Kinetics and thermodynamics of Cu(II) adsorption on oil shale wastes


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ABSTRACT

The oil shale waste material, retorted shale, was utilized as an adsorbent for Cu(II) removal from aqueous solution. The kinetics and thermodynamic adsorption was investigated during a series of batch adsorption experiments. The removal efficiency was controlled by solution pH, temperature, initial ion concentration and contact time. Two simple kinetic models, pseudo-first-and second-order, were used to investigate the adsorption mechanisms. The pseudo-second-order chemical reaction kinetics provides the best correlation with the experimental data. Langmuir and Freundlich models were used to fit the equilibrium data, which showed that Langmuir best-fitted these data. Thermodynamic parameters such as free energy, enthalpy and entropy were calculated to predict the nature of the adsorption process.

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1. Introduction

The removal of heavy metals ions from wastewater has been widely studied in the last decade mainly because they can be readily adsorbed by living organisms. In particular, copper has received considerable attention because although it is an essential trace element for human beings, it can cause harmful and acute effects. The major effects of excessive large doses of copper in the human body include high blood pressure, severe mucosal irritation, widespread capillary damage, anemia, hepatic damage, necrotic changes in the liver and kidney [1,2]. The main sources of water contamination with copper ions are industrial waste from metal cleaning and plating baths, wood pulp production, mining and metallurgy activities, electrical device manufacturing, and the fertilizer industry.

Various processes are available for removing copper from water and wastewater including chemical precipitation, ion-change, and activated carbon adsorption. A wide range of adsorbents for the treatment of Cu(II) rich effluents has been studied as low-cost alternatives to activated carbon [3,4], including clays [5] polymerized peanut skins with formaldehyde [6], sawdust [7], peat [8], chitosan [9] and others.

In the present investigation, retorted shale (RS), a solid residue of the thermal transformation of oil shale, was studied as a possible cost-efficient and non-conventional adsorbent to remove copper from wastewater. Parameters that influence adsorption, such as copper initial concentration, contact time, temperature and pH were investigated. A review of the literature shows that RS has not been used so far as an adsorbent to remove Cu(II) from wastewater. Moreover, the technological development for the beneficial use of this material is needed, since oil shale is abundant in 31 countries [10], and Brazil has the second largest reserve in the world.

2. Materials and methods

2.1. Materials

The retorted shale used in this study was obtained from São Mateus do Sul, State of Paraná, Southern Brazil. It was ground,
sieved down to 75 µm and used without any previous treatment. All the chemicals were of reagent grade purity. Deionized water (DI) was used to prepare all solutions.

2.2. Adsorption experiments

The synthetic solutions of Cu(II) at different concentrations were prepared by dissolving Cu(NO₃)₂·3H₂O in deionized water. Batch adsorption experiments were carried out by shaking 1 g of adsorbent with 100 mL of Cu(II) solution of the desired concentration at constant temperatures (30, 40 and 50 °C) and 260 rpm. The samples were taken at specific time intervals and then the adsorbent was removed by filtration through filter paper. The concentration of Cu(II) ions in the supernatant solution was measured by atomic absorption spectroscopy (Varian, Espectr AA-110 model). Each experiment was repeated three times to check the reproducibility for statistical purposes. The effect of pH on adsorption treatment. All the chemicals were of reagent grade purity.

2.3. Mathematical procedures

The amount of Cu(II) adsorbed on the adsorbent was calculated using the following expression:

\[ q_t = (C_0 - C_1) V / W \]  

(1)

And the percentage adsorption of Cu(II) was calculated according to

\[ \text{adsorption} = \frac{C_0 - C_t}{C_0} \times 100 \]  

(2)

where \( q_t \) is the amount of Cu(II) adsorbed (mg/g) at different times (t), \( V \) is the volume of the solution (L), \( W \) is the weight of the adsorbent (g), \( C_0 \) and \( C_t \) are the Cu(II) concentration (mg/L) at the initial and at a time t, respectively.

In order to quantify the extent of uptake in adsorption kinetics two simple kinetic models were tested: Lagergren’s first-order rate equation [11] based on solid capacity is generally expressed as follows:

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

(3)

where \( k_1 \) (1/min) is the equilibrium rate constant of the pseudo-first-order adsorption, \( q_t \) and \( q_e \) (mg/g), are the amount of metal ions adsorbed at equilibrium and at any time t. The integrated pseudo-first-order rate equation is written as

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

(4)

A pseudo-second-order adsorption kinetic equation is [11]:

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

(5)

where \( k_2 \) (g/(mg min)) is the rate constant of the pseudo-second-order adsorption. Integrating Eq. (5) and applying boundary conditions (\( t = 0 \) to \( t = t \) and \( q_t = 0 \) to \( q_t = q_e \) gives

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

(6)

The values of \( k_2 \) and \( q_e \) can be obtained from the intercept and slope of the plot of \( (t/q_t) \) versus t.

The activation energy for Cu(II) adsorption onto retorted shale can be calculated by using the Arrhenius equation

\[ k = A e^{-E_a/RT} \]  

(7)

where, \( k \) is the rate constant at temperature of T (K), \( A \) is the frequency factor, \( R \) is the universal gas constant (8.314 J/(mol K)) and \( E_a \) (kJ/mol) is the activation energy for the adsorption process. The magnitude of activation energy can indicate the type of sorption. The activation energy for physical adsorption is usually no more than 4.2 kJ mol⁻¹, since the forces involved are weak. Chemical adsorption is specific and involves forces much stronger than physical adsorption. So the activation energy for chemical adsorption is of the same magnitude as the heat of chemical reactions. Two kinds of chemical adsorption are encountered, activated and, less frequently, nonactivated. Activated chemical adsorption means that the rate varies with temperature according to finite activation energy (between 8.4 and 83.7 kJ mol⁻¹) in the Arrhenius equation. In non-activated chemical adsorption, chemisorption occurs very rapidly, suggesting the activation energy is near zero [12,13].

Adsorption data for a wide range of adsorbate concentrations are most conveniently described by adsorption isotherms, such as the Langmuir or Freundlich, which relate amounts adsorbed to the equilibrium adsorbate concentration in the bulk fluid phase. The Langmuir isotherm suggests that the adsorbed metals form monolayer coverage on the adsorbent surface and there is no interaction between adsorbed molecules. The linear form of the Langmuir isotherm is represented by the following equation:

\[ \frac{C_s}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \]  

(8)

where \( C_s \) is the solution concentration at equilibrium (mg/L), \( q_e \) is the amount adsorbed at equilibrium (mg/g), \( b \) is the Langmuir constant (L/mg) which can be considered as a

![Fig. 1 - Effect of pH on the Cu(II) adsorption by RS.](image)
measure of the adsorption energy and \( q_m \) is the maximum adsorption capacity (mg/g) corresponding to complete monolayer coverage. A plot of \( C_o/q_e \) versus \( C_o \) over the entire concentration range produces a straight line, which is an indication of the applicability of the Langmuir isotherm for the system under consideration.

To confirm the favorability of the adsorption process, the essential features of Langmuir’s isotherms can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, \( R_L \), which can be calculated by the following equation [14].

\[
R_L = \frac{1}{1 + bC_o}.
\]

where \( C_o \) is the highest Cu(II) concentration (mg/L), and \( b \) is Langmuir’s constant. The value of \( R_L \) indicates whether the isotherm is irreversible (\( R_L = 0 \)), favorable (\( 0 < R_L < 1 \)), linear (\( R_L = 1 \)) or unfavorable (\( R_L > 1 \)).

The Freundlich model assumes that different sites with several adsorption energies are involved in the adsorption process. The Freundlich isotherm is shown as the following equation:

\[
q_e = K_FC_e^{1/n}
\]

The linear form of the equation can be written as:

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

where \( K_F \) and \( n \) are the Freundlich constants related to the adsorption capacity and adsorption intensity, respectively [15]. The intercept and the slope of the linear plot of \( \ln q_e \) versus \( \ln C_e \) at given experimental conditions provide the values of \( K_F \) and \( 1/n \), respectively.

Thermodynamic parameters such as Gibbs free energy (\( \Delta G^0 \)), enthalpy (\( \Delta H^0 \)) and entropy (\( \Delta S^0 \)) for the adsorption process can be calculated from the van’t Hoff equation [16].

\[
\Delta G^0 = -RT \ln b
\]

where \( R \) is the ideal gas constant, \( T \) is temperature (K) and \( b \) is Langmuir’s constant. The slope and intercept of the plots of \( \ln K_F \) versus \( 1/T \) were used to determine \( \Delta H^0 \) and \( \Delta S^0 \).

\[
\ln b = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}
\]

3. Results and discussion

3.1. Characterization of adsorbent material

The characteristics of the retorted shale were as follows: surface area (B. E. T), 65.083 m²/g; apparent density, 0.9982 g/cm³; average particle size, 19.1 μm, pore size 32.5 Å and chemical composition: SiO₂ (55.6%), Al₂O₃ (11.4%), TiO₂ (0.6%), Fe₂O₃ (8.6%), MgO (1.8%), CaO (3.5%), Na₂O (1.6%), K₂O (2.85%) in addition to minor components including MnO, V₂O₅, SrO, CuO, ZnO, ZrO₂, NiO and sulfur. It is observed that the retorted shale is mainly composed of acids, bases and amphoteric oxides, which assures the presence of active groups of mineral species.
and organic residues on the grain surface, suggesting good adsorption behavior.

3.2. Effect of initial pH

The pH dependence of Cu(II) uptake onto RS was studied. The results obtained are represented in Fig. 1. It is observed that the percentage adsorption increases with increasing pH and then reaches a maximum at about 5.5. For higher values, Cu(II) ions precipitate in the form of metallic hydroxides. At lower pH values, the amount of adsorption decreases with decreasing pH, because the aluminol and silanol groups are more protonated and, hence, they are less available to retain the copper. Such pH trends are in agreement with earlier observations [17,18].

3.3. Effect of contact time and initial concentration

The experimental results for Cu(II) adsorption on RS for various concentrations at 30 and 50 °C are shown in Figs. 2 and 3. Increasing contact time increases copper uptake and adsorption equilibrium is attained relatively earlier in the solution containing lower Cu(II) concentrations. The equilibrium time required for a maximum Cu(II) removal were 180, 210, 240 and 270 min for initial concentrations of 200, 300, 400 and 500 mg/L, respectively. As expected, the increase in initial metal ion concentration increased the amount of metal uptake per unit weight of the adsorbent (mg/g). The plots of metal uptake as a function of time are single, smooth and continuous leading to saturation, suggesting the possible monolayer coverage of Cu(II) ions on the surface of the adsorbent.

3.4. Kinetics studies

Fig. 4 shows the pseudo-second-order plot for Cu(II) adsorption at an the initial concentration of 200 mg/L at three temperatures. The experimental points are shown along with the theoretically generated lines. The constants calculated for different concentrations and temperatures using both rate equations are shown in Table 1. The regression coefficients for the linear plots from the pseudo-second-order equation were greater than those obtained for the pseudo-first equation indicating that this one was not applicable for all the results.

| Cu(II) concentration (mg/L) | Temperature(°C) | First order | | | Second order | | |
|----------------------------|----------------|-------------|---|---|----------------|---|
|                            |                | k₁          | R²| | k₂ (g/(mg min)) | qₑ (mg/g) | R²|
| 200                         | 30             | 0.0076      | 0.9758| | 0.0018 | 11.70 | 0.9990 |
| 300                         | 30             | 0.0143      | 0.8262| | 0.0017 | 12.15 | 0.9975 |
| 400                         | 30             | 0.0076      | 0.9788| | 0.0016 | 13.52 | 0.9943 |
| 500                         | 30             | 0.0104      | 0.9726| | 0.0010 | 15.75 | 0.9964 |
| 200                         | 40             | 0.0069      | 0.9822| | 0.0024 | 13.36 | 0.9966 |
| 300                         | 40             | 0.0131      | 0.8078| | 0.0015 | 13.81 | 0.9957 |
| 400                         | 40             | 0.0069      | 0.9822| | 0.0017 | 16.29 | 0.9959 |
| 500                         | 40             | 0.0102      | 0.9130| | 0.0018 | 19.02 | 0.9956 |
|                            | 50             | 0.0056      | 0.9876| | 0.0030 | 15.06 | 0.9941 |
| 200                         | 50             | 0.0068      | 0.6844| | 0.0027 | 16.17 | 0.9907 |
| 300                         | 50             | 0.0056      | 0.9876| | 0.0024 | 18.15 | 0.9917 |
| 400                         | 50             | 0.0079      | 0.8719| | 0.0025 | 21.42 | 0.9867 |

Table 1 – Kinetic parameters of Cu(II) adsorption on RS at different temperatures

![Fig. 5 – Arrhenius plot for the Cu(II) adsorption by RS.](image)

![Fig. 6 – Freundlich and Langmuir adsorption isotherms of Cu(II) on RS.](image)
Therefore, no further consideration was given to it. The pseudo second-order reaction model, instead, fitted quite well the experimental results. The equilibrium rate constant, \( k_2 \), increased with an increase in temperature for the initial Cu(II) concentrations indicating that the adsorption process becomes slower for higher temperatures. This result may be interpreted as an indication of some specific interaction between the solid adsorbent and the copper ions.

The specific adsorption at equilibrium, \( q_e \), increases with an increase in temperature for the initial Cu(II) concentrations of 200–500 mg/L. The increase in the equilibrium adsorption capacity of Cu(II) with temperature indicates that a higher temperature favors Cu(II) removal by adsorption on RS. Therefore, this results suggests that the adsorption Cu(II) on RS involved some activated or chemisorption process. Another reason that may account for the pseudo-second-order rate is the real heterogeneity of the surface sites.

The activation energy was obtained from slope of the plot of \( \ln K \) values versus \( 1/T \) (Fig. 5) according to Eq. (7) and was found to be 21.24 kJ/mol. This value confirms that the adsorption process involves some chemical forces [12,13].

### 3.5. Adsorption isotherms

The adsorption isotherms are shown in Fig. 6. Linearized isotherms are also represented in Figs. 7 and 8 corresponding to Langmuir and Freundlich models, respectively. The parameters are shown in Table 2. In general, the Langmuir model fitted the results slightly better than the Freundlich model with all \( R^2 \) values greater than 0.98. This suggests that the adsorption of Cu(II) ions by RS is monolayer-type and agrees with the observation that the adsorption from an aqueous solution usually forms a layer on the adsorbent surface [19]. To a lesser extent, the equilibrium data was also well described with the Freundlich model, probably due to the real heterogeneous nature of the surface sites involved in the metal uptake. The values of Langmuir constants, \( b \) and \( q_m \), increased with increasing the temperature, showing that the adsorption capacity and intensity of adsorption are enhanced at higher temperatures and suggesting that there is a chemical interaction between adsorbent and adsorbate. As seen from Table 3, the monolayer adsorption capacity \( (b) \) was 23.86 mg/g (0.37 mmol/g) at optimum pH (5.5) and temperature (50 °C).

The values of \( R_L \) for Cu(II) adsorption onto RS were found to be 0.21, 0.19 and 0.16 at 30, 40 and 50 °C, respectively. As can be observed, the value of \( R_L \) decreased with increasing temperature, indicating that the Cu(II) adsorption on RS is more favorable at 50 °C. In addition, for 0.1<\( 1/n <1.0 \) the adsorption process is favorable.

### 3.6. Thermodynamics studies

As seen from Table 3, the negative values of \( \Delta G^\circ \) indicate the spontaneous nature of the adsorption process. The increase in free energy change with increasing temperature shows an

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>ln b</th>
<th>( \Delta G^\circ ) (kJ/mol)</th>
<th>( \Delta H^\circ ) (kJ/mol)</th>
<th>( \Delta S^\circ ) (l/(mol K))</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>6.098</td>
<td>–15.370</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>6.454</td>
<td>–17.340</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
increase in the feasibility of adsorption at higher temperatures. The positive value of $\Delta H^\circ$ indicates the endothermic nature of adsorption and suggests the possibility of weak bonding between adsorbate and adsorbent. The positive value of $\Delta S^\circ$ suggests some structural changes in adsorbent and adsorbate.

4. Conclusions

- The adsorption capability of retorted shale resulted of the presence of ionic species in the particle surface and a net of negative load on the structure of the fine grains of mineral silicates.
- The values of the correlation coefficients indicate that the results obtained from Langmuir’s isotherms are better than those obtained from Freundlich’s isotherms.
- Thermodynamic parameters indicate that the Cu(II) adsorption on RS is endothermic and kinetic studies suggest that adsorption involved some activated or chemisorption process.
- The results showed that the retorted shale can be used as an efficient adsorbent material in Cu(II) removal from wastewaters.

Acknowledgments

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Appendix A

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Frequency factor</td>
</tr>
<tr>
<td>b</td>
<td>Langmuir constant (L/mg)</td>
</tr>
<tr>
<td>C_e</td>
<td>Metal ion concentration at equilibrium (mg/L)</td>
</tr>
<tr>
<td>C_0</td>
<td>Initial metal ion concentration (mg/L)</td>
</tr>
<tr>
<td>C_t</td>
<td>Metal ion concentration at time t (mg/L)</td>
</tr>
<tr>
<td>E_a</td>
<td>Activation energy (kJ/mol)</td>
</tr>
<tr>
<td>$\Delta G^\circ$</td>
<td>Gibb’s free energy change (kJ/mol)</td>
</tr>
<tr>
<td>$\Delta H^\circ$</td>
<td>Enthalpy change (kJ/mol)</td>
</tr>
<tr>
<td>k_1</td>
<td>Equilibrium rate constant of the pseudo-first-order model (L/min)</td>
</tr>
<tr>
<td>k_2</td>
<td>Equilibrium rate constant of the pseudo-second-order model (g/(mg min))</td>
</tr>
<tr>
<td>K_F</td>
<td>Freundlich constant (mg/g)</td>
</tr>
<tr>
<td>q_e</td>
<td>Amount of Cu(II) adsorbed per gram of adsorbent at equilibrium (mg/g)</td>
</tr>
<tr>
<td>q_m</td>
<td>Maximum adsorption capacity (mg/g)</td>
</tr>
<tr>
<td>q_t</td>
<td>Amount of Cu(II) adsorbed per gram of adsorbent at any time (mg/g)</td>
</tr>
<tr>
<td>R</td>
<td>Universal gas constant (8.314 J/g mol K)</td>
</tr>
<tr>
<td>R^2</td>
<td>Correlation coefficient</td>
</tr>
<tr>
<td>R_L</td>
<td>Dimensionless separation factor</td>
</tr>
<tr>
<td>$\Delta S^\circ$</td>
<td>Entropy change (kJ/mol)</td>
</tr>
<tr>
<td>t</td>
<td>Time</td>
</tr>
<tr>
<td>T</td>
<td>Absolute temperature (K)</td>
</tr>
<tr>
<td>V</td>
<td>Volume of the solution (L)</td>
</tr>
<tr>
<td>W</td>
<td>Weight of the adsorbent (g)</td>
</tr>
<tr>
<td>1/n</td>
<td>Adsorption intensity</td>
</tr>
</tbody>
</table>

REFERENCES