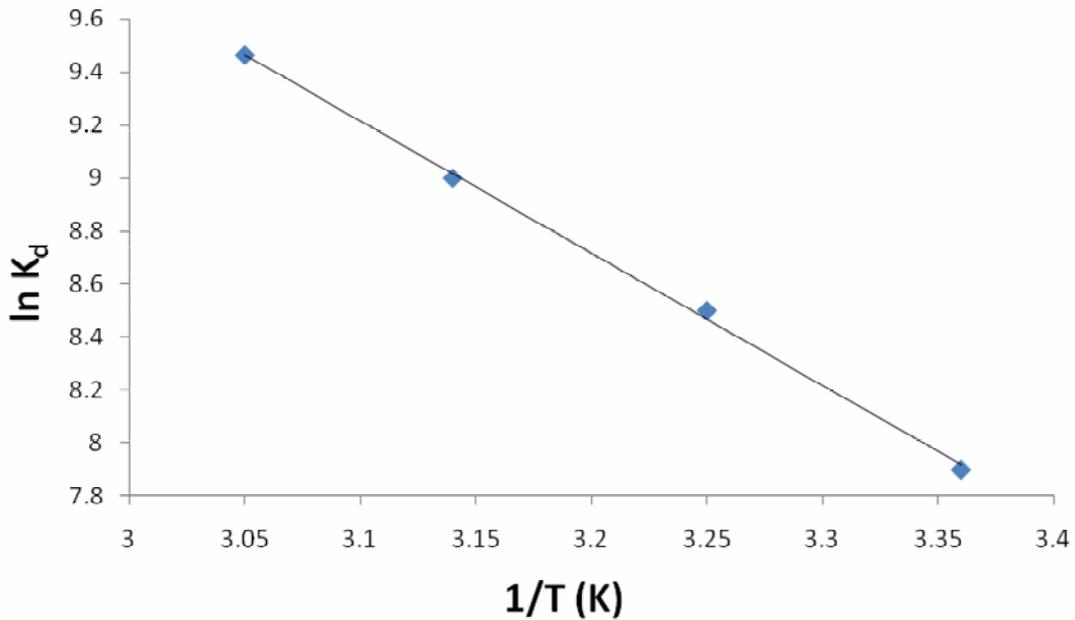


Fig. 6 – The effect of temperature on the thermodynamic behavior of adsorption of Pb(II) at sodium montmorillonite.

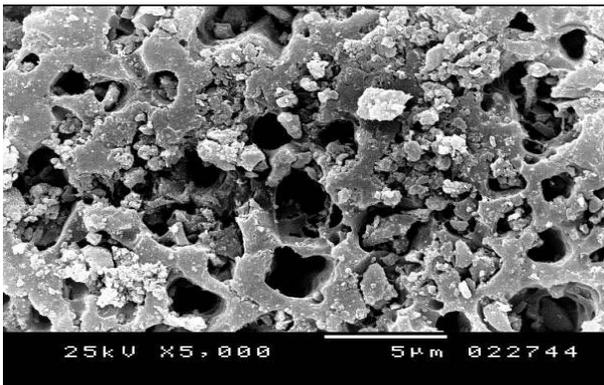


Fig. 7a – Sodium montmorillonite before adsorption.

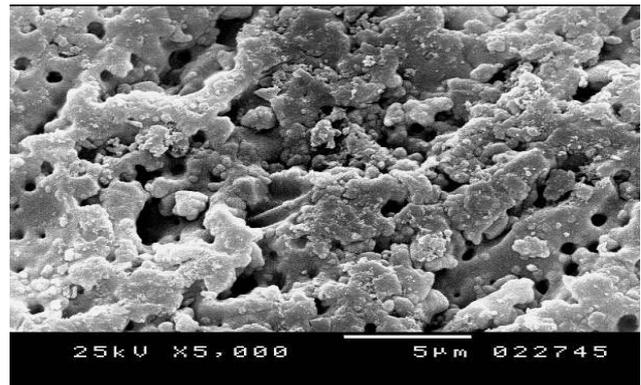


Fig. 7b – Sodium montmorillonite after adsorption of Pb(II).

The changes in Gibbs free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ), and entropy ( $\Delta S^\circ$ ) for the adsorption process were obtained using the following equations:<sup>38</sup>

$$\ln K_d = \Delta S^\circ / R - \Delta H^\circ / RT \quad (5)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (6)$$

where  $R$  is the ideal gas constant ( $J \text{ mol}^{-1} \text{ K}^{-1}$ ), the equilibrium constant ( $K_d = K_c = q_e / C_e$ ) and  $T$  is the temperature in (K).

The enthalpy of adsorption ( $\Delta H^\circ$ ) is a measure of the energy barrier that must be overcome by reacting molecules. The values of  $\Delta H^\circ$  were found to be  $22.5 \text{ kJ mol}^{-1}$  was positive. One possible explanation of positive  $\Delta H^\circ$  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 supersedes 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. This suggests that the adsorption reaction of Pb(II) onto sodium montmorillonite adsorbent is endothermic in nature, meaning that increasing temperature will favor the adsorption of Pb(II) onto sodium montmorillonite adsorbent. The value of  $\Delta S^\circ$  is an indication of whether or not the adsorption reaction is by an associative or dissociative mechanism. The entropy measures the width of the saddle point of the potential energy surface over which reactant molecule must pass as activated complex. Entropy change is  $140 \text{ J.K}^{-1} \text{ mol}^{-1}$  and generally implies a dissociative mechanism. The value of

$\Delta S^\circ$  is unexpected for the adsorption of lead ions on sodium montmorillonite adsorbent. Associative mechanism is expected. The abnormality may not necessarily mean that the adsorption of lead ions on sodium montmorillonite adsorbent is dissociative in nature, but that there could be some structural changes in the adsorbate and adsorbent during the adsorption reaction.<sup>39</sup>

The negative value of the Gibbs free energy ( $\Delta G^\circ$ ) for lead adsorption by sodium montmorillonite process is spontaneous. A more negative value of  $\Delta G^\circ$  at higher temperatures, as was observed in this study, implies a greater driving force for adsorption at higher temperature.

### Surface characterization

The SEM micrographs were shown in Fig. 7. The SEM images for the sodium montmorillonite before and after adsorption of Pb(II) showed that the surface morphology of adsorbent changed. Before adsorption (Fig. 7a), the surface of sodium montmorillonite is of an irregular form, rough and more cracks appeared and the surface contains a large number of pores. After adsorption (Fig. 7b), the surface appears smoother, regular and compact which indicate the high affinity between sodium montmorillonite and lead ions.

### CONCLUSIONS

Pb (II) could be adsorbed and thus higher significant amounts removed by sodium montmorillonite from aqueous solutions.

In batch mode adsorption studies, the removal of Pb (II) increased with the increase of contact time, and reached its maximum within about 30 min.

The percentage of adsorption increased with increasing the adsorbent dose.

$q_e$  (adsorbed amount,  $\text{mg g}^{-1}$ ) decreased with increasing in adsorbent dosage.

The adsorption percentage increases by increasing the pH value and reaches a plateau at pH values of 6.0.

Kinetic modeling results showed that the pseudo second-order equation was appropriate for the description of this type of adsorption and removal.

Depending on the negative value of  $\Delta G^\circ$ , the adsorption of Pb (II) on sodium montmorillonite surfaces was spontaneous and from ( $\Delta H^\circ$ ) process was endothermic process.

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