Uranium Adsorption from Aqueous Solution Using Sodium Bentonite Activated Clay

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Abstract

Due to extensive variety of nuclear applications, the cost efficient adsorbent is extremely needed for radioactive liquid waste solutions treatment. Bentonite which consists essentially of clay minerals of the smectite group; have a wide range of industrial uses. In this study, a simple approach to adsorb uranium (VI) from aqueous solution by exchangeable cation by sodium bentonite clay is presented. The effects of contact time, pH of the solution, initial uranium (VI) concentration, adsorbent dosage, and solution temperature on the adsorption of uranium (VI) ions from radioactive liquid solution were investigated. Adsorption isotherms were expressed by Langmuir and Freundlich adsorption models. The theoretical capacity of sodium bentonite clay adsorbent is about 12 mg/g. The optimum adsorption conditions were recommended. About 89% of the loaded Uranium (VI) on modified clay adsorbent was eluted by CH3COONa as an efficient eluent. The preferred adsorption and elution conditions were applied on real waste sample and the obtained capacity was determined.

Keywords: Uranium; Adsorption; Sodium bentonite; Elution

Introduction

Bentonites, which contain essentially of clay minerals of the smectite group, have a wide range of industrial uses. A particular feature of this group of minerals is the substitution of Si4+ and Al3+ in the crystal structure by lower valancian cation. This leaves unsatisfied negative charges which are balanced by loosely-held "exchangeable" cation such as Na+, Ca2+, Mg2+ and H+ located mainly on the interlayer crystal surface. The structure, chemical composition, exchangeable ion type and small crystal size of smectite are responsible for several unique properties, including a large chemically active surface area, a high cation exchange capacity, and interlayer surface having unusual hydration characteristics, and sometimes the ability to modify strongly the flow behavior of liquid [1].

Depending on the dominant exchangeable cation present the clay may be referred to as either calcium Bentonites or sodium Bentonite, the two varieties exhibiting markedly different properties and thus use. The terms non-swelling Bentonites and swelling Bentonites are identical with calcium Bentonites and sodium Bentonites respectively. When mixed with water, swelling bentonite exhibit a greater degree of dispersion and better plastic and rheological properties than non-swelling bentonite. Natural sodium Bentonites, such as those in Wyoming, USA (Wyoming or western bentonite), are comparatively rare although the cation-exchange properties of smectite enable the more widespread calcium from to be easily converted to high-swelling sodium bentonite by a simple sodium exchange process.

Since the exchangeable cation present in bentonite are easily replaceable, Na+ is readily replaced by Ca2+ and Mg2+ under leaching condition [1]. Natural sodium bentonite have medium to low green strengths but high dry strengths, which increase the resistance to erosion by molten metal, wet tensile strengths are high. Sodium bentonite usually shows good [2].

Clay minerals are known with a wide variety of cations and organic molecules by adsorption, interaction and cation exchange capacity. These minerals may serve as a cost-effective sorbents for the removal of heavy metals. Their sorption capacities are usually less than those of synthetic sorbents; these materials could provide an inexpensive substitute for the treatment of heavy metal for wastewaters. To enhance the the sorption capacity; the clays are modified in various ways, such as treatment by inorganic and organic compounds, acids and bases [3,4]. For example, montmorillonite, coated and intercalated by aluminum hydroxide exhibits much higher adsorption capacity for some heavy metal ions, than that of natural montmorillonite [5]. Treatments of zeolites by NaCl solution converts them into a near homoionic state in Sodium form, and improves the exchange capacity for lead and zinc ions [6]. Adsorption capacity of clay minerals can also be enhanced by replacing the natural exchangeable cations with organic cations, which makes the clay surface more hydrophobic [7,8]. Uranium is one of the most serious contamination concerns because of its radioactivity and heavy-metal toxicity [9-11]. Numerous techniques have been applied for uranium removal from liquid solution and radioactive solution. Chemical precipitation, ion exchange, liquid membrane, solvent extraction and adsorption are the most commonly used methods [12-16]. Absorption technique has attracted attention in recent decades because of its effective and economic method with high potential for the removal uranium, recovery and recycling of metal ions from liquid solution. A number of materials (as adsorbent) were tested. The latter were involved activated carbon [17], zeolite, olivine rock, coir pith, smectites, bentonite [18] sepiolite, montmorillonite, biomass, goethite, and polymeric materials [14,19].

This work aimed to explore the ability of using sodium bentonite clay (SBC) for uranium (VI) removal from the radioactive liquid waste as a low cost adsorbent. Batch experiments were carried out to choice the preferred adsorption conditions. Uranium (VI) adsorption efficiency was studied as a function of the following parameters: contact time, initial uranium concentration, solution pH, and temperature. Equilibrium adsorption isotherms were analyzed to obtain the
Langmuir and Freundlich constants. The obtained results gave a better understanding of the sodium bentonite clay adsorption (uranium) phenomenon. For desorption (or elution) of the loaded uranium (upon the prepared sodium bentonite clay), many eluents were tested (Table 1).

**Experiment**

**Materials and analytical procedure**

The working aqueous experimental sample used in this study was provided by the Nuclear Material Authority, Egypt. The chemical composition of the studied raffinate solution has the following chemical composition: 60 mg/l U, 141.1 g/l HNO₃ (2.2 M), 1.9 g/l Ca²⁺ and 0.6 g/l Fe₂O₃. A uranium stock standard solution assaying 1000 mg/L was prepared by dissolving 0.16556 g of uranyl nitrate UO₂(NO₃)₂ of BDH Chemicals Ltd. Poole, England in 100 ml distilled water. Uranium was analyzed in the different working aqueous solution using the Arsenazo III spectrophotometric method [20]. Absorbance of the formed uranium Arsenazo III complex was measured at 650 nm against proper standard solutions using a Perkin-Elmer, USA UV/VIS spectrophotometer. The initial pH of the working solution was adjusted by addition of a buffer solution. Commercial bentonite clay sample after and before activation (8.20, 8.14 m²/g) respectively was supplied from Al Amier Ceramic Co. Cairo; with chemical composition listed in Table 2 and the XRF pattern was plotted in Figure 1. The provided clay sample was crushed, ground and sieved to the used grain size of 0.09 mm (200 mesh size). The XRF analysis for bentonite shows that this type of clays consists mainly for aluminum silicate, with Na and Ca as exchangeable cations, so it is considered as intermediate bentonite with moderate swelling capacity [21].

**Preparation of the sodium bentonite**

Sodium bentonite was prepared as described by Galabutskaya and Deb. [3,4]. The thoroughly-wetted clay (20-40 mg) is treated with a fresh 4% sodium chloride solution of pH 5.8-6.0 (adjusted by sodium hydroxide solution) at ~ 40-45°C for 15 minutes. The clay is then treated with 0.05 N hydrochloric acid at ~ 40°C for 3 minutes, re-centrifuged, and the supernatant liquid collected in a separate beaker. This complete with 0.05 N hydrochloric acid at ~ 40°C for 3 minutes, re-centrifuged, and the supernatant liquid collected in a separate beaker. This complete.

**Equilibrium studies**

For studying the relevant adsorption factors, several series of experiments have been achieved using synthetic uranium solution.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>%</th>
<th>Constituent</th>
<th>%</th>
</tr>
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<tbody>
<tr>
<td>Al₂O₃</td>
<td>16.7</td>
<td>MgO</td>
<td>2.13</td>
</tr>
<tr>
<td>SiO₂</td>
<td>56.34</td>
<td>CaO</td>
<td>10.15</td>
</tr>
<tr>
<td>TiO₂</td>
<td>2.04</td>
<td>K₂O</td>
<td>2.6</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>11.36</td>
<td>V₂O₅</td>
<td>0.046</td>
</tr>
<tr>
<td>MnO</td>
<td>0.27</td>
<td></td>
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</table>

**Table 1: Chemical composition of the working Bentonite sample before treatment.**

These factors involved contact time, initial uranium concentration, pH, solid/liquid ratio, g/ml and the adsorption temperature. From the attained results, Langmuir and Freundlich isotherms were determined. These batch adsorption experiments were implemented by shaking 0.1 g of the SBC sample with 15 ml of the uranium synthetic solution (200 ppm) using a magnetic stirrer. The adsorbed amounts of uranium were calculated by the difference between its equilibrium and initial concentrations.

For eluting or desorption of the loaded uranium from SBC sample, the different eluents were studied, namely, Sodium acetate (CH₃COONa), Nitric acid (HNO₃), Hydrochloric acid (HCl) and Sodium chloride (NaCl).

**Equilibrium calculation**

All uranium speciations in this study were performed with Hydra-MEDUSA, a chemical equilibrium calculation program [22].

**Results and Discussion**

**Results of uranium adsorption study**

Effect of pH: The influence of solution pH on the adsorption of uranium on SBC was investigated by contacting a fixed weight of the prepared SBC (0.1 g) with 15 mL of uranium standard solution of 200 ppm at 25°C for 60 minutes. The investigated pH ranged from 0.5 to 8.5. The attained data were shown in Figure 3. From this figure the uranium adsorption efficiency increases gradually with increasing pH values till pH 4.2 with 84% adsorption efficiency. By increasing the pH beyond 4.2, the uranium adsorption efficiency was deceasing from 4.2 to 8.5. Thus, we can recommend the use of solution pH having pH value of 4.2.

It is significant to designate that uranium adsorption is powerfully liable on the solution pH. At low pH ≤ 4.2, the number of H₃O⁺ ions exceeds that of the UO₂⁺ several times and the surface is most likely covered with H₃O⁺ ions, reducing the number of binding sites for
the adsorption of UO$_2^{2+}$. When pH increases >4.2, more H$_3$O$^+$ ions leave the clay mineral surface making the sites available to the cation to the formation of complexes in aqueous solution, i.e., UO$_2$(OH)$_2^+$, (UO$_2$)$_2$(OH)$_2$ and UO$_2$(OH)$_2^+$, which increase uranium (VI) adsorption [23,24].

The aqueous speciation distribution of uranium was calculated and represented in Figure 4. The results showed that the complexes of UO$_2$(NO$_3$)$_2^+$ and UO$_2$(OH)$_2^+$ were the predominant species at the pH range from 0.0 - 0.03 with mean total percent of 17 and 83% respectively. U-hydroxide complexes start to dominate the aqueous phase at pH near 3 of (UO$_2$)$_2$(OH)$_2$ and (UO$_2$)$_2$(OH)$_2$. At pH 5, the UO$_2$(OH)$_2$.H$_2$O(C) became the major species with about 100% of total concentration at pH range from 4.5 to 11 while at pH 12, UO$_2$(OH)$_2$ at pH 13, UO$_2$(OH)$_2^+$ the major species within a total percent 100% of the total concentration.

Effect of contact time: The effect of the contact time was investigated by performing a serious of experiments by contacting a fixed weight (0.1 g) of SBC with 200 mg/l uranium solution (15 ml) at room temperature and pH 4.2. The studied time ranged from 1 up to 180 minutes. The obtained results were plotted in Figure 5. It was observed that the uranium adsorption efficiency attained about 22.5% at the first contact of 1 min. By increasing the contact time from 1 to 120 min. the uranium adsorption efficiencies obtained increases significantly 22.5 to 91% from 1 to 120 min. respectively. Beyond 120 minutes contact time there is slight increase to 92%. Therefore, the 120 minutes contact time could be selected as the suitable time.

Effect of adsorbent dosage: To study the effect of SBC dosage amount a series of adsorption experiments were performed under fixed conditions namely, uranium with initial concentration of 200 mg/L at room temperature (≈ 25°C) and pH=4 (± 0.2), and the contact time of 2 h. The studied ratios are ranging from 1.66 to 26.66 g SBC /L. From the obtained results plotted in Figure 6, it is clearly obvious that uranium adsorption efficiency increased steadily with increasing the temperature. For this reasons, room temperature (≈25 °C) was chosen as the optimum temperature.

Effect of initial uranium concentration: To investigate the effect of initial uranium concentration on its adsorption efficiency onto SBC, a series of experiments were performed by contacting a fixed weight (0.1 g) for 120 min at room temperature (= 25°C) and pH 4.2. The studied initial uranium concentrations used ranged from 50 up to 800 mg/L.

To study the effect of SBC dosage amount a series of experiments were performed under fixed conditions namely, uranium with initial concentration of 200 mg/L at room temperature (≈ 25°C) and pH=4 (± 0.2), and the contact time of 2 h. From the obtained results plotted in Figure 7, it is clearly obvious that uranium adsorption efficiency increased steadily with increasing the weight of the adsorbent from 92 down to 49% at 1.66 and 26.66 g SBC /L respectively. This was interpreted that by increasing in the adsorbent amount may cause aggregation of adsorbent. Consequently, adsorptive capacity of adsorbent available was not fully employed at a higher adsorbent amount (dose) in comparison to lower adsorbent amount were the available adsorption sites may decrease [25-27].

Effect of adsorption temperature: To study the effect of temperature upon the uranium adsorption onto the prepared adsorbent sample, a series of adsorption experiments were performed using different temperatures ranging from 25 up to 60°C. In these experiments the other parameters were kept constant, at an initial uranium concentration of 200 mg/L a constant pH of 4.2 and a contact time of 2 h. From the obtained results plotted in Figure 7, it is clearly obvious that uranium adsorption efficiency increased steadily with increasing the temperature. For this reasons, room temperature (=25 °C) was chosen as the optimum temperature.
The obtained results were plotted in Figure 8 from the obtained data, it was clearly obvious that uranium adsorption efficiency decreases with increasing its initial concentration. Therefore the uranium solution of 200 mg/L could be chosen as the most favorable concentration. Another result could be concluded from Figure 8, which is the experimental capacity of the adsorbent which was determined by 11.8 mg uranium/g SBC.

**Adsorption isotherm:** Several common adsorption isotherm models were considered to fit the obtained isotherm data under the equilibrium adsorption of the SBC. Examples of these models are Langmuir and Freundlich isotherms.

**Langmuir isotherm:** According to the Langmuir model, adsorption occurs uniformly on the active sites of the sorbent, and once a sorbate occupies a site, no further sorption can take place at this site. Thus, the Langmuir model is given by the following equation [28,29].

\[
\frac{C_e}{q_e} = \frac{1}{bQ_o} + \frac{C_e}{Q_o}
\]

where: \(Q_o\) and \(b\), the Langmuir constants, are the saturated monolayer sorption capacity and the sorption equilibrium constant, respectively. A plot of \(C_e/q_e\) versus \(C_e\) would result in a straight line with a slope of \((1/Q_o)\) and intercept of \(1/bQ_o\) as seen in Figure 9. The Langmuir parameters given in Table 3 can be used to predict the affinity between the sorbate and sorbent using the dimensionless separation factor \(R_L\) [30,31].

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

The values of \(R_L\) for adsorption of uranium (VI) onto Modified bentonite are shown in Figure 10, which indicate that adsorption of uranium(VI) is more favorable at higher initial uranium(VI) concentrations than at lower concentrations.

**Freundlich isotherm:** The Freundlich model stipulates that the ratio of solute adsorbed to the solute concentration is a function of the solution. The empirical model was shown to be consistent with exponential distribution of active centers, characteristic of heterogeneous surfaces. The amount of solute adsorbed at equilibrium, \(q_e\), is related to the concentration of solute in the solution, \(C_e\), following [28,29],

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sorption capacity and sorption intensity, respectively. A plot of (log$q$) versus (log$C_e$) would result in a straight line with a slope of (1/n) and intercept of (logK) as seen in Figure 11. Freundlich constants are given in Table 3. The experimental data shows that the adsorption of uranium onto SBC fitted well with Langmuir than Freundlich isotherm.

**Choice of the optimum adsorption conditions**

From the obtained results of the relevant factors affecting uranium adsorption onto the sodium bentonite, careful selection of the optimum values of these results would depend primarily on economic considerations. In the light of the studied factors, it would seem economic to select the following conditions for uranium removal by the prepared bentonite followed in Table 4.

**FT-IR**

The infrared spectrum of sodium bentonite clay before adsorption is shown in Figure 12a. The spectral regions of interest are: (i) The broad absorption band in region 3868-3480 cm$^{-1}$ can be attributed to the stretching of lattice OH (Si-OH, Al-OH) and OH of the physically adsorbed water [33] and the overtone of the bending vibration of water observed at 1622 cm$^{-1}$. (ii) The deep band of about (1034) cm$^{-1}$ in the stretching mode region is due to Si-O-Si stretching frequencies. (iii) Bands centered around (537-787) cm$^{-1}$ in the stretching mode are due to Si-O-Al and Si-O-Na stretching frequency, and Si–O bending frequencies [34,35].

After adsorption of U, some bands disappeared (Figure 12b); such as that bands of Si-O-Al, Si-O-Na stretching frequency, and Si-O bending frequencies, in addition, the deep band at 1034 cm$^{-1}$ of Si-O-Si stretching frequencies. This is due to the binding of metal ions mainly located on the clay lattice region, so basically affected the Si-O vibrations. In addition, there was a strong broadening band of water, which may be due to the moisture after adsorption experiments.

**SEM**

The SEM images of the SBC before and after adsorption for U (VI) ions are presented in Figure 13. As shown in Figure 13a, the surface of SBC before adsorption was flat and uniform. However, its surface became uneven and was covered with some material containing uranium, as shown in Figure 13b. It can also be observed that there were some cleavage and small opening after adsorption. The reason for this may be due to the rehydration of SBC in the aqueous solution resulted in the improvement of the d-spacing [36-39].

**Uranium desorption**

**Effect of strip agent:** The subsequent solutions NaCl, HCl, HNO$_3$, and CH$_3$COONa were tested for uranium elution from the loaded SBC for 30 minutes. The elution experiments were carried out by 0.1 g of loaded SBC sample with eluent portions of 20 mL. A systematic calculation of the eluted uranium amounts was carried out after its analysis. Table 5 summarizes the obtained data, it is clearly obvious that the CH$_3$COONa elution solution is the finest solution tested as an eluent for uranium from the loaded SBC.

**Effect of stripping agent concentration**

To studying the effect of stripping agent concentration, a series of stripping experiments were performed by shaking different concentrations of CH$_3$COONa ranged from 0.1 up to 2 M. with the loaded SBC of 5 g SBC / L phase ratio for 30 min. shaking time. The results were plotted in Figure 14. From the obtained data, it is obvious that 1 M CH$_3$COONa (stripped about 90% of the loaded uranium) could be chosen as a suitable concentration.

**Effect of shaking time upon uranium stripping**

For studying the effect of contact time upon uranium stripping from the uranium–loaded SBC, a series of experiments was performed using time intervals varying from 15 minutes up to 90 minutes. The performed experiments were carried out using fixed CH$_3$COONa concentration of 1 M and 5 g SBC / L phase ratio. The results were plotted in Figure 15. From the obtained results, one can observe that 30 min. shaking time would be quite sufficient for stripping uranium from the loaded SBC and don’t show no significant improvement in latter time.

**Effect of volume/mass upon uranium stripping**

To investigating the result of Volume/Mass upon uranium stripping from the uranium loaded SBC, investigates from 1 g SBC/L up to 5 g SBC/1000 ml under fixed CH$_3$COONa concentration of 1 M and 30 min. The results were plotted in Figure 16. and detected that 5 g SBC / L will be suitable for stripping uranium from the loaded SBC.

**Case Study: Uranium Removal from the Raffinate Waste Solution**

**Uranium adsorption**

As previously mentioned, the prepared adsorbent has a satisfactory
uranium adsorption capacity (about 11 mg U/g SBC). In the present work, the study of uranium removal from liquid raffinate was carried out using batch experiment by contacting 0.1 g SBC with 20 ml of the raffinate solution for 120 min. by calculating the loaded uranium content from its analysis in the effluent samples revealed that only 8.7 mg U/g SBC was adsorbed. Comparing this loading capacity with the theoretical capacity of the prepared SBC (about 11.8 mg U/g SBC), indicated that under the working conditions, 73.7% of the theoretical capacity was realized. The decrease in the SBC capacity after contacting with the working sample may be due to the competition between uranium and different ions in the studied nuclear waste sample (as iron).

**Uranium elution**

Using the 1.0 M CH₃COONa as an eluent was found effective in uranium elution from the loaded SBC adsorbent bed. By calculating of the eluted uranium amounts revealed that this elution solution gave about 90% uranium elution efficiency (7.83 mg U were eluted).

<table>
<thead>
<tr>
<th>Eluent type</th>
<th>Elution Efficiency, %</th>
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<tbody>
<tr>
<td>1.0M NaCl</td>
<td>15</td>
</tr>
<tr>
<td>1.0M HNO₃</td>
<td>60</td>
</tr>
<tr>
<td>1.0M HCl</td>
<td>68</td>
</tr>
<tr>
<td>1.0M CH₃COONa</td>
<td>89.7</td>
</tr>
</tbody>
</table>

**Table 5:** Elution yields using different eluent reagents.
uranium conc. of 200 mg/L. The Langmuir model sufficiently described optimum conditions of 120 min shaking time, pH about 4.2, with initial are also of great importance. The best results were obtained under minerals) constituting approximately 93% of the samples.

The ability of the material to elements and the nature of the materials. The ability of the material to adsorbed uranium is mainly due to the micro-porous minerals (clay minerals) constituting approximately 93% of the samples.

The texture and the physical properties (porosity, etc.) of the SBC are also of great importance. The best results were obtained under optimum conditions of 120 min shaking time, pH about 4.2, with initial uranium conc. of 200 mg/L. The Langmuir model sufficiently described the adsorption data with R, values of adsorption is greater than 0.97 and this implies that the adsorption of the metal ions from their aqueous solutions proceeds by monolayer adsorption.

The results suggested that Na bentonite is suitable as sorbent material for adsorption of uranium ions from aqueous solutions. We succeeded to elute about 90% of the loaded uranium using 1.0 M CH₃COONa as an eluent solution.

References


