Removal lead Pb (II) from wastewater using kaolin clay

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Abstract. In this experiment’s kaolin clay was applied as adsorbent material for remove lead (Pb\textsuperscript{II}) from simulated wastewater. Many experiments were done at variance conditions, such as pH, initial concentration of Pb ions and adsorbent weight. Highest removal efficiency (85.1) % was obtained at 2g adsorbent weight, 10 mg/L initial metal concentration with pH5. Consequences appeared that kaolin clay is perfect in removing Pb\textsuperscript{II} from wastewater. Adsorption isotherm of Pb\textsuperscript{II} ions by kaolin clay was conducted with Freundlich and Langmuir isotherms which had good effects, that reported. FTIR images of kaolin clay before and after adsorption were completely verified the uptake of Pb\textsuperscript{II}. The aim of current work is to use kaolinite clay for investigating adsorption properties of Pb\textsuperscript{II} from polluted water.

Keywords: kaolin, Pb\textsuperscript{II}, Adsorption, Freundlich and Langmuir isotherms

1. Introduction
Heavy metals are nondegradable at atmosphere and could be toxic toward the number of the living organism. For this purpose, metals removal from waste-water also waters are essential for protecting environment and community health [1]. Via their waste effluents, many manufacturing practices like plating metal, fertilizers industry, Mining and tinting activities in the textile industry add heavy metals to atmosphere [2]. Therefore, the amount of these metals used with agriculture from water, wastewater and drinking water must be minimized to ultimate allowable concentration. Over the years, many approaches were used for removing heavy metal found in soils as well as industrial wastewater. Ion exchange, ultrafiltration, phytoextraction, solvent extraction, electrodialysis, reverse osmosis, chemical precipitation and adsorption are standard procedures in extracting heavy metals of polluted water [3]. one of essential technique for extracting heavy metal from the ecological system is adsorptions. Major adsorbent properties are a good attraction with elevated loading potential in heavy metals removal. Generally, naturalists’ adsorbents own these characteristics. To extract various heavy metals from polluted water, adsorption and ion-exchange mechanisms by clay minerals were used [4]. lead (Pb\textsuperscript{II}) is conceded part of the main ecological contaminants due to its existence through automotive fuel and consequent atmospheric leakage of exhaust gases [5]. In addition, by Lead smelting wastes, battery producers, industries in the pulp, paper as well as ammunition, they penetrate the water system [6]. Adsorption Pb\textsuperscript{II} from polluted water were evaluated using different adsorbents [7].

However, it is worthwhile to use kaolin material as an economical, abundant substance to adsorb heavy metal from polluted water, composed of 1:1 structure layer with strong bonding between them, with Al\textsubscript{2}Si\textsubscript{2} O\textsubscript{5} (OH)\textsubscript{4} formula [8]. Only the essence of its surface and edges defines the sorption properties of this clay. Kaolinite clay has a variance charge which connected to the interaction between the edges of surface ionizable groups and ions in polluted water [9]. It was used in adsorption
process of different heavy metals as an adsorbent material [10].

2. Materials and methods

2.1. Material

Kaolin clay supplied from the local market at Baghdad city and sieved by (1.18mm) net diameter after that air-dried at room temperature. Table 1 explains the chemical texture. SiO2, comprised 48.57% maximum chemical component while the lowest one was 0.08 %for K2O. Physical analysis for kaolin clay found that the surface area and cation exchange capability (CEC) were respectively 22.34m2 / g and 20 meq/100 g.

| Composition | Content (Wt %) |
|-------------|----------------|
| SiO2        | 48.57          |
| Al2O3       | 35.05          |
| CaO         | 0.6            |
| Fe2O3       | 1.34           |
| K2O         | 0.08           |
| TiO2        | 1.19           |
| MgO         | 0.77           |

2.2 Equipment

To control pH values in polluted water, a pH meter was used (WTW- 3110 / Germany). Concentration of metals was measured using the Atomic Absorption Spectrometer (AAS). By using X-ray Fluorescence (XRF), the chemical composition of the clay sample was identified, also, adsorbent characterized at room temperature through FT-IR spectrophotometer. By using nitrogen gas adsorption, surface area calculated according to Brunauer-Emmett - Teller (BET) process while NH4Cl-50% CH3CH2OH. observed cation exchange power (CEC).

2.3. Batch adsorption procedure

Many parameters are taken in this study (pH, clay mass and initial heavy metal concentration) were used to estimate the most significant adsorption factor effect. At pH ranges (5, 7, and 9), adsorption tests were performed by adding 0.1N HCL, 0.1N NaOH to achieve the desired pH and different adsorbent weight (0.2, 0.5, 1, 1.5, and 2) gm at room temperature was used. Different initial concentrations (1050  ppm were provided by proper dilution from a stock solution of 1000 mg / L which was prepared by adding1.6 gm of Pb (NO3)2 to 1000 ml deionized water as shown in figure 1. Then electrical balance was used to applied the required quantity of kaolin clay also a component of flasks were shaken at 200 rpm through 30 minutes contact time. Then filtered by filter paper of (0.45 μm) diameter. The concentration of lead remainder was measured with (AAS). Batch equilibrium tests were performed using a solution with a concentration of 10 mg / L, 0.5 g of kaolin, mixing speed 200 rpm and 30 min contact time in 300 ml volume of (Pb II).

The percentage removal of metal ion was found as illustrated:

\[ R (%) = \left( \frac{C_0 - C_e}{C_0} \right) \times 100 \]  

Where,

- \( R \) % is removal efficiency,
- \( C_0 \) and \( C_e \) the primary as well as final concentrations of metal, consequently. Then, adsorption capacity in mg/g can be found from equation:

\[ Q = \frac{(C_0 - C_e)V}{m} \]
\[ q_e = \frac{V(C_0 - C_e)}{M} \]  

Where, 
- \( q_e \) is the mass concentration of adsorbed metal ions in mg/g;  
- \( M \) is mass adsorbent in g;  
- \( V \) is solution volume in l.

Figure 1. Pb\(^{+2}\) stock solutions.

3. Results and Discussion
3.1. Effect of pH
The most critical determinants regulating lead adsorption on the surface of natural clay samples is the initial solution pH which was selected from (3 to 9) with a speed of 200 rpm, 30-minute contact time, 10 ppm initial dye concentration, 1 gm adsorbent weight. The results are shown in figure 2.

Figure 2. Impact of pH on removal efficiency of Pb\(^{+2}\).
It was observed, when pH rising, the maximum removal efficiency was achieved in kaolin clay. At pH=9, the highest removal efficiency 95.5 % was obtained due to precipitate of lead ions in solution in the formula of lead hydroxide so pH 5 was selected in this study because the rivalry between the metal and H+ ions in solution on active site of kaolin clay minimizes and electrostatic force occurs between the negative and positive charge of kaolin surface with metal ions, consequently [11].

3.2. Effect of adsorbent mass
Effectiveness of kaolin weight onto lead removal with a contact time 30 min in 300 ml volume of metal solution was studied through changing adsorbent mass from (0.2 to 2) g in 10 ppm initial concentration of (Pb II) at room temperature. Figure 3 offering the result.

![Figure 3. Effect of kaolin weigh on removal efficiency.](image)

From the figure, the removal efficiency on kaolin clay increased from 76.6 to 85.1% to Pb+2 ions an increasing in adsorbent weight enhancing the percentage removal of lead ions until arrives equilibrium state at 0.5gm which implies to increase the surface area of kaolin clay, followed by an increase in a number of binding sites [12].

3.3. Effect of initial metal concentration
The initial concentration of metal had a significant impact on ability of kaolin clay to adsorb heavy metal ions as illustrated in figure 4, with Ph 5 and 0.5 gm weight of adsorbent clay obtained from previous test with the same operation conditions.
Therefore, it seems that removal efficiency decreasing at high concentration of lead ion from (85.1 to 70.8) % because adsorption sites are limited resulting in retained lead on available adsorption location on adsorbent kaolin, so maximum percentage was achieved at low concentration 10 mg/l which presented the perfect concentration in this study [12, 13].

3.4. Adsorption isotherms

To determine the quantity of Pb (II) removed by kaolin clay and its balance concentration in aqueous solution, Langmuir and Freundlich isotherm models were used. Experimental data conformed to the linear form expressed in equation 3 of the Langmuir model:

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

Where, \(q_m\) : monolayer adsorption capacity in mg/g, \(K_L\) : Langmuir constant in L/mg. The Freundlich isotherm is explained as:

In logarithmic data given in equation 4, the sorption equilibrium data was also applied to Freundlich model:

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

Where, \(K_F\) is Freundlich adsorption isotherm constant, indicating the amount of adsorption, and \(n\) is a Freundlich constant associated with adsorption intensity.
Figure 5. Langmuir adsorption isotherm for lead (linear equation).

\[ y = 4.4475x - 3.3837 \]
\[ R^2 = 0.8921 \]

Figure 6. Freundlich adsorption isotherm for lead (linear equation).

\[ y = 0.1067x + 0.9678 \]
\[ R^2 = 0.7977 \]

The correlation factor for Langmuir and Freundlich models are 0.8921 and 0.7977, respectively, as exposed in table 2.
Table 2. Parameters of Langmuir and Freundlich isotherm to lead by kaolin clay.

| Pollutant | Langmuir Isotherm | Freundlich Isotherm |
|-----------|-------------------|---------------------|
| Pb^{2+}   | q_m (mg/g) 0.3    | K_L (L/mg) 0.98     | R^2 0.8921 |
|           |                   | KF (mg/g)(L/mg)^1/n | N 9.37    | R^2 0.7977 |

3.5. FTIR analysis

From figure 7 the bands at 3695.61 as well as 3622.32 cm\(^{-1}\) referring to the O–H stretching vibration of (Si–OH) silanol groups while HO–H is a vibration molecule of water absorbed on the silica surface. The range 1824.66 and 1635.64 cm\(^{-1}\) clarify H–OH bond of water molecules kept in silica layer. The wavelength at 1107.14, 1033.85 and 1006.84 represent the Si–O–Si collections of tetrahedral sheets, in addition, those at 914.26, (792.74 and 754.17) and 694.37 cm\(^{-1}\) signify Al–OH bending vibrations, Si–O stretching and Si–O bond respectively. While the band 538.14 due to Al–O–Si stretching vibration as well as 470.63 and 428.20 cm\(^{-1}\) represented Fe–O stretching. Water in kaolin produces broadband at 3429.2cm\(^{-1}\) corresponding to the H2O-stretching vibrations [14].

![Figure 7. FTIR of kaolin before and after adsorption to lead.](image)

4. Conclusion

The experimental results showed that adsorption of Pb (II) from polluted water can be successfully used with kaolin clay. To achieve the highest removal for Pb (II) from polluted water via kaolin clay, experimental limits such as solution pH, adsorbent weight and initial
concentration have to be optimally selected. The linear Langmuir and Freundlich models well followed by balance data. The removal is effected by pH and the adsorbed quantity increases with rising pH until the ions are precipitated at pH > 7 as the insoluble hydroxides. More Pb$^{+2}$ ions have been found to be adsorbed by kaolinite at low initial metal concentrations.

5. References
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