Sorption of Pb(II) Ions by Kaolinite Modified with Humic Acids

Khansaa Al-Essa¹ and Fawwaz I. Khalili²

1. Department of Chemistry, The University of Jerash, Jerash 26150, Jordan
2. Department of Chemistry, The University of Jordan, Amman 11942, Jordan

Abstract: Sorption of Pb(II) onto modified Jordanian kaolinite clay by Fluka Humic Acid (FHA) or humic acid extracted from King Talal Dam sediments (KTD) was studied using batch technique at different time, concentration, temperatures and pH. The kinetic studies showed that the uptake increases with time and reached the equilibrium in less than 2 hours and fitted pseudo second-order model for the two modified humic acid kaolinite clay. The Pb(II) uptake properties on both modified kaolinite clay fit Langmuir, Freundlich and Dubinin-Radushkevich sorption models. The energy of sorption process calculated from Dubinin-Radushkevich showed that the sorption was a physical one. The values of ΔG° indicated that the sorption process was favorable, while ΔH° values indicated an endothermic process. On the other hand, the process has positive ΔS° which drives the sorption process. Kaolinite clay modified by (FHA) showed higher uptake for Pb(II) than that modified by KTD.

Key words: Kaolinite, humic acid, Pb(II) sorption isotherm, thermodynamics, kinetics.

1. Introduction

The pollution of water with toxic substances is a major problem because it affects the environmental quality and living systems. Heavy metals are one of the toxic substances and are hazardous even at very low concentrations [1] because they are non-biodegradable and bio-accumulate [2]. For that reason, the removal of these metals from water and wastewater is important in terms of protection of public health and the environment [3]. Lead is an important metal from the viewpoint of environmental toxicology, since it has find its way into air and water from a multitude of sources like lead smelter, battery manufacturer, paper and pulp industry, boat and ship fuel and ammunition industry [4-6]. Therefore, lead levels in wastewater, drinking water and water used for agriculture should be reduced to the maximum allowed concentration.

Several methods have been applied over the years for the elimination of toxic metal ions present in wastewaters, such as chemical precipitation, ion-exchange, solvent extraction, ultrafiltration, reverse osmosis, electrolysis and sorption [7, 8]. The sorption technique is favorable in terms of cost, flexibility, simplicity of design, ease of operation, insensitivity to toxic pollutants and better removal efficiency [9].

Natural adsorbents have strong affinity and high loading capacity for the removal of heavy metals [10, 11]. For example, clay minerals, zeolites [12], activated carbon [12], activated bleaching earth [13], bentonite [14], montmorillonite [15], smectite [16] and kaolinite [16-20] have been used to remove different heavy metals from aqueous solution.

Kaolinite has relatively low cation-exchange capacity (CEC) [3-15 meq for 100 g of clay] and a smaller surface area ranging from 10 to 20 (m²·g⁻¹) [19], so it is often modified from its natural state by physical or chemical treatments to enhance the properties of the material, and to improve its sorption capacity [21].

Corresponding author: Fawwaz I. Khalili, professor, Ph.D., main research field: environmental chemistry.
Modification of kaolinite can be achieved by either impregnation or grafting of organic/inorganic molecules on its surface. Kaolinite clay was modified by tripolyphosphate [21], sodium tetraborate [22], sulfate- and phosphate [11] and tetrabutylammonium [23].

Humic Acids (HA’s) are complex aggregates of dark-colored amorphous high molecular weight substances extracted from the natural degradation products of plant and animal residues. HA contains carboxyl (−COOH), amine (−NH2), hydroxyl (−OH), and phenol (Ar −OH) functional groups, and has negative charge in weakly acidic-to-basic media because of deprotonation [24].

Previously, the modification of bentonite by sorption of humic acid and it’s uptake of heavy metals was studied in our laboratory [25]. This is part of a study seeking to introduce modified kaolinite clay as a new low-cost and more efficient adsorbent for humic acid and toxic metal ions [26], since Jordan has a huge reserve of kaolinite, estimated to be 9.7 billion metric tons at Al-Mudawwara [27]. In this work, the modification of Jordanian kaolinite clay by two types of humic acids having different characteristics and origin was done in order to understand the role of kaolinite in nature in terms of removing different types of humic acids from brown water. Then the sorption behavior of Pb(II) ions into the two modified kaolinite was studied at different pH and temperatures. The kinetic and thermodynamic parameters were calculated in order to understand the effect of each type of humic acid.

2. Materials and Methods

2.1 Materials

All chemicals were obtained from commercial sources as either analytical reagent grade or chemically pure grade and were used as received. The chemicals were purchased from the corresponding companies: sodium hydroxide NaOH (LOBA), sodium perchlorate anhydrous (Alfa Aesar), perchloric acid 65% (VWR), anhydrous potassium chloride KCl (Puriss) and silver nitrate AgNO₃ (Puriss). Two types of HA were used; one was from Fluka Company (FHA) and the other was extracted from King Talal Dam sediments (The King Talal Dam was built in 1978 on the Az Zarqa River) [28]. Kaolinite clay was obtained from the Al-Mudawwara region in east of Jordan.

2.2 Instrumentation

Concentrations of the metal ions were determined by using (Varian Spectra AA-250 pulse) atomic absorption spectrometer (AAS). Concentrations of HA were determined by using UV-VIS Spectrophotometer (Varian Cary100). Drying of the modified kaolinite clay was done by freeze-dryer (ALPHA 1-4). Shaking of samples was done by using Clifton shaker equipped with thermostat and the pH was measured by using METROHM 605 pH-meter.

2.3 Methods

2.3.1 Humic Acid- Kaolinite Clay Complex Preparation

The > 250 µm kaolinite clay fractions were obtained by wet sedimentation and subsequently exchanged with K⁺ by washing four times with 0.5 M KCl solution. The excess KCl was removed by repeatedly washing with deionized water until a negative chloride test was obtained by AgNO₃ solution. The clay suspensions were quickly frozen, freeze-dried and stored in a closed container prior to use [15].

The modification of kaolinite by HA was done by dissolving 1.0000 g ± 0.1 mg of either Fluka humic acid (FHA) or King Talal Dam humic acid (KTD) in 1.0 L of 0.5 M KCl solution at pH 4 and 45 °C, followed by mixing with 10.0000 g ± 0.1 mg of the corresponding K⁺-kaolinite for 1 week. The HA-kaolinite adduct was separated by centrifugation, and mixed with 0.5M KCl solution (three times) to saturate the cation-exchange sites in HA, and then dialyzed against deionized water and washed (twenty times) with deionized water until neither light
brown-colored humic substances in supernatants nor HA particulates accumulating on the top of kaolinite fractions after centrifugation were visualized. The HA-kaolinite complex was quickly frozen and freeze-dried.

2.3.2 Preparation of Stock Solutions of Metal Ion

Stock solutions of 1,000 ppm for the metal ion were prepared separately by dissolving specific amount of Pb(NO₃)₂ in 0.01 NaClO₄ and was adjusted by 0.10 HClO₄ and/or 0.10M NaOH to the desired pH. The stock solutions were used to prepare solutions with different concentrations (10, 20, 30, 40, 50, 60, 80 and 100 ppm). The dilution is achieved by using 0.01M NaClO₄ to keep the ionic strength constant.

2.3.3 The Rate of Metal Ion Uptake by Batch Techniques

Experiments for determination of the equilibrium time of the sorption process were studied by shaking 0.2000 g ± 0.1 mg of the modified kaolinite with 20.0 mL of 100 ppm metal ion solution at a pH of 5.00 for kinetic purposes. The contact time was varied from 30 minutes to 24 hr at 35 °C. The mixture was filtered and the concentration of the metal ion remaining was determined using AAS. Every measurement was repeated three times to make sure of the accuracy and reproducibility of the results.

2.3.4 Sorption Isotherms Experiments

The sorption of Pb(II) on both modified kaolinite was studied in the initial pH range of 4.00, 5.00, 6.00, at different temperatures of 25, 35, 45 °C for 0.2000 g ± 0.1 mg adsorbent dose and 20.0 mL of different initial concentrations of 10, 20, 30, 40, 50, 60, 80 and 100 ppm at a constant ionic strength of 0.01M NaClO₄. Every measurement was repeated three times to make sure of the accuracy and reproducibility of the results, and then the average was taken. The metal ion percentage uptake by the kaolinite (q) was obtained using the Eq. (1):

\[ q = \frac{(C_i - C_e)}{m} V \times 100\% \]  

where;
- \( q \): metal ion uptake by kaolinite in (mg/g);
- \( C_i \): initial metal ion concentration (ppm) in the solution;
- \( C_e \): the residual concentration of the metal ion in solution at equilibrium in (ppm);
- \( V \): volume of solution (L);
- \( m \): mass of kaolinite (g).

3. Results and Discussion

3.1 Kinetics of Sorption

Sorption kinetics is used in order to explain the sorption mechanism and sorption characteristics. Two kinetic models, Lager green pseudo-first-order and pseudo-second-order reaction, were tested to find out which model is in agreement with the experimental results of kinetic study [17].

3.1.1 Pseudo-first-order Reaction Kinetic

The sorption rate constant was first proposed by Lager green in 1898 [29]. The first order reaction kinetic equation is shown as Eq. (2):

\[ \frac{dq}{dt} = k_1 (q_e - q_t) \]  

where \( k_1 \) (min⁻¹) is the Pseudo-first-order sorption rate constant for the first order sorption, \( q_e \) and \( q_t \) (mg·g⁻¹) are the amount of metal ions adsorbed per unit mass at equilibrium and at any time \( t \), respectively, and is the amount of metal ions adsorbed at (mg·g⁻¹).

After definite integration by applying the conditions \( q_e = 0 \) at \( t = 0 \) and \( q_e = q_t \) at \( t = t \), Eq. (2) becomes the Eq. (3):

\[ \ln (q_e - q_t) = \ln q_e - k_1 t \]  

The values of \( k_1 \) can be obtained from the slopes of the linear plots of ln(\( q_e - q_t \)) versus \( t \). The validity of the first-order kinetics and hence the Lager green equation could be tested by comparing \( q_e \) values obtained from the intercepts of the plots with those obtained. If the validity is weak, the kinetics can be tested for following second-order mechanism [17].
3.1.2 Pseudo-second-order Reaction Kinetic

The pseudo-second-order reaction assumes that the rate limiting step may be chemical sorption [30]. Sorption data was evaluated according to the pseudo-second-order reaction kinetic proposed by Ho and McKay [31]:

\[
\frac{dq}{dt} = k_2 (q_e - q_t)^2
\]  

(4)

where \( k_2 \) is the second order reaction constant (g·mg\(^{-1}\)·min\(^{-1}\)). For the boundary conditions, \( t = 0 \) to \( t = t \) and \( q_t = 0 \) to \( q_t = q_e \), the integrated linear form of the equation is written as:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]  

(5)

The plot of \( t/q_t \) vs. \( t \) gives a linear relationship, allowing for computation of \( q_e \) and \( k_2 \).

The validity of this model can be tested by comparing values of the experimental \( q_e \) (mg·g\(^{-1}\)) values (when \( q_e \) reach’s plateau) with the calculated \( 1/ \) slope of the pseudo-second-order kinetic plots as obtained from Eq. (5) [17].

Sorption of the metal ion at (308.15 K) was initially very fast and the maximum uptake was recorded within 30 min. The initial uptake rate for the metal ion was very high as a large number of sorption sites (e.g. carboxyl and phenolic hydroxyl sites on the clay) were available for sorption at the beginning of the process, where sorption proceeded with a high rate. As the sites were gradually filled up, the number of sites became less and metal ion had to fiercely compete among themselves for getting adsorbed, so sorption became slow and the kinetics became more dependent on the rate at which the metal ionic species were transported from the exterior to the interior sites of the clay mineral particles or from the bulk of the solution to the clay surface.

The linearity of the plots of the pseudo-second-order model with \( R^2 \) values greater than 0.90 for Pb(II), indicating that one of the mechanisms or the rate determining step of the sorption of Pb(II) by modified kaolinite was by chemisorption [6].

Moreover, the experimental \( q_e \) values (when \( q_e \) reach’s plateau) were equal to the calculated values of the pseudo-second-order kinetic plots as obtained from Eq. (5). Table 1, which indicates that pseudo-second-order kinetic model, is considered appropriate to represent the kinetic data.

3.2 Sorption Isotherms

The isotherm plots for lead(II) ions sorption on both modified kaolinite with a fixed adsorbent dose at different pH values of 4.00, 5.00 and 6.00 and different temperature of 25, 35 and 45 °C are shown in Figs. 1, 2. They were analyzed using Langmuir, Freundlich (For examples see Fig. 4, 5) and D-R isotherm models.

It is clear from Figs. 1, 2 that as the metal ion concentration remaining in the metal ion solution decreased, sorption increased first rapidly, and then slowed down, and finally the saturation was reached. This is because of the more efficient utilization of the adsorptive capacities of the adsorbent. The shape of isotherm for Pb(II) sorption on both modified kaolinite is L-curve, which is the most common type and it describes the case where the solid (modified kaolinite) has a high affinity for the solute (metal ion) especially in the initial stages of the isotherm. As more sites in the substrate (modified kaolinite) are filled, it becomes increasingly difficult for solute

| Table 1 Calculated and experimental qe values for both modified kaolinite. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Kinetic model   | Type of modified clay | Value of qe (mg·g\(^{-1}\)) | \( k_2 \) (g·mg\(^{-1}\)·min\(^{-1}\)) | \( R^2 \)        |
| Pseudo-first-order kinetic | FHA-kaolinite | 0.74 | 2.77 | ----- | 0.0656 |
|                  | KTD-kaolinite   | 0.80 | 5.68 | ----- | 0.4731 |
| Pseudo-second-order kinetic | FHA-kaolinite | 2.80 | 2.80 | 0.0208 | 0.9963 |
|                  | KTD-kaolinite   | 2.10 | 2.10 | 0.1388 | 0.9998 |
molecules to find a vacant site available. This means that the surface becomes covered and saturated from the first monolayer molecules, so there are no more available sites [32, 33].

To discriminate whether surface precipitation of Pb(II) accompanies ion exchange process or not, Apak, et al. [34] introduced the limiting pH of metal ion solubility term as the pH where precipitation of metal ions start. For this purpose, the limiting pH of metal ion solubility for 10 ppm Pb(II) must be calculated. Once the limiting pH of solubility (i.e., pH*) is known, sorption experiments are carried out below this predetermined pH. Computing the critical pH of the initiation of bulk precipitation (pH*) is allowed to measure true sorption and the removal of the metal ions concerned by providing ample space for all kinds of sorption of soluble complex species, including polynuclearhydroxo-metal cations. Thus the mass
balance equation of James-Healy modeling [35] should be applied and the exemplification of pH* vs pMt (where Mt is the total free metal ions concentration that can exist in aqueous solution in equilibrium with M(OH)2(s)) correlations has been undertaken as mentioned by Apak, et al. [34].

If a series of Mt values are calculated for specified pH using the stability constants of lead-hydroxide complexes system obtained from the literature [36-38] as log β₁ = 6.2, log β₂ = 10.3, log β₃ = 13.3, and pKₚ for (Pb(OH)₂) = 15.10 and pMt are correlated with pH by linear regression analysis, then a simple logarithmic equation of the form (pH* = 0.500pMt + 6.452) may be derived, which will suffice for estimating the limiting pH of solubility (pH*) of the lead ion with reasonable accuracy, given the total lead

Fig. 2 Sorption isotherms of Pb(II) on KTD-kaolinite at (a) 25 °C, (b) 35 °C and (c) 45 °C and different pH.
Fig. 3  Limiting pH of solubility of lead ion as a function of total Pb(II) concentration in the absence of complexing ligands except OH\(^-\) at pH 6.

3.2.1 Langmuir Sorption Isotherm Model

The Langmuir isotherm is a valid monolayer sorption on completely homogeneous surfaces containing a finite number of binding sites. It assumes uniform energies of sorption on the surface and no transmigration of adsorbate in the plane of the surface, with negligible interaction between adsorbed molecules [39].

The linear forms of the Langmuir equation are written as Eq. (6) [40]:

\[
\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{6}
\]

where \(q_e\) is the amount of solute adsorbed per unit weight of adsorbent (mg·g\(^{-1}\)), \(C_e\) is the equilibrium concentration of solute (ppm), \(q_m\) is the sorption capacity (mg·g\(^{-1}\)), or monolayer capacity, and \(K_L\) is the Langmuir equilibrium constant related to the affinity of binding sites and energy of sorption (L·mg\(^{-1}\)) [41]. From these equations we can calculate the values of \(q_m\) and \(K_L\).

One of the essential characteristics of the Langmuir isotherm model can be explained in terms of the dimensionless constant called equilibrium parameter \(R_L\) [42] which is defined as:

\[
R_L = \frac{1}{1 + K_L C_o} \tag{7}
\]

where \(C_o\) is the highest initial concentration (ppm).

The Linearized Langmuir isotherms parameters for the sorption of Pb(II) on modified kaolinite have the highest correlation coefficients and are shown in Fig. 4 and Table 2.

The sorption of Pb(II) on modified kaolinite fitted Langmuir model. From the Langmuir constant, the values of \(R_L\) indicates the type of the isotherm to be either unfavorable sorption (\(R_L > 1\)), linear sorption (\(R_L = 1\)), favorable sorption (0 < \(R_L < 1\)) or irreversible sorption (\(R_L = 0\)) [21, 43]. So as shown in Table 2, the \(R_L\) values for Pb(II) are between 0.0118 and 0.0293. The \(R_L\) values for metal ion adsorbed by both modified kaolinite are between 0 and 1, so the sorption process of Pb(II) is favorable. From Table 2, the values of \(q_m\) which is related to sorption capacity indicated that the increase of temperatures and pH led to the increase in the sorption capacities of both modified kaolinite for Pb(II).

This is can be explained as follows: the surface of the kaolinite contains a large number of active sites
Fig. 4 Plots of linearized Langmuir isotherm (II) for Pb(II) adsorbed by FHA-kaolinite at (a) 25 °C, (b) 35 °C and (c) 45 °C.
Sorption of Pb(II) Ions by Kaolinite Modified with Humic Acids

Table 2  Linearized Langmuir isotherm parameters for Pb(II) adsorbed by both KTD-kaolinite and FHA-kaolinite.

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>pH</th>
<th>Langmuir isotherm (Ce/qe vs. Ce)</th>
<th>Langmuir isotherm (Ce/qe vs. Ce)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>K_L</td>
<td>q_m</td>
</tr>
<tr>
<td>4.00</td>
<td>4.00</td>
<td>0.3662</td>
<td>0.0266</td>
</tr>
<tr>
<td>25</td>
<td>5.00</td>
<td>0.5511</td>
<td>0.0178</td>
</tr>
<tr>
<td></td>
<td>6.00</td>
<td>0.5228</td>
<td>0.0187</td>
</tr>
<tr>
<td>4.00</td>
<td>4.00</td>
<td>0.4466</td>
<td>0.0219</td>
</tr>
<tr>
<td>5.00</td>
<td>5.00</td>
<td>0.4798</td>
<td>0.0204</td>
</tr>
<tr>
<td>6.00</td>
<td>6.00</td>
<td>0.5031</td>
<td>0.0195</td>
</tr>
<tr>
<td>35</td>
<td>5.00</td>
<td>0.4798</td>
<td>0.0204</td>
</tr>
<tr>
<td>4.00</td>
<td>4.00</td>
<td>0.6034</td>
<td>0.0163</td>
</tr>
<tr>
<td>6.00</td>
<td>6.00</td>
<td>0.8343</td>
<td>0.0118</td>
</tr>
</tbody>
</table>

Units for the parameters: K_L (L·mg⁻¹), q_m (mg·g⁻¹) and R_L unitless.

and may become positively charged at a very low pH, thus increasing the competition between H⁺ and the metal ions for available sorption sites. However, as pH increases, this competition decreases as these surface active sites becomes neutral and/or more negatively charged due to the deprotonation of humic acid, which enhances the sorption of the positively charged metal ions through electrostatic force of attraction [22]. So, Pb(II) ions sorption increases by the combined action of aluminol, carboxyl and phenol groups at a higher pH [44].

3.2.2 Freundlich Adsorption Isotherm Model

The Freundlich isotherm theory says that the ratio of the amount of solute adsorbed onto a given mass of sorbent to the concentration of the solute in the solution is not constant at different concentrations [19]. The Freundlich isotherm can be used for non-ideal sorption that involves heterogeneous sorption surface and active sites with different energies [45].

The logarithmic linear form of the Freundlich equation is given as [46, 47]:

\[ \log q_e = \log K_F + \frac{1}{n} \log C_e \]  

where K_F is the Freundlich constant (mg·g⁻¹) indicating the adsorption capacity and n (g·L⁻¹) is the adsorption intensity [6]. Both K_F and n are empirical constants; where K_F indicates the adsorbate priority for adsorption [48, 49]. On the other hand, greater values of K_F indicate higher capacity for the adsorption than smaller values [14]. Theoretically, the Freundlich equation represents a situation in which the quantity of solute adsorbed increases indefinitely with increasing concentration. This will occur when multilayer is formed and heterogeneous adsorption sites are implied [50].

The Freundlich isotherm plots and parameters for the sorption of Pb(II) on modified kaolinite are shown in Fig. 5 (for example) and Table 3.

The sorption of Pb(II) ions by modified kaolinite clay fitted Freundlich model, and the Freundlich isotherm plots had excellent linearity (R² > 0.90). The adsorption coefficients (K_F, n) agreed well with the conditions supporting favorable adsorption. From the Freundlich model, better adsorption has higher K_F value. With reference to Table 3, K_F values increase with increasing both temperature and pH for Pb(II). The values of n are greater than one which is shown in Table 3 for Pb(II) between 0.672-5.287, indicating that the adsorption is favorable [22, 51].

3.2.3 Dubinin-Radushkevich (D-R) Adsorption Isotherm

The D-R equation is an adaptation of the earlier Polanyi potential theory of adsorption [52], which is for the volume filling of microspores. The idea that the mechanism for adsorption of gas molecules in microspores is that of pore filling rather than a layer-by-layer formation of a film on the walls of the
Fig. 5 Plots of linearized Freundlich isotherm for Pb(II) adsorbed by FHA-kaolinite at (a) 25 °C, (b) 35 °C and (c) 45 °C.
Table 3  Freundlich isotherm parameters for Pb(II) adsorbed by both KTD-kaolinite and FHA-kaolinite.

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>pH</th>
<th>n</th>
<th>Kf</th>
<th>R²</th>
<th>n</th>
<th>Kf</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>4.00</td>
<td>3.398</td>
<td>2.74</td>
<td>0.9639</td>
<td>0.629</td>
<td>0.88</td>
<td>0.9898</td>
</tr>
<tr>
<td>5.00</td>
<td>3.599</td>
<td>3.20</td>
<td>0.9151</td>
<td>0.764</td>
<td>1.86</td>
<td>0.9987</td>
<td></td>
</tr>
<tr>
<td>6.00</td>
<td>1.919</td>
<td>1.62</td>
<td>0.9730</td>
<td>0.804</td>
<td>2.78</td>
<td>0.9659</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>4.00</td>
<td>1.919</td>
<td>1.62</td>
<td>0.9730</td>
<td>0.804</td>
<td>2.78</td>
<td>0.9659</td>
</tr>
<tr>
<td>5.00</td>
<td>2.085</td>
<td>1.99</td>
<td>0.9726</td>
<td>0.808</td>
<td>2.18</td>
<td>0.9881</td>
<td></td>
</tr>
<tr>
<td>6.00</td>
<td>2.161</td>
<td>2.19</td>
<td>0.9492</td>
<td>0.835</td>
<td>2.90</td>
<td>0.9991</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>4.00</td>
<td>2.045</td>
<td>1.89</td>
<td>0.9575</td>
<td>0.799</td>
<td>2.25</td>
<td>0.9980</td>
</tr>
<tr>
<td>5.00</td>
<td>2.886</td>
<td>2.99</td>
<td>0.9662</td>
<td>0.672</td>
<td>3.59</td>
<td>0.9874</td>
<td></td>
</tr>
<tr>
<td>6.00</td>
<td>4.492</td>
<td>6.19</td>
<td>0.9156</td>
<td>0.548</td>
<td>4.99</td>
<td>0.9773</td>
<td></td>
</tr>
</tbody>
</table>

Units for the parameters: n (g L⁻¹) and Kf (mg g⁻¹).

The D-R isotherm model can be used to describe adsorption on both homogeneous and heterogeneous surfaces [54] with the Eq. (9) [55]:

\[
\ln q = \ln q_{\text{max}} - \beta \varepsilon^2
\]

where \( \beta \) is the activity coefficient constant related to mean sorption energy (mol²·kJ⁻²), \( \varepsilon \) is the Polanyi potential [52].

\[
\varepsilon = R T \ln \left(1 + 1 / C_{eq}\right)
\]

where: R is the ideal gas constant (8.3145 J·mol⁻¹·K⁻¹) and T is the absolute temperature (Kelvin).

The D-R adsorption isotherm is applied on the adsorption data in order to distinguish between chemical and physical adsorption. The adsorption mean free energy (EkJ·mol⁻¹) is the energy required to transfer one mole of the adsorbate from infinity in solution to the surface of solid and is widely used for estimating the type of adsorption [56]. It is calculated as Eq. (11):

\[
E = \frac{1}{2\beta}^{0.5} - 0.5
\]

The D-R isotherm plots and parameters for the adsorption of Pb(II) on modified kaolinite are shown in Fig.6 (as an example) and Table 4.

The \( R^2 \) values shown in Table 4 are greater than 0.90, indicating that D-R model can describe the adsorption data very well, which means that the sorption is on homogeneous and heterogeneous surfaces as mentioned in 3.2.1 and 3.2.2. If notice the trend of \( q_m \) values for Pb(II) and both modified kaolinite vs. temperature and pH, authors will see that as temperature and pH increases, \( q_m \) values will increase. Similar trend was obtained by Langmuir parameter (\( q_m \)), and Freundlich parameter (\( K_f \)) (Notice that there are no significant differences between \( q_m \) values obtained from Langmuir and D-R models). As shown in Table 4, the values of E for Pb(II) are between 0.784 and 1.619 kJ·mol⁻¹, and all these values are less than 8.00 kJ·mol⁻¹, indicating that physical forces affect the adsorption [14, 51]. The obtained sorption data showed very well fitting for Langmuir more than other adsorption isotherm models, which means both modified kaolinite have homogeneous surface with monolayer adsorption.

3.3 Sorption Thermodynamics

3.3.1 Effect of Temperature

The effect of temperature on sorption is important not only because it affects the rate and extent of sorption but also due to the fact that temperature dependence of sorption provides information about possible adsorbate-adsorbent interaction. The Pb(II) sorption isotherms onto both modified kaolinite were conducted at temperatures of 25, 35 and 45°C, and the sorption capacity was determined. The results of the studies on the influence of temperature on Pb(II) sorption are presented in Table 5. Since, the sorption increased with temperature, the sorption process is an endothermic one [57, 58].

3.3.2 Thermodynamic Parameters

Thermodynamic parameters include Gibbs free energy changes \( AG^0 \), enthalpy changes \( AH^0 \) and
Sorption of Pb(II) Ions by Kaolinite Modified with Humic Acids

Table 4  D-R isotherm parameters for Pb(II) adsorbed by both KTD-kaolinite and FHA-kaolinite.

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>pH</th>
<th>β</th>
<th>E</th>
<th>q_m</th>
<th>R²</th>
<th>β</th>
<th>E</th>
<th>q_m</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>4.00</td>
<td>0.561</td>
<td>0.944</td>
<td>6.62</td>
<td>0.9664</td>
<td>0.814</td>
<td>0.784</td>
<td>7.07</td>
<td>0.9510</td>
</tr>
<tr>
<td></td>
<td>5.00</td>
<td>0.434</td>
<td>1.073</td>
<td>6.95</td>
<td>0.9848</td>
<td>0.470</td>
<td>1.031</td>
<td>7.23</td>
<td>0.9895</td>
</tr>
<tr>
<td></td>
<td>6.00</td>
<td>0.762</td>
<td>0.820</td>
<td>8.06</td>
<td>0.9951</td>
<td>0.327</td>
<td>1.237</td>
<td>7.89</td>
<td>0.9630</td>
</tr>
<tr>
<td>35</td>
<td>4.00</td>
<td>0.271</td>
<td>1.358</td>
<td>7.68</td>
<td>0.9345</td>
<td>0.515</td>
<td>0.986</td>
<td>7.44</td>
<td>0.9806</td>
</tr>
<tr>
<td></td>
<td>5.00</td>
<td>0.676</td>
<td>0.860</td>
<td>7.09</td>
<td>0.9814</td>
<td>0.397</td>
<td>1.123</td>
<td>7.60</td>
<td>0.9589</td>
</tr>
<tr>
<td></td>
<td>6.00</td>
<td>0.685</td>
<td>0.855</td>
<td>9.23</td>
<td>0.9588</td>
<td>0.319</td>
<td>1.253</td>
<td>8.06</td>
<td>0.9798</td>
</tr>
<tr>
<td>45</td>
<td>4.00</td>
<td>0.191</td>
<td>1.619</td>
<td>7.35</td>
<td>0.9848</td>
<td>0.394</td>
<td>1.127</td>
<td>8.03</td>
<td>0.9869</td>
</tr>
<tr>
<td></td>
<td>5.00</td>
<td>0.378</td>
<td>1.150</td>
<td>7.38</td>
<td>0.9576</td>
<td>0.253</td>
<td>1.405</td>
<td>8.49</td>
<td>0.9595</td>
</tr>
<tr>
<td></td>
<td>6.00</td>
<td>0.240</td>
<td>1.443</td>
<td>9.86</td>
<td>0.9738</td>
<td>0.202</td>
<td>1.572</td>
<td>8.68</td>
<td>0.9599</td>
</tr>
</tbody>
</table>

Units for the parameters: β (mol²•kJ⁻²), E (kJ•mol⁻¹) and q_m (mg•g⁻¹).

entropy changes ΔS°. The Eq. (12) was used for ΔG° calculation:

\[ ΔG° = -RT\ln K \]  

where R is the gas constant (8.3145 J•mol⁻¹•K⁻¹), T is the temperature in Kelvin and K is the equilibrium constant which is equal to:

\[ K = \frac{q_e}{C_e} \]  

The K value was obtained from the intercept of the plot of ln(q_e/C_e) versus q_e.

The values of enthalpy (ΔH°) and entropy (ΔS°) are calculated using the Eq. (14):

\[ \ln K = \frac{ΔS°}{R} - \frac{ΔH°}{RT} \]  

The plot of ln K against 1/T gives a linear relationship, then authors can obtain (ΔH°) and (ΔS°) from the slope and intercept of this plot, respectively. These values are shown in Table 5.

Spontaneity of the sorption process is established by decrease in Gibbs free energy (ΔG) values. They were found to be small or negative indicating that the sorption of metal ion onto both modified kaolinite clay was spontaneous and energy favorable (Table 5) with small amount of energy required to convert reactants into products [59]. This is agreeing with values of n which represent the degree of favorability of sorption.

As shown in Table 5, all ΔH values are positive (endothermic); this agrees with those obtained in Langmuir parameter (q_m) (Table 2), Freundlich
constant ($K_T$) (Table 3), and $(q_m)$ values from the D-R model (Table 4). One possible explanation of the endothermic enthalpy of sorption is the well-known fact that heavy metal ions used are well solvated in water. This can be explained by the fact that each ion of adsorbate has to release more than one molecule of water. This dehydration process of ions requires energy, which exceeds the exothermic energy of the ions adsorbed on the surface [60].

The endothermic interactions between both modified kaolinite and Pb(II) were accompanied by small positive values of entropy, which was the driving force for sorption. The positive values of $\Delta S$ signify an increased state of randomness at the solid-solution interface following sorption. Also positive entropy of sorption reflects the affinity of adsorbent for Pb(II) used. The adsorbed water molecules, which are displaced by the adsorbate species, gain more translational energy than that lost by the adsorbate ions, thus allowing the prevalence of randomness in the system [14]. The entropy changes were most likely due to structural changes and adjustments in the adsorbate as well as the adsorbent. The structural changes arise from the release of ions like $H^+$ and $K^+$ from the clay surface into the solution and also from partial solvation of the metal ions in water [15]. The sorption of Pb(II) on both modified kaolinite were associated with entropy decrease in conformity with the general situation of ions existing in a more chaotic random distribution in aqueous solution compared to their adsorbed and immobilized states.

These results were consistent with previous kinetic, equilibrium and thermodynamic studies of sorption of heavy metal ions onto clays. It has been reported that the modification of kaolinite with sodium tetraborate reagent (NTB-modified kaolinite) increased the sorption capacity of kaolinite for Pb(II) and Cd(II) at 298 K, because its specific surface area was increased. Increasing temperature was found to increase the sorption of both metals onto both adsorbents suggesting an endothermic sorption reaction. The thermodynamic calculations for the modified kaolinite sample indicated an endothermic nature of sorption for Pb(II) and Cd(II) and an increase in entropy as a result of sorption of both metal ions. The small positive values of $\Delta G$ indicated that the sorption of Pb(II) and Cd(II) onto the modified adsorbent may require some small amount of energy to make it more feasible. Modeling equilibrium adsorption data obtained suggested that NTB-modified adsorbent sample has homogeneous adsorption sites and fit very well with Langmuir adsorption model [22]. Bhattacharyya and Gupta investigated the removal of Cu(II) ions from an aqueous solution by kaolinite, montmorillonite, and their poly (oxozirconium) (ZrO) and tetrabutylammonium (TBA) derivatives. Adsorption increased with pH till Cu(II) ions became insoluble in alkaline medium. The kinetics of the interactions suggests that the interactions could be best represented by a mechanism based on second order kinetics. The adsorption followed Langmuir isotherm model. The process was endothermic accompanied by increase in entropy and decrease in $\Delta G$ [15]. Amer, et al. determined the potential application of sodium polyphosphate-modified kaolinite clay as an adsorbent for the removal of Pb(II), Zn(II) and Cd(II) from aqueous solutions. The adsorption isotherms of all three metal ions followed well Langmuir equation. The thermodynamic

<table>
<thead>
<tr>
<th>pH</th>
<th>$\Delta G$ (kJ/mol)</th>
<th>$\Delta H$ (kJ/mol)</th>
<th>$\Delta S$ (J/mol K)</th>
<th>$R^2$</th>
<th>$\Delta G$ (kJ/mol)</th>
<th>$\Delta H$ (kJ/mol)</th>
<th>$\Delta S$ (J/mol K)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.00</td>
<td>1.54</td>
<td>11.54</td>
<td>33.7</td>
<td>0.9413</td>
<td>0.82</td>
<td>37.44</td>
<td>123.5</td>
<td>0.9181</td>
</tr>
<tr>
<td>5.00</td>
<td>1.03</td>
<td>8.10</td>
<td>23.7</td>
<td>0.9974</td>
<td>-1.03</td>
<td>15.16</td>
<td>54.2</td>
<td>0.9816</td>
</tr>
<tr>
<td>6.00</td>
<td>0.81</td>
<td>6.49</td>
<td>19.0</td>
<td>0.9997</td>
<td>-2.04</td>
<td>3.18</td>
<td>17.5</td>
<td>0.9991</td>
</tr>
</tbody>
</table>
parameters, $\Delta G^\circ$, $\Delta H^\circ$ and $\Delta S^\circ$ calculated using the Langmuir constants for metal ions adsorption on the modified kaolinite clay showed that the adsorption process is spontaneous and endothermic in nature [9].

### 3.3.3 Comparing KTD-kaolinite Clay with FHA-kaolinite Clay

Modification of kaolinite by KTD and FHA increased the uptake of Pb(II). From Table 1, the $q_e$ value for FHA kaolinite is greater than that for KTD kaolinite. While Table 5 showed that $\Delta G^\circ$ for FHA kaolinite is less than that for KTD kaolinite, which means more energy favorable and spontaneous process. Also the greater $\Delta S^\circ$ values for FHA kaolinite than for KTD kaolinite drives the sorption in favor of the first. All of these are due to the larger increase in oxygen content of FHA (70.6%) than that of KTD (31.9%), and the presence of oxygenated functional groups, which enhance the interaction with Pb(II) ions.

### 4. Conclusions

Kaolinite showed relatively high capacity to adsorb humic acid, which then acted as an adsorbent of Pb(II) ions. The best conditions for Pb(II) adsorption on modified kaolinite clay were at pH = 6.00, 45 °C and initial metal concentration of 10 ppm. The Pb(II) ions kinetic data fitted pseudo second-order model for the two modified humic acid kaolinite clay. The obtained sorption data showed fitting for Langmuir, Freundlich and Dubinin-Radushkevich adsorption isotherm models. The sorption was a physical process on both homogeneous and heterogeneous surfaces, which was well shown from the values of E for Pb(II). All these values were less than 8.00 kJ·mol$^{-1}$. The thermodynamic parameters showed that the sorption process was favorable, but it was more favorable in FHA-kaolinite clay than in KTD-kaolinite clay, and the sorption of Pb(II) was an endothermic process.

### References


Colloid and Interface Science 286: 43-52.
Sorption of Pb(II) Ions by Kaolinite Modified with Humic Acids

497-508.


