Adsorption of U(VI) from Aqueous Solution onto Hydrotalcite-Like Compounds

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Abstract: Uranium adsorption by the synthesized compound of magnesium aluminum hydroxide hydrate – layered double hydrotalcite (STH)-like compounds was studied. The calcinated STH was proven to be a highly effective in U(VI) adsorption in pH range from 6.5 to 7. The time dependent experimental data were found to be fit to the pseudo-second-order model. The equilibrium data have been modeled using Langmuir and Freundlich isotherms. The results showed that both model provide the best correlation with equilibrium data. The highest adsorption capacity, approximated 62.5 mg/g, was observed in the calcinated STH at 500 °C. The positive value of enthalpy change indicated that adsorption reaction of U(VI) on STH was endothermic process. The regeneration experiments of STH using 0.1M Na₂CO₃ solution was successfully demonstrated multiple times without any significant effect on the initial adsorption capacity.

Keywords: Uranium, Adsorption, Hydrotalcite like compounds, Isotherms.

Introduction

Uranium pollution in aquatic environment has been a subject for extensive studies because of its high toxicity and radioactivity. Recently published studies in animals and humans show effect of chronic uranium exposure at low levels in drinking water. Primary carcinogenic effect of uranium is on the kidneys.

Although uranium could be naturally present from natural deposits leaching, it only poses a limited threat to environment. However, large amount of uranium is released from various human activities such as mill tailing discharge and nuclear industry emission as well as the use of fossil fuel in automobile and phosphate fertilizer in agriculture, which are also sources of uranium pollution.

Clean uranium polluted water remains a challenge, in which, most of the efforts focus on uranyl ion adsorbents, which need to be effective in uranium removal as well as environmental friendly. Natural absorbents such as clays and minerals have been the subjects of many U(VI) adsorption studies. Recently, a class of synthetic clay known as
the magnesium aluminum hydroxide hydrate layered double hydroxides, or hydrotalcite-like compound, has been demonstrated as a potential adsorbent because of its high adsorption capacity with cationic and anionic species. Moreover, this clay is easily synthesized from inexpensive chemicals. Those advantages indicate that synthesized hydrotalcite clay (STH) would be a potential adsorbent for U(VI), however, the lack of published data about U(VI) adsorption on STH hinders its usefulness. Therefore, our main goal of this study is to obtain some characteristic information on U(VI) adsorption by STH allowing a better use of STH for recovering and removal of uranium from aqueous solution.

Experimental

All chemicals used in this work were of analytical grade. The standard solution of uranium (1.0 mg mL⁻¹) was prepared by dissolving 0.10 g of uranium metal (99.99%) in 15 mL of conc. HNO₃ and evaporated to dryness on a water bath. The residue was dissolved with 10 mL of 1M HNO₃ and transferred to a 100 mL measuring flask. The solution was diluted with water to the mark and shaken well. The solution of arsenazo III (0.07%) was prepared by dissolving 0.07 g of arsenazo III (Merck Co.) in 100 mL of 0.05 M HCl solution and kept in a polyethylene vessel. The mixture solution of MgCl₂.6H₂O and AlCl₃.6H₂O (solution A) was prepared by dissolving 29.02 g of MgCl₂.6H₂O and 14.48 g of AlCl₃.6H₂O (Merck Co.) in 200 mL of distilled water. The mixture solution of NaOH and Na₂CO₃ (solution B) was prepared by dissolving 64.0 g of NaOH and 11.44 g Na₂CO₃ (Merck Co.) in 4 L of distilled water.

Preparation of STH

The STH was prepared by the co precipitation method. The procedure of the method was carried out as follows: the solution A was slowly added into the solution B under continuously stirring condition. pH of the mixture was maintained from 9 to 10 by adjusting with HCl or NaOH diluted solutions. The precipitates were separated by centrifuging and washed several time with distilled water. The precipitates were mixed with 200 mL of distilled water and kept in an oven at 80 °C for 48 h and then separated from the liquid phase by centrifuging and dried at 100 °C for 24 h. The dried solid was ground to fine powder using a manual hand grinding mills and stored in closed container, ready for use. About 5 g each of STH were calcinated at individual temperature (100, 200, 300, 400 and 500 °C) for 3 h. The calcinated STHs at different temperature were labeled as STH-100, STH-200, STH-300, STH-400 and STH-500, in which the number indicates the calcination temperature.

The synthesized STH was characterized as single crystal of Al₂O₃ and Mg₂O using X-ray diffraction spectra, which was recorded with Sciffert 3000 using CuKα radiation. The scanning electron microscope (SEM) surface image was obtained using HITACHI S – 3400 N. Compositions of MgO and Al₂O₃ in STH were determined using X-ray fluorescence (XRF) using Phillips PW 1480 spectrometer. The BET surface areas of calcinated STH samples were measured by N₂-adsorption using micromeritics ASAP 2000.

Uranium analysis

Determination of U(VI) in the liquid phase after equilibriums was based on measuring the color complex of U(VI) with arsenazo III in the medium of 10⁻³ M HClO₄. A test solution containing U(VI) was placed into a 50 mL measuring flash. 1 mL of 0.07 % arsenazo III and 10 mL of 3 M HClO₄ was added. The mixture was shaken for two min and 3 M HClO₄ solution then added to the measuring volume. The mixture was shaken for three min. The absorbance of the absorbing solution was measured at 650 nm using a Libra S32 Perkin Elmer spectrophotometer. Uranium content in the test solution was determined from a calibration curve, which was constructed using a uranium standard solution.
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Adsorption studies

Batch adsorption experiments were conducted in a series Erlenmeyer flasks containing 0.1 g of STH with 50 mL aqueous solution of U(VI) of desired initial concentration (10 - 100 mg/L) at constant pH of 6.5. The reaction solutions were shaken in a water bath using an Innova model 3000 lab shaker at 30±1 °C. The flasks containing reaction solution were tightly closed to reduce dissolution of CO₂ from air. Samples were withdrawn after a definite time interval and liquid phase is separated by centrifuging. Similar experiments were repeated with varying solution pH and temperature. Effect of individual calcination temperature of STH was obtained by shaking 0.1 g of the adsorbent in 50 mL of 100 mg/L U(VI) at pH 6.5. Shaking time for reaching to equilibrium adsorption was selected from previous experiments. For study of regeneration ability of STH, batch experimental mode was performed in a glass beaker containing 0.1 g of exhausted STH used in previous experiments and 20 mL of 0.1 M Na₂CO₃ solution. The mixture was mixed by a mechanical mixer for 120 min. The solid phase was then separated by centrifuging and washed with distilled water until free of CO₃²⁻. The resulting STH was dried at 80 °C in a furnace for three hours. This step was considered as a first cycle. In the next cycle, resulting STH obtained in the first cycle was placed in a 100 mL beaker containing 50 mL of uranium solution (100 mg U / L). pH of the reaction solution was adjusted to 6.5. The mixture was shaken for 60 min. After equilibrium, the solid phase was separated by centrifuging. The similarly experiments of sorption/ desorption were carried out in the third and fourth regeneration cycles.

Percentage adsorption of U(VI) on STH and the adsorption capacity defined as amount of adsorbate per unit mass of adsorbent is calculated by formulas: is calculated by relationships:

\[
\% \text{ adsorption} = \frac{C_i - C_e}{C_i} \times 100 \tag{1}
\]

and

\[
q_e = \frac{C_i - C_e}{C_i} \times \frac{V}{m} \tag{2}
\]

Where, \(C_i\) is initial concentration of U(VI) in mg.L⁻¹ and \(C_e\) is concentration of U(VI) at equilibrium (mg.L⁻¹), \(V\) is volume of adsorbate (dm³), \(m\) is the mass of adsorbent (g).

Results and Discussion

Characteristics of STH

Table 1 shows the composition and ratios of Mg and Al in STH. The surface areas of STH are also included in table 1. Ratios of Mg and Al obtained in STH prepared by our method was found to be 2:1 and in an agreement with those, which had been reported. The surface area of STH were observed to increase with increasing calcination temperature. The highest value of the surface area of calcinated STH at 500°C was found to be 182 m²/g. The increase of the surface area of calcinated STH may be due to dehydroxylation and loss of interlayer anions, which cause a collapse of the layered structure. The SEM imagine of STH gives in Figure 1, which is shown that the amorphous and rough surface of the STH was observed. X-ray diffraction (XRD) patterns of noncalcinated STH and calcinated STH (STH-500) are shown in Figure 2a and 2b, respectively. The diffraction peaks of noncalcinated STH (Figure 2a) are typical of the layered double hydroxide structure with the characteristic basal spacing \(d = 7.73 \text{Å}\), which corresponds to interlayer CO₃²⁻. On the contrary, the peaks at 7.73 and 3.87 Å in X-ray diffraction pattern of the calcinated STH (Figure 2b) are not present. At
high temperature of calcinations, $\text{CO}_3^{2-}$ in the interlayer of STH was completely removed and the layered structure was destroyed\textsuperscript{16}. It means that heating of STH leads to yield a periclase MgO phase in addition to amorphous aluminum.

**Table 1.** Characteristic of synthesized STH.

<table>
<thead>
<tr>
<th>$\text{Al}_2\text{O}_3$, %</th>
<th>MgO, %</th>
<th>Ratio Mg/Al</th>
<th>Surface areas, m\textsuperscript{2}/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Noncalcinated STH</td>
</tr>
<tr>
<td>15.70 ± 0.98</td>
<td>39.08 ± 1.03</td>
<td>2:1</td>
<td>158</td>
</tr>
</tbody>
</table>

**Figure 1.** SEM imagine of the synthetic STH.

**Figure 2a.** The diffraction spectra of the noncalcinated STH.
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Effect of contact time

The time dependence curves of U(VI) removal are illustrated in Figure 3. It can be seen that percentage uptake of U(VI) increases with the elapse time. At initial contact time (up to 30 min), adsorption rate of U(VI) took place rapidly and thereafter the rate of adsorption was found to be slow. There is only somewhat different in adsorption rate of STH with different concentration of U(VI). Initial slow rate was found when concentration of U(VI) is about 100 mg/L. This may be due to competition between uranium ions for diffusing onto the adsorbent surface. However, the equilibrium adsorption with maximum adsorption capacity (in percentage) in all different concentration of U(VI) was reached more than 99% at 120 min. This time was used for the other experiments in this study.

Effect of pH

Figure 4 illustrates the effect of pH on U(VI) adsorption. It can be seen that adsorption of U(VI) by STH is a function of pH values. The maximum adsorption percentage achieved more than 97.0% at pH from 6.5 to 7 and reduced to 85.5-80% and lower at pH ≥ 8. At pH ≤ 5, the percentage adsorption is rapidly reduced for all concentration used in this test. This adsorption behaviors can be explained by the existence of different uranium species which may have responsibility to uptake U(VI) by STH.
In the range of pH ≤ 5, U(VI) primarily exists in the cationic form as UO$_2^{2+}$, which competes against H$^+$ ions for adsorption process. Increasing of high H$^+$ ion concentration leads to gradually protonation of the adsorbent surface. Therefore, the positive charge uranyl ions are repelled from adsorbed sites.

In the slight acid and neutral medium (pH 6.5 - 7), the competition of H$^+$ ions is negligible. Furthermore, in this pH range, U(VI) primarily exists in the form of hydrolyzed ion such as UO$_2$(OH)$^+$, (UO$_2$)$_2$(OH)$_2$$^{2+}$ and (UO$_2$)$_3$(OH)$_5$$^+$ which have low ionic charge that causes decreasing in secondary solvation energy. This phenomenon makes U(VI) in the form of (UO$_2$)$_3$(OH)$_5$$^+$ easily diffusing to the sorption sites of the adsorbent.

At pH ≥ 8, U(VI) primarily exists in the anionic complexes with OH$^-$ and CO$_3^{2-}$ (formed by dissolution of CO$_2$ from air) such as (UO$_2$)CO$_3$(OH)$_3^-$, UO$_2$(CO$_3$)$_2$$^{2-}$, UO$_2$(CO$_3$)$_3$$^{4-}$, etc. These complexes are very stable in the solution. The existence of the stable carbonate complexes of U(VI) with CO$_3^{2-}$ and OH$^-$ in the alkaline medium leads to reducing adsorption capacity of the STH.

**Adsorption kinetics**

In this research, two kinetic models used for fitting experimental data are the pseudo-first-order, pseudo-second order models. The pseudo-first order model:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$$

Where, $k_1$ is the pseudo-first-order constant (min$^{-1}$), $q_t$ is amount adsorbed at time t (mg/g) and $q_e$ is the amount adsorbed at equilibrium (mg/g). The pseudo-second-order model:

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

Where, $k_2$ is the pseudo-second-order constant (g/mg.min). The plots of log($q_e$-$q_t$) from Eq.(3) and $t/q_t$ from Eq.(4) against t give a linear relationship, which allow to calculate $k_1$, $k_2$ and predict $q_e$. The linear plots for the pseudo-first-odder and the pseudo-second-order models are presented in Figure 5 and 6, respectively. Table 2 lists the parameters of two models. The correlation coefficients values, $R^2$, of the pseudo-first-order and the pseudo-second-order models were found to be 0.987 and 0.999, respectively. These values are very high for both models. However, there is only an agreement between
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$q_{e,\text{exp}}$, experimental and $q_{e,\text{th}}$, predicted values for the pseudo-second-model. Thus, the best fit was achieved by the pseudo-second-order model for the U(VI) adsorption by STH.

**Figure 5.** Plots of pseudo-first-order equation for U(VI) adsorption ([U] = 20 mg/L, pH=6.5, T=303K).

**Figure 6.** Plots of pseudo-second-order equation for U(VI) adsorption ([U] = 20 mg/L, pH=6.5, T=303K).

<table>
<thead>
<tr>
<th>Pseudo-first-order model</th>
<th>Pseudo-second-order model</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$</td>
<td>$q_{e,\text{exp}}$, mg/g</td>
</tr>
<tr>
<td>0.033</td>
<td>19.7</td>
</tr>
</tbody>
</table>

**Table 2.** Parameters of pseudo-second-order model for U(VI) adsorption.

**Adsorption Isotherm**

The experimental equilibrium data for the adsorption of U(VI) by STH are described according to the Langmuir and Freundlich models. The linear form of Langmuir model:

$$\frac{C_e}{q_e} = \left( \frac{1}{K_lQ_{\text{max}}} \right) + \left( \frac{C_e}{Q_{\text{max}}} \right)$$

Where, $q_e$ is adsorption capacity (mg/g), $C_e$ is uranium concentration in liquid phase after equilibration (mg/L), $K_l$ is Langmuir constant related to the binding energy between the adsorbent and the adsorbate, L.mg$^{-1}$ and $Q_{\text{max}}$ is maximum adsorption capacity (mg.g$^{-1}$).

The linearized form of the Freundlich model:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

Where, $K_f$ is the Freundlich constant (g/L), $n$ is the a measure of the adsorption intensity, $C_e$ and $q_e$ have the same definition as stated in equation 4.

The values of $K_l$ and $Q_{\text{max}}$ in Eq. 5 and $K_f$ and $n$ in Eq. 6 can be calculated from the slope and the intercept of linear plots $C_e/q_e$ and log $q_e$ vs. $C_e$, respectively. Figures 7 and 8 show the comparative of Langmuir, Freundlich isotherms with correlation coefficient values.
are 0.9905 and 0.9997, respectively. From the results, it can be seen that the equilibrium adsorption capacity for both models, $q_e$, increased with the increase in U(VI) concentration.

**Figure 7.** Langmuir adsorption isotherm of U(VI) onto STH (pH=6.5, T=303K).

**Figure 8.** Freundlich adsorption isotherm of U(VI) onto STH (pH=6.5, T=303K).

**Table 3.** Langmuir and Freundlich isotherm constants.

<table>
<thead>
<tr>
<th>Langmuir model</th>
<th>Freundlich model</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_l$</td>
<td>$Q_{max}$</td>
</tr>
<tr>
<td>0.131</td>
<td>62.5</td>
</tr>
</tbody>
</table>

The linear type of the Langmuir model at different temperature is shown in Figure 9. The values of parameters in Langmuir model were determined and reported in Table 4. From results, it was found that the adsorption of U(VI) by STH is increased with increasing temperature. To determine Gibbs free energy ($\Delta G^0$), standard enthalpy change ($\Delta H^0$), and standard entropy change ($\Delta S^0$) of the adsorption reactions between U(VI) and STH at different temperature, the thermodynamical equations $^{17}$ were used:

$$\ln K_f = A - \frac{\Delta H^0}{RT}$$ (7)

$$\ln K_f = -\frac{\Delta G^0}{RT}$$ (8)

$$\Delta S^0 = \frac{(\Delta H^0 - \Delta G^0)}{T}$$ (9)

Where, $R$ is universal gas constant (8.314 J/mol.K), $T$ is absolute temperature (K). Figure 10 shows the linear plot of $\ln K_f$ against constant $1/T$ of the equation (7). The value of enthalpy change ($\Delta H^0$) for the adsorption of U(VI) by STH could be obtained from the slope of the plot. The values of the Gibbs free energy ($\Delta G^0$) and the standard entropy change ($\Delta S^0$) were calculated using equations (8) and (9). The thermodynamic parameters obtained in this study are given in Table 4.
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**Figure 9.** The linear type of the Langmuir model at different temperature.

**Figure 10.** The variation of the Langmuir constant with temperature.

**Table 4.** Parameters of Langmuir equation for the U(VI) adsorption.

<table>
<thead>
<tr>
<th>T, K</th>
<th>K_l, L/mg</th>
<th>A, mg/g</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>0.131</td>
<td>18.281</td>
<td>0.997</td>
</tr>
<tr>
<td>313</td>
<td>0.205</td>
<td>19.762</td>
<td>0.963</td>
</tr>
<tr>
<td>323</td>
<td>0.296</td>
<td>23.09</td>
<td>0.933</td>
</tr>
</tbody>
</table>

**Table 5.** The thermodynamic parameters for the adsorption of U(VI) on STH.

<table>
<thead>
<tr>
<th>T, K</th>
<th>ΔH, kJ/mol</th>
<th>ΔS, J/mol.K</th>
<th>ΔG (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>45.26</td>
<td>130</td>
<td>5.87</td>
</tr>
<tr>
<td>313</td>
<td>131</td>
<td>130</td>
<td>4.03</td>
</tr>
<tr>
<td>323</td>
<td>130</td>
<td>130</td>
<td>3.19</td>
</tr>
</tbody>
</table>

The positive values of enthalpy change (ΔH^0) indicates the endothermic nature of the adsorption process of U(VI) by STH. Positive values of Gibbs free energy (ΔG^0) indicate that the adsorption process depended on temperature. As shown in results, ΔG^0 values
obtained are very small and decrease with increasing temperature. The adsorption of U(VI) by STH. The values of the entropy change (ΔS°) are positive and remain almost constant with temperature. This reflects the affinity of the STH for U(VI) and suggest increased randomness at the adsorbent / solution surface during the adsorption.

Effect of calcination temperature

Based on the Langmuir model, the maximum adsorption capacities for U(VI) by STH calcinated at 100, 200, 300, 400 and 500 °C were found to be 23.0, 24.8, 25.1, 47.8 and 51.2 mg /g, respectively. There are two factors that may have contribution to the increase of the adsorption capacity of calcinated STH: (i) the high available sorption sites due to high surface areas of the calcinated STH; (ii) the structural memory effect of hydrotacite. According to Erickson et al\(^6\) when exposition to water, the calcinated STH induces the reconstruction of its original structure by taking anion from aqueous solutions. It means that, anionic complexes of U(VI) with OH\(^-\) and CO\(_3\)^{2-} such as (UO\(_2\))CO\(_3\)(OH)\(_3\), UO\(_2\)(CO\(_3\))\(_2\)^{2-}, UO\(_2\)(CO\(_3\))\(_3\)^{4-} at pH ≥ 6 will participate in the reconstruction of the calcinated STH, and enhance the adsorption capacity.

Regeneration of STH

From characteristics of the STH including the high adsorption capacity, the structural memory effect and the stability of the anion carbonate complexes of U(VI), the 0.1 M Na\(_2\)CO\(_3\) solution was selected for regeneration of the noncalcinated STH. The results of four regeneration cycles of the exhausted STH are presented in Table 5. The percentage adsorption was only slightly reduced from the third and the fourth cycles. From the results obtained, it can be concluded that STH could be reused for recovery and removal of U(VI) in aqueous solution.

<table>
<thead>
<tr>
<th>Number of Regeneration cycle</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>U (VI) adsorption capacity, %</td>
<td>98.3</td>
<td>98.0</td>
<td>97.5</td>
<td>97.2</td>
</tr>
</tbody>
</table>

Table 6. The generation results of the exhausted STH.

Conclusion

Synthesized clay (STH) was prepared with high adsorption capacity with U (VI). There was difference adsorption capacity between different calcination temperatures of STH. The pH values were also effect on adsorption capacity of STH. The suitable pH ranges for uranium adsorption by STH is from 6.5 to 7. The time dependent experimental data were found to be fit to the pseudo-second-order model. The Langmuir and Freundlich models showed that both model provide the best correlation with equilibrium data. The measured adsorption isotherm at the different temperature were found to be fit to the Langmuir model with correction coefficients, R\(^2\) = 0.997, 0.963 and 0.933 at 303K, 313K and 323K respectively. From Langmuir model, the adsorption maximum capacity of STH was calculated. It is 51.2 mg U(I) per g of STH. For regeneration studies, the results obtained were shown that the adsorption capacity is only slightly reduced after fourth cycle. From results obtained, it could be concluded that the STH is a potential adsorbent for removal of U (VI) in contaminated water as well as from wastewater containing uranium.
Acknowledgment

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References

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