Adsorption of Cd(II) From Solution By Nsu Clay: Kinetic and Thermodynamic Studies

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Abstract
The work reports the utilization of Nsu Clay as a cheaper alternative for the removal of Cd(II) ions from industrial effluent, the significance of this study is to reduce the harmful effect of Cadmium to man, aquatic life and microorganisms, since most developing Nations faced with the problem of high cost involved in treating industrial waste can make use of the adsorptive properties of the clay as a cheaper alternative. The effect of contact time, sorbent dose and temperature on the adsorption process were investigated using batch method. The results showed an increase in adsorption with increase in these parameters. Maximum uptake was obtained at a contact time of 20 minutes. The kinetic study showed that the adsorption of Cd(II) on Nsu clay can be described by both the Pseudo-first order and Pseudo-second order models. The Entropy change ∆S0 and Enthalpy change, ∆H0 obtained from thermodynamic study are 59.29J/molK and 16.93kJ/mol respectively. These results indicate that the adsorption of Cd(II) by Nsu clay is spontaneous and endothermic in nature and the clay can be used as a cheap adsorbent for the removal of Cd(II) from aqueous effluents.

Keywords: adsorption, Cd(II), cadmium, isotherm, kinetic, thermodynamic

INTRODUCTION
The pollution of water with toxic heavy metals is of major concern to the environment as well as human health. These metals get into the aqueous environment through effluents from various industrial operations such as metal plating, explosives manufacturing, dying, mining, smelting and printing. Cadmium for instance is one of the most toxic and is used in chemical industries in manufacturing of pesticides, herbicides and fungicides (Zahra et al., 2008). Cadmium is responsible for kidney tubular impairment, affects ion regulation, calcium metabolism and skeletal calcification. Cadmium poisoning also causes severe abdominal pain, vomiting, diarrhea and a choking sensation (Igwe and Abia, 2007).

Various methods have been used for the removal of cadmium from effluents such as filtration, ion exchange, membrane separation, reverse osmosis, solvent extraction and activated carbon adsorption (Molinari et al., 2004; Gode and Pehlivan, 2006). These techniques are usually expensive or ineffective especially when the concentrations of heavy metal ions are less than 10mg/l. This led to the use of low cost agricultural waste and clay materials for the adsorption of Cadmium. (Aksu, 2001; Ajmal et al., 2003; Horsfall et al., 2004; Gupta and Bhattacharyya, 2008; Zahra et al., 2008). In order to utilize cheaper alternatives for the removal of Cadmium from wastewaters, Nsu clay obtained from Imo State, Nigeria was tested. Most clay materials have been found to be effective in Cadmium removal from effluents, but Nsu clay was used in this study because of its abundance and easy accessibility. This work reports the study of the removal of Cd(II) ions from aqueous solution by Nsu clay, the effect of contact time, temperature, sorbent dose as well as the kinetics and thermodynamics were studied.

MATERIALS AND METHOD
Sample Preparation
The sample of Nsu clay was collected from Okigwe Zone, Imo state, Nigeria in September 2011. It was crushed and passed through a 100μm mesh sieve, oven dried at 100°C for 2 hours, then kept until use.

Adsorption Experiment
The research was carried out at Projects Development Institute (PRODA), Enugu, Nigeria. The adsorption process was performed using batch technique. Analytical grade of Cd(NO₃)₂ was used to prepare the standard solution of Cadmium. De-ionized water was also used for preparing and dilution of all solutions. The stock solution was diluted to the required concentration and appropriate pH with a drop wise addition of 0.1M HNO₃ and 0.1M NaOH using a pH meter. Freshly diluted stock solutions were used for each experiment.

In order to achieve optimal conditions, the adsorption studies were performed for different contact time, (5-120 minutes), temperature, (27-45°C), pH, (1-7) and sample dose (1-5g). Each batch study was carried out
by adding 2.0g of the prepared sample to 20ml of a given concentration of Cadmium ion solution in a thermostat water bath (Haake Wia model) for temperature regulation. In each study, a parameter was varied while others were kept constant. At the end of the given contact time, the solution was filtered and the filtrate analyzed for the cadmium ion concentration using an Atomic Absorption Spectrophotometer (AAS) (Buck scientific model 210 VGP). Each experiment was repeated and the mean value calculated.

The amount of Cd(II) ion adsorbed and the percentage removed were calculated from equation (1) and (2) respectively

\[ q_e = \frac{V(Co-Ce)}{M} \]  
\[ \%R = \frac{Co-Ce}{Co} \times 100 \]

Where \( q_e \) (mg/g), \( Co \) (mg/l), \( Ce \) (mg/l), \( V \) (litres) and \( M \) (g) are the equilibrium adsorption capacity, initial metal ion concentration, equilibrium concentration, volume of solution and mass of clay used respectively.

**RESULTS AND DISCUSSION**

The chemical characterization of Nsu clay was analyzed by classical methods and the use of the Atomic Absorption Spectrophotometer (AAS). The result of the analysis is shown in Table 1. It is seen that the main constituents are SiO\(_2\) and Al\(_2\)O\(_3\).

<table>
<thead>
<tr>
<th>Constituents</th>
<th>SiO(_2)</th>
<th>Al(_2)O(_3)</th>
<th>CaO</th>
<th>Fe(_2)O(_3)</th>
<th>MgO</th>
<th>Loss on Ignition</th>
</tr>
</thead>
<tbody>
<tr>
<td>% By Weight</td>
<td>46.25</td>
<td>38.41</td>
<td>0.87</td>
<td>0.71</td>
<td>0.39</td>
<td>13.37</td>
</tr>
</tbody>
</table>

**Effect of Contact Time**

The effect of contact time on the adsorption of cadmium on Nsu clay was investigated in order to determine the minimum necessary time to achieve the sorption equilibrium. The experiment was performed at an optimum pH of 5.0. Figure 3 describes the adsorption of cadmium on the clay as a function of contact time. The studies on the effect of contact time on the adsorption of most metal ions were achieved within 10-40 minutes. As shown in Figure 1, this adsorption process followed the same pattern, optimum adsorption of Cadmium was achieved sharply within the first 20 minutes remaining fairly stable thereafter. Equilibrium sorption experiments were conducted at a contact time of 2hrs, hence we ensured that equilibrium conditions were attained. The fast initial uptake reflects the accumulation of Cadmium ions on the surface and the availability of abundant active sites on the surface of the clay. The adsorption process slows down with time as the active sites were used up. The fast metal uptake observed is of particular importance in process design and operation in practical uses.

![Figure 1: Effect of contact time on adsorption of Cd(II) on Nsu clay (Concentration, 10mg/l, Temp, 300K, pH, 5.0).](image1.png)

**Influence of Temperature**

The effect of temperature on the sorption of Cadmium on Nsu clay was investigated and the result is shown in Figure 2. As observed, there is an increase in the sorption of Cadmium with increase in temperature from 27\(^\circ\)C to 45\(^\circ\)C. This indicates that the adsorption process is endothermic in nature. The increase in adsorption intensity reflects chemical interactions between cadmium and Nsu clay. Similar results have been reported (Ajmal et al., 2003; Amer et al., 2009). However, using various adsorbents, the effect of temperature on adsorption processes found in literature presents different types of behaviors. Temperature-independent effect on adsorption has been reported (Ahuja et al., 1999). In contrast, a decrease in the adsorption capacity with increase in temperature was also obtained (Aksu., 2001).

![Figure 2: Effect of temperature on the adsorption of Cd(II) on Nsu clay (Concentration, 10mg/l, Time, 2hrs, pH, 5.0).](image2.png)
Influence of Sorbent Dose
The result for the effect of sorbent dose on the adsorption of Cadmium on Nsu clay is shown in Figure 3. There is an observed increase in the percentage removed or adsorbed with increase in amount of sorbent dose. The increased percentage adsorption may be due to increase in surface negative charge and decrease in the electrostatic potential near the solid surface, which favors sorbent-solute interactions (Amer et al., 2009). The increase is also due to the increase in the number of active sites responsible for sorption.

Figure 3: Effect of sorbent dose on adsorption of Cd(II) on Nsu clay (Concentration,10mg/l, Temp, 300K, Time, 2hrs, pH, 5.0).

Kinetic Study
The kinetic model is the most important factor in predicting the rate at which sorption takes place for a given system and also very essential in understanding sorbent design, with sorbate residence time and reactor dimensions (Horsfall and Spiff., 2004). The sorption kinetics show a large dependence on the physical and chemical characteristics of the sorbent material which influences the sorption process and its mechanism (Ho et al., 1995). The pseudo-first order and Pseudo-second order models were applied in this study.

Table 2: Pseudo-first and Pseudo-second order kinetic parameters for the adsorption of Cd(II) on Nsu clay (Time, 5-25mins, Concentration, 10mg/l, Temp., 300K, pH, 5.0)

<table>
<thead>
<tr>
<th>PSEUDO-FIRST ORDER MODEL</th>
<th>qe(calculated)</th>
<th>K</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.135</td>
<td>0.19</td>
<td>0.96</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PSEUDO-SECOND ORDER MODEL</th>
<th>ho</th>
<th>qe</th>
<th>K₂</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.005</td>
<td>0.112</td>
<td>0.396</td>
<td>0.917</td>
<td></td>
</tr>
</tbody>
</table>

Pseudo-First Order Model
The kinetic of sorption described by the pseudo-first order expression given by Lagergren was adopted (Ho et al., 1996). The linearized form of the equation is given in equation (3).

\[
\ln(qe-qt) = \ln qe - Kt
\]  
(3)

Where \( qt \) is the mass of metal ion adsorbed at time \( t \) and \( K(\text{min}^{-1}) \) is the Lagergren rate constant. The plot of \( \ln(qe-qt) \) against \( t \) is shown in Figure 4, the constants \( K \) and \( qe(\text{calculated}) \) are obtained from the slope and intercept respectively. The linearity of the plot is indicated by \( R² = 0.96 \), this shows the applicability of the model for this sorption process. Therefore, the kinetic parameters are shown in Table 2.

Figure 4: Pseudo-First Order plot for the Adsorption of Cd(II) on Nsu Clay( Time,5-25mins, Conc, 10mg/l, pH, 5.0, Temp, 300K).

Pseudo-Second Order Model
This model is based on the assumption that adsorption follows a Second order mechanism, so the rate of occupation of adsorption site is proportional to the square of the number of unoccupied site (Zafar et al; 2006). The Pseudo-second order equation for the sorption of divalent metal ions was adopted (Ho et al; 1995). The linear form of the equation is given by equation (4)

\[
t/qt = 1/h_0 + t/q_e
\]  
(4)

Where \( h_0(\text{mg/gmin}) \) is the initial sorption capacity given in equation(5)

\[
h_0 = K_2 q_e^2
\]  
(5)

\( K_2 \) (g/mgmin) is the Pseudo-second order rate constant. A linear plot of \( t/qt \) against \( t \) is shown in Figure 5 and the pseudo-second order parameters obtained are shown in Table 2. The constants \( qe \) and \( h_0 \) were obtained from the slope and intercept. The \( R² \) value obtained shows that this model also provided a good fit to the experimental data, although the pseudo-first order gave a better fit. This model indicates that the rate-limiting step is a chemical sorption process between Cadmium ions and Nsu
clay, where metal removal from solution is due to purely physicochemical interactions between metals and the adsorbents (Aksu, 2001).

Figure 5: Pseudo-Second Order plot for the Adsorption of Cd(II) on Nsu Clay (Time, 5-25 mins, Conc, 10 mg/l, pH, 5.0, Temp, 300K).

**Thermodynamics of Adsorption**

The thermodynamics was deduced from the data obtained on the effect of temperature on sorption. The thermodynamic parameters (changes in standard Gibbs free energy, ∆G°, Enthalpy, ∆H° and Entropy, ∆S°) were calculated using equations (6) - (8).

\[ \Delta G^0 = -RT \ln K_{ad} \]  \hspace{1cm} (6)

\[ K_{ad} = \frac{C_{ad}}{C_e} \]  \hspace{1cm} (7)

\[ \Delta G^0 = -\Delta S^0(T) + \Delta H^0 \]  \hspace{1cm} (8)

Where R is the universal gas constant (8.314J/molK) and T is the temperature (K). The plot of ∆G° against T is shown in Figure 10. The entropy, ∆S° and enthalpy, ∆H° are obtained from the slope and intercept. The value of the Regression (R²) = 0.995 (≈ 1) shows the agreement between the change in free energy and temperature. The thermodynamic parameters obtained are shown in Table 3. The adsorption process is highly disordered as indicated by the positive value of entropy change, ∆S°. The positive value has been reported to be associated with increase in the dehydration steps of the metal ions, which are known to possess relatively high energies of solvation thereby resulting in the stabilization of water sheaths in the absence of the sorbent. Similarly, the Enthalpy change, ∆H° is positive which indicates an endothermic process. Consequently, it is expected that increase in temperature should favor the process, this is in agreement with our result obtained in Figure 2 were an increase in adsorption with temperature was observed.

CONCLUSION

Nsu clay has much potential as an adsorbent for the removal of Cd(II) ions from effluents. The time, sorbent dose, and temperature proved to be important parameters on the sorption process. The kinetic study revealed that the pseudo-first and pseudo-second order models were appropriate in describing the adsorption process. The thermodynamic study indicated an endothermic process with a positive entropy change of adsorption.

REFERENCES


