

Towards a More Safe Environment: (5) Disposability of Uranium by Some Clay Sediments in Egypt

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Abstract: To accurately predict contaminant transport through the subsurface, it is essential that the important geochemical processes affecting contaminant transport be identified and accurately described. Dissolution/precipitation and adsorption/desorption are usually the most important processes affecting contaminant interaction with soils. In current study, adsorption and desorption of Uranium by clay sediments was take place in Egypt. Obtained results indicated that Uranium can be sorbed upon Kalabsha kaolinite, Abu Tartur bentonite and El-Hafafit vermiculite. The amount of adsorbed uranium increases with the increase of U concentration, pH and equilibration time till 3 hrs. It decreases with the increase of the solid/liquid ratio. Pretreatment of the clay sediments by roasting, HCl and NaOH proved to increase the U adsorption efficiency. Release of U from the loaded clay sediments was possible to different extents depending upon clay type and desorbing agent. The IR analyses proved that considerable mineralogical changes occurred after U adsorption and desorption.

Key words: adsorption-desorption – clay sediments – I.R - nuclear - pollution- uranium – Egypt.

INTRODUCTION

Radionuclides exist in the environment naturally and in recent times, have added by nuclear power and weapons. The carcinogenic nature and long half-lives of many radionuclides make them a potential threat to human health, morton *et al.* (2002), vandenhove *et al.* (2007) and runping Han *et al.* (2007).

Uranium introduced into environment from the processing of uranium ores into nuclear fuels and materials. Uranium mining, milling, processing, enriching and disposal all have the potential to contaminate the environments.

Clay sediments represent excellent natural barriers due to their small grain size, their specific surface area and their diagenetic processes (which cause high natural density). Besides, their ability to close fissures and cracks (which may form paths for leachates). In addition, their chemical reactivity permits them to immobilize important contaminants i.e. uranium, wang *et al.* (2003), seaman *et al.* (2001), prikryl *et al.* (2001),abdallah (2004 and 2006).

It is important to note that soil scientists and geochemists knowledgeable of sorption processes in natural environments have long known that generic or default partition coefficient values found in the literature can result in significant errors when used to predict the absolute impacts of contaminant migration or site-remediation options.

The aim of study was to obtain some necessary data about the adsorbability and desorbability of uranium to be utilized for the improvement of uranium extraction technology as follows:

1- During the leaching of uranium from its ores, the mineralogical composition of these ores especially the gangue mineral content affects the uranium leaching efficiency. The ores having higher clay minerals content are lower in uranium extraction efficiency because clay minerals immobilize some uranium. The latter may reach 10% of the initial uranium content.

2- In the uranium heap leaching process, it is strongly recommended to use clayey layer under the heap to prevent the ground water contamination by the leached uraniferous solution. It is very important to know the suitable clay mineral type, which has the highest uranium adsorbability and immobilization and in the same time which one have high affinity with uranium to prevent its losses.

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3- The uranium ores, which have higher contents of clay minerals, could face filtration problems during the separation of the spent ore from the leached uranium solution. That is because clay minerals are mostly present in the clayey or silty size and hence block the filter pores. The determination of the uranium adsorbability by clay minerals will help in developing new methods for desorbing uranium from the spent ores as well as adding special filter aids to solve the solid / liquid separation problem.

MATERIALS AND METHODS

Clay Sediments:

Three natural clay sediments differ in their mineralogical composition were selected. The samples collected from either the exploitation localities or from nearby radioactive occurrences in Egypt. Full characterization of these sediments including location, radiometric analysis, X-ray diffraction analysis, Infra-red spectroscopy analysis, Differential Thermal Analysis and full chemical analysis (major oxide and trace elements) by X-ray fluorescence, were carried out in separate study by abdallah *et al.* (2007).

The collected samples were grinded in a porcelain ball mill, washed with distilled water to remove soluble impurities and wet sieved through 350 mesh sieve (45 μm), homogenized and < 45 μm fraction was collected.

Radioactive element:

A synthetic stock solution of uranyl nitrate $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich product) was prepared to be utilized in the adsorption experiments. The concentration of the prepared solution ranged from 0.074 – 1.45 mmol/L.

Disposability Procedure Experiments:

To achieve the aim of the current study two experiments were set. Adsorption and desorption experiments were carried out according to abdallah *et al.* (2005). In desorption experiments the initial uranium concentration was 0.74 mmol/l. In each experiment, the analysis of uranium was performed by fluorimetric method.

Uranium Analysis:

The fluorimetric method of uranium analysis was adopted in this work using a Jarrel – Ash fluorimeter (model 26 – 010, USA). The method mainly based upon the dilution technique as the interference from other elements based upon their concentration and not on their ratio to the uranium content. In addition, the internal standard technique was also used in order to assure accuracy and reproducibility of the analytical results. Thus, for each analysis, a number of aliquots of the uranium solution to be analyzed each measuring 0.1 ml were transferred to special Pt-dishes and were evaporated to dryness under infra red light using a special pellet-maker. A suitable amount of the flux material (sodium carbonate / sodium fluoride in the ration of 9/1) was then added to each Pt-dish including that containing the blank. After fusion at about 900 °C, the fused pellets were cooled and their fluorescence was measured. The concentration of uranium in the analyzed solution calculated from the following equation: $C = c(X-B) / (Y-X)$ where:

C = uranium conc. in the analyzed solution, c= uranium conc. of the standard solution, X = mean fluorescence value of the analyzed solution, B = mean fluorescence value of the blank solution, and Y = mean fluorescence value of the analyzed solution containing 0.1 ml of the standard solution (internal standard).

RESULTS AND DISCUSSION

The data obtained from studying the effect of uranium concentration upon its adsorption efficiency by the studied Egyptian clay samples shown in Fig. (1) and table (1).

From these results, it is clear that at low U concentration (until 0.5 mmol/L), Kalabsha kaolinite adsorbed more U than the other two sediments. When the initial concentration rises above (0.5 mmol/L), Abu Tartur bentonite adsorbs more U than the other two sediments. At low U concentration, kaolinite selectivity and exposed surface charges may be the reason. After that, CEC does not play the main role in U adsorption that was 12.8, 71.0 and 90.0 cmol/kg for Kalabsha kaolinite, Abu Tartur bentonite and El Hafafit vermiculite respectively as recorded in table (2) by abdallah(2007).

Figure (2) and table (2) describe the U adsorption on the studied clay samples by Langmuir equations and their constants, respectively. It is evident that the U adsorption maxima arranged in the descending order: Abu Tartur bentonite, El Hafafit vermiculite and Kalabsha kaolinite. There are some differences between this arrangement and that based on the CEC figures recorded in abdallah *et al.* (2007) especially for bentonite. This may be attributed to the presence of montmorillonite (as the predominant clay mineral in the bentonite

sediment) which will swell on exposure to water, so filling the voids between tailing particles in addition to their uranium sorption, Al-Hashimi *et al.* (1996) supported the previous finding. However, this work confirms the absence of correlation between the adsorption maxima B and the cation exchange capacity.

The binding energy (b) calculated from Langmuir equation has opposite trend relative to the adsorption maxima (B). Kalabsha kaolinite exhibits the lowest adsorption maxima with highly binding energy. It means that although bentonite has the highest adsorption maxima the uranium may release easier. This may explain why the geologists search for uranium ores in the kaolinite sediments.

Factors Controlling Uranium Adsorption:

Equilibration Time:

The results obtained from studying the effect of equilibration time upon U adsorption shown in Fig. (3). From the obtained data, one can notice that the uranium adsorption increased with increasing the equilibrium time from 15 min, to 3 hours and then almost constant. In case of Abu Tartur bentonite and Kalabsha kaolinite, the increase has a gentle curve, while in case of El Hafafit vermiculite the increase has a straight line.

It is worthy to mention that Barnett *et al.*, (2000) reported that the rate of U^{+6} adsorbed on the illite, kaolinite, smectite and vermiculite samples was rapid over the first few hours of the adsorption time and then slowed appreciably after 24 to 48 hours. The adsorption of U^{+6} to the samples was also non-linear suggesting a decreasing attraction for the surface adsorption with increased surface loading.

pH:

Variations in pH affect both the solution specification and the preferred type of sorption sites on the clay mineral surface, Hennig *et al.*(2002). The data presented in Fig. (4), shows the effect of pH upon the uranium adsorption efficiency, by clay sediments. From the obtained results, it is clear that the U adsorption efficiency increased by increasing the pH until pH (6) or (8) depend on clay type then decreased. In case of Kalabsha kaolinite, the U adsorption efficiency increased from 38.3% at pH (2) until 98.12% at pH (8) then decreased to 56.3 % at pH (12). While, in case of Abu Tartur bentonite, the U adsorption efficiency increased from 52.5 % at pH (2) until 75.3 % at pH (8) then decreased to 61.0 % at pH (12). In the case of El Hafafit vermiculite, the U adsorption efficiency increased from 74.5 % at pH (2) until 93.6 % at pH (4) then decreased to 56.0 % at pH (12). Obtained data was highly supported by Gadelle *et al.* (2001) and Barnett *et al.* (2000).

It is worthy to mention herein, that the pH dependent aqueous speciation of uranyl ions was an important factor determining the magnitude of U adsorption. At low pH, the adsorption by fixed-charge sites was predominant. The decrease in U adsorption with increasing the pH caused by the formation of the monovalent aqueous uranyl species, which are weakly bound to the fixed charge sites. At higher pH, the most significant adsorption reaction is the binding of $(UO_2)^{+2}$ to Al OH and $(UO_2)_3(OH)^{+5}$ to Si OH edge sites. Near saturation of Al₂OH sites by $(UO_2)^{+2}$, significant contribution of Si OH sites to uranyl adsorption was allowed Mckinley *et al.*, (1995).

Hennig *et al.*(2002) demonstrated that with increasing pH the uranyl unit becomes more hydrolyzed and forms oligomeric solution species. The thermodynamic calculations predict the formation of solid hydrated uranyl oxides at pH > 5.4. However, the formation of surface sorption complexes can be kinetically favored in comparison to hydrated uranyl precipitates.

Solid/liquid ratio:

The obtained data from studying the effect of solid/liquid ratio upon U adsorption by some clay samples are shown in Table (3). From the obtained results, it is clear that by increasing the solid/liquid ratio from 1:100 to 1: 2, the U adsorption efficiency decreased from 71.4 to 34.5% for Kalabsha kaolinite, from 62.5 to 53% for Abu Tartur bentonite and from 62.7 to 45% for El Hafafit vermiculite sample. This may be attributed to the well-known fact that at low solid/liquid ratio more surface area of the clay particles is available to the adsorbant solution. Thus, higher U adsorption efficiencies are predicted.

Electrolyte Background:

The effect of NaClO₄ concentration upon U adsorption was studied in the range of 0.001, 0.01 and 0.1M NaClO₄. The obtained results are shown in Table (4). From the obtained data, it is clear that Kalabsha kaolinite behaves differently than the other two sediments. In the former case, by increasing the NaClO₄ concentration from 0.001 to 0.1M, the uranium adsorption slightly decreased from 71.4% to 56.0%. This result is in harmony with that of Mckinley *et al.*, (1995). The decrease in U adsorption attributed to the competition of Na⁺ with U to be adsorbed on the fixed charge sites.

However, in case of Abu Tartur bentonite and El Hafafit vermiculite, the U adsorption slightly increased by the increase of NaClO₄ concentration from 0.001 to 0.1M. This may be attributed to the increase the edge sites for exchange over the fixed charge sites of the bentonite and the vermiculite samples. The clays with higher proportion of edge sites retained more uranium. And / or due to there was no conflicting between the sites for sodium and these for uranium adsorption.

Clay Pretreatment:

The data obtained from studying the effect of pretreating of used clay sediments by means of roasting at 1000°C for two hours, agitating with 50% HCl and 20% NaOH for two hours upon U adsorption are tabulated in Table (5). From these data, it is clear that, in case of Kalabsha kaolinite, the roasting pretreatment led to the increase of U adsorption from 71.4 to 91.0 %. While, the pretreatment by HCl and NaOH led to the decrease of U adsorption from 71.4% to 53.0 and 62.0%, respectively. The crystalline structure of kaolinite thermally transformed to amorphous oxides by temperature used. Additional Al-OH and Si-OH bonds formed also will act as cation exchange centers. Suraj *et al.* (1998) concluded the same trend when they trying to obtain amorphous derivatives oxides of kaolinite by thermal modification followed by acid activation, which improved the exchangeability properties of kaolinite.

In case of Abu Tartur bentonite, the pretreatment with 50% HCl improved the U adsorption from 62.57 % to 77.2 %. While, the pretreatment by roasting and with 20 % NaOH was decreased the U adsorption from 62.57 % to 48.00 and 56.00 % respectively. The transformation of bentonite to illite with roasting may be led to decrease CEC and may be decreased U adsorption. While increasing the adsorption efficiency by Hcl treatment refer to increasing the surface area of bentonite, Christidis *et al.*, (1997) reported that the acid activation with HCl of two bentonites from Greece resulted in 4-5-fold increase of the surface area of the raw materials, and thus increases their anion and cation exchange capacities. The same phenomenon was observed also by Barrios *et al.*, (1995) and Breen and Watson (1998).

In case of El Hafafit vermiculite, the pretreatment by neither roasting nor acidic and alkaline treatments did not improve the U adsorption. Thus, the pretreatment led to the decrease of U adsorption from 62.75% to 43.4%, 55.00% and 44.0%. These data are completely different from those obtained by Raiz *et al.*, (1997) and Kang *et al.*, (1998). The transformation of poorly crystalline vermiculite with the treatments used may be the reason.

Uranium Desorption:

The obtained data from performing the U desorption experiments are presented as cumulative curves of the released U percentage relative to the initial adsorbed amounts in Fig.(5). From these data, it is clear that: about 34.0,53.1 and 43.8% from the initial adsorbed U can be desorbed by H₂O leaching after four successive times from Kalabsha kaolinite, Abu Tartur bentonite and El Hafafit vermiculite, respectively. When applying 0.1M HCl as desorbing agent, the released U percentage was increased to reach 45.3, 82.8 and 76.0 % from the studied clay samples, respectively. In addition, the leached U percentage was further increased to reach 58.9 and 83.4% for kaolinite and bentonite samples, while decreased in vermiculite sample to 69.9% by performing the alkaline desorbing agent. These results showed that U is fairly binded to the Egyptian clay samples because four successive H₂O leachings did not desorb more than 50 % from the initial adsorbed U. In fact, this amount of U desorption by H₂O could be attributed to the capture of some U droplets in the clay samples. These droplets themselves are easily washable by water, as detected by I.R spectroscopy, which discussed after.

Comparing the U desorption from the loaded clay samples, it can be arranged generally in the order: Abu Tartur bentonite > El Hafafit vermiculite > Kalabsha kaolinite. By matching this arrangement with the calculated binding energy (b), one can notice that except bentonite there is positive correlation between them. The swelling structure of montmorillonite in water which was the main component in the bentonite sediment, fig.(3) in abdallah *et al.* (2007), may be the responsible the increasing the desorbed amount than expected from binding energy through weakens the bond via increasing the distance between u and clay mineral.

Infrared Spectroscopic Studies:

To monitor the changes occurred in the clay sediments after U adsorption and desorption by each desorbing agent the clays subjected to IR analysis. The obtained IR spectra represented in Figs. (6), while the additional reported vibrational frequencies obtained from the IR analysis tabulated in Table (6). Summarized data revealed the following:

Table 1: Initial and equilibrium U concentration and its adsorbed amount in the studied clay sediments

| Initial conc. (m mol/l) | Equilibrium conc. C (m mol/l) | | | Adsorbed amount X/M, (c mol/kg) | | | C/XM | | |
|----------------------------|----------------------------------|-------------|-------------|------------------------------------|-------------|-------------|-----------|-------------|-------------|
| | Kaolinite | Bentonite | El Hafafit | Kalabsha | Bentonite | El Hafafit | Kaolinite | Bentonite | El Hafafit |
| | Kalabsha | Abu Tarture | vermiculite | Kaolinite | Abu Tarture | vermiculite | Kalabsha | Abu Tarture | vermiculite |
| 0.074 | 0.007 | 0.011 | 0.018 | 0.66 | 0.63 | 0.56 | 0.011 | 0.017 | 0.032 |
| 0.148 | 0.022 | 0.016 | 0.037 | 1.26 | 1.32 | 1.11 | 0.017 | 0.012 | 0.037 |
| 0.222 | 0.023 | 0.037 | 0.059 | 1.99 | 1.85 | 1.63 | 0.011 | 0.020 | 0.036 |
| 0.370 | 0.040 | 0.090 | 0.088 | 3.30 | 2.80 | 2.82 | 0.012 | 0.032 | 0.031 |
| 0.518 | 0.122 | 0.153 | 0.146 | 3.96 | 3.65 | 3.72 | 0.030 | 0.041 | 0.039 |
| 0.740 | 0.212 | 0.177 | 0.175 | 5.28 | 5.63 | 6.65 | 0.040 | 0.031 | 0.030 |
| 1.11 | 0.392 | 0.350 | 0.416 | 7.18 | 7.60 | 6.94 | 0.054 | 0.046 | 0.059 |
| 1.48 | 0.572 | 0.480 | 0.700 | 9.08 | 10.00 | 7.80 | 0.062 | 0.048 | 0.089 |

Table 2: The constants of Langmuir equations and R² of U adsorption by studied clay sediments.

| Sample | Adsorption Maxima (B) | Binding energy (b) | Equation | R ² |
|-------------|-----------------------|--------------------|----------------------|----------------|
| Kaolinite | 10.52 | 7.3 | Y = 0.0954 X +0.0131 | 0.94 |
| Bentonite | 14.08 | 4.0 | Y = 0.0711 X +0.0192 | 0.88 |
| Vermiculite | 11.90 | 3.0 | Y = 0.0840 X +0.0264 | 0.93 |

Table 3: Effect of solid/liquid ratio upon U adsorption efficiency (%)

| S/L | Kaolinite Kalabsha | Bentonite Abu Tartur | Vermiculite El Hafafit |
|----------|--------------------|----------------------|------------------------|
| 1 : 100 | 71.4 | 62.5 | 62.7 |
| 1 : 40 | 44.1 | 60.1 | 57.6 |
| 1 : 20 | 41.5 | 59.2 | 52.0 |
| 1 : 13.5 | 39.4 | 58.0 | 47.0 |
| 1 : 5 | 38.4 | 55.0 | 46.0 |
| 1 : 2 | 34.5 | 53.0 | 45.0 |

Table 4: Effect of electrolyte concentration on U adsorption efficiency (%)

| Electrolyte | Kaolinite Kalabsha | Abu Tartur | Bentonite | Vermiculite El-Hafafit |
|-------------|--------------------|------------|-----------|------------------------|
| 0 | 71.4 | 62.57 | | 62.75 |
| 0.001 | 70 | 87 | | 82.5 |
| 0.01 | 65 | 90.2 | | 92.5 |
| 0.1 | 56 | 93.5 | | 93 |

Table 5: Effect of clay pretreatment on U adsorption efficiency (%)

| Treatment | Kalabsha kaolinite | Abu Tartur bentonite | El hafafit vermiculite |
|-------------------|--------------------|----------------------|------------------------|
| Without treatment | 71.4 | 62.57 | 62.75 |
| Roasting | 91.00 | 48.00 | 43.4 |
| HCl | 53.00 | 77.20 | 55.00 |
| NaOH | 62.00 | 56.00 | 44.00 |

Table 6: IR spectra interpretation of clay sediments used after U adsorption and desorption experiments.

| Adsorption | Kalasha Kaolinite | | | Abu Tartur bentonite | | | El Hafafit vermiculite | | | | |
|------------|-------------------|--------|--------|----------------------|--------|--------|------------------------|--------|--------|--------|--------|
| | Desorption | | | Adsorption | | | Desorption | | | | |
| | H ₂ O | HCl | NaOH | H ₂ O | HCl | NaOH | H ₂ O | HCl | NaOH | | |
| -- | -- | 3906.2 | -- | -- | -- | 3906.2 | -- | 3904.2 | 3905.2 | -- | |
| -- | -- | -- | -- | -- | -- | 3858.0 | -- | 3858.2 | 3858.7 | -- | |
| -- | -- | -- | -- | -- | -- | 3838.0 | -- | 3838.5 | 3839.0 | -- | |
| -- | -- | -- | -- | -- | -- | -- | -- | 3822.8 | 3822.5 | -- | |
| -- | -- | -- | -- | -- | -- | 3802.9 | 3802.9 | 3803.1 | 3803.5 | -- | |
| -- | -- | -- | -- | -- | -- | -- | -- | -- | 3752.5 | -- | |
| -- | -- | -- | -- | 3695.7 | -- | -- | -- | -- | -- | -- | |
| -- | -- | -- | -- | 3651.4 | -- | -- | -- | -- | -- | -- | |
| * | -- | -- | -- | 2927.4 | 2928.2 | -- | -- | -- | -- | 2927.0 | |
| -- | -- | -- | -- | 2856.5 | -- | -- | -- | -- | -- | -- | |
| -- | -- | -- | -- | 2340.7 | 2340.8 | 2340.7 | 2340.4 | 2340.3 | 2340.6 | 2340.6 | 2340.7 |
| 1828.4 | 1829.5 | 1829.5 | 1829.1 | -- | -- | -- | -- | -- | -- | -- | -- |
| -- | -- | -- | -- | -- | -- | -- | 1562.7 | -- | 1563.2 | 1562.8 | -- |
| -- | -- | -- | -- | -- | -- | -- | -- | 1543.5 | 1543.6 | 1543.4 | -- |
| -- | -- | -- | -- | -- | -- | -- | -- | 1458.6 | -- | -- | -- |
| -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | 1422.7 | -- |
| * | 1114.2 | -- | 1114.9 | -- | -- | -- | -- | -- | -- | -- | -- |
| -- | -- | -- | -- | -- | 1028.7 | 1031.3 | 1032.1 | -- | -- | -- | -- |
| * | 1007.6 | -- | 1007.7 | 1008.1 | -- | -- | -- | -- | -- | -- | -- |

Table 6: Continue

| | | | | | | | | | | |
|----|----|----|----|-------|-------|-------|-------|-------|-------|-------|
| -- | -- | -- | -- | -- | -- | -- | -- | -- | 967.2 | -- |
| -- | -- | -- | -- | -- | 915.3 | -- | 915.5 | -- | -- | -- |
| * | -- | -- | -- | -- | 797.5 | 792.1 | 797.3 | -- | -- | 796.8 |
| -- | -- | -- | -- | 754.7 | -- | -- | -- | 755.4 | -- | 758.6 |
| * | -- | -- | -- | 689.2 | 693.3 | 692.8 | 693.6 | 685.6 | -- | 690.1 |
| -- | -- | -- | -- | -- | -- | -- | -- | -- | 677.3 | -- |
| -- | -- | -- | -- | 537.4 | -- | -- | -- | -- | -- | 531.6 |
| * | -- | -- | -- | -- | 522.3 | 526.4 | 524.6 | -- | -- | -- |
| * | -- | -- | -- | -- | 425.1 | 427.4 | 426.0 | -- | -- | -- |

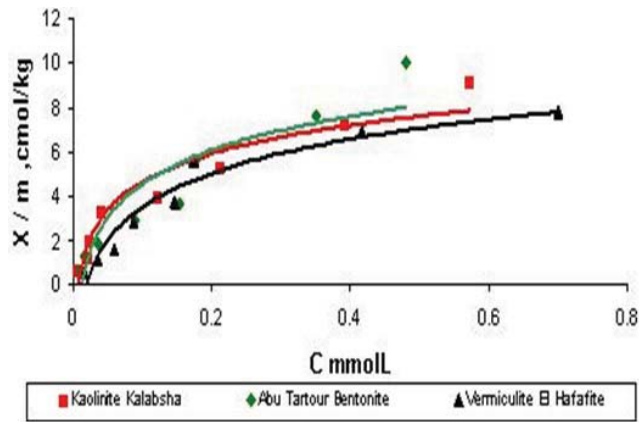


Fig. 1: Adsorbed amount of U on different clay sediments

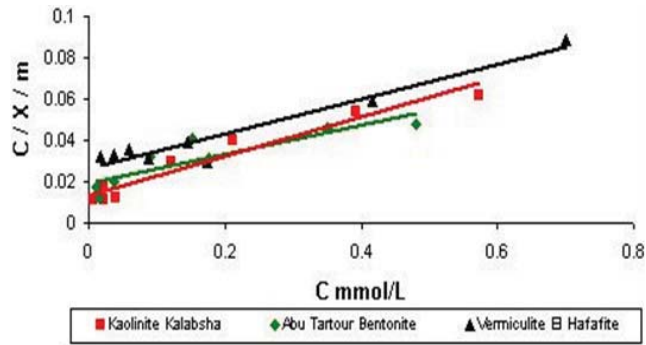


Fig. 2: Langmuir adsorption isotherm of U on different clay sediments

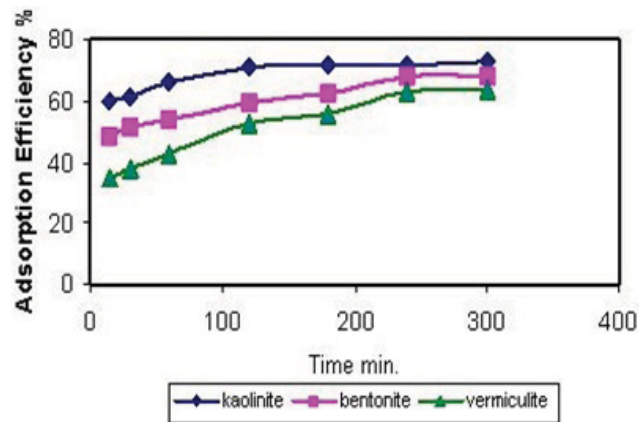


Fig. 3: Effect of equilibrium time on U adsorption

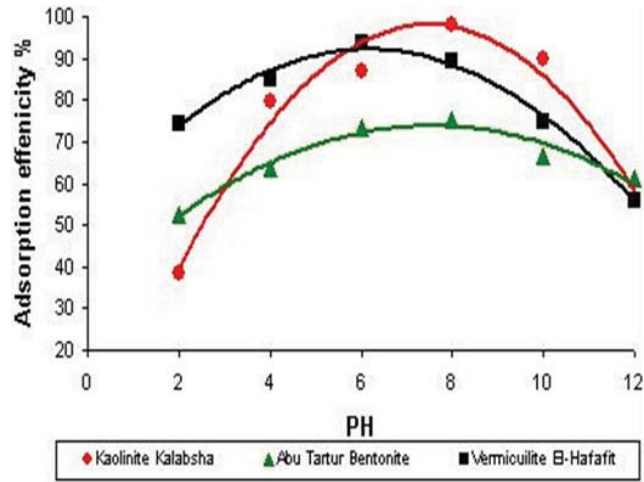


Fig. 4: Effect on pH on U adsorption

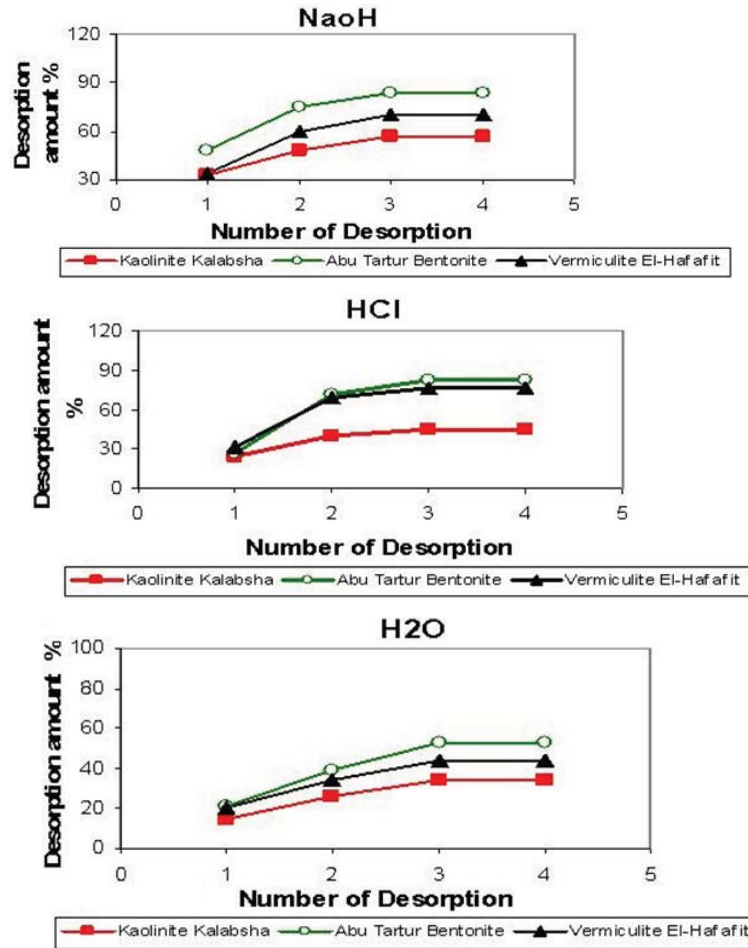


Fig. 5: Cumulative curves of U desorbed by different desorping agents

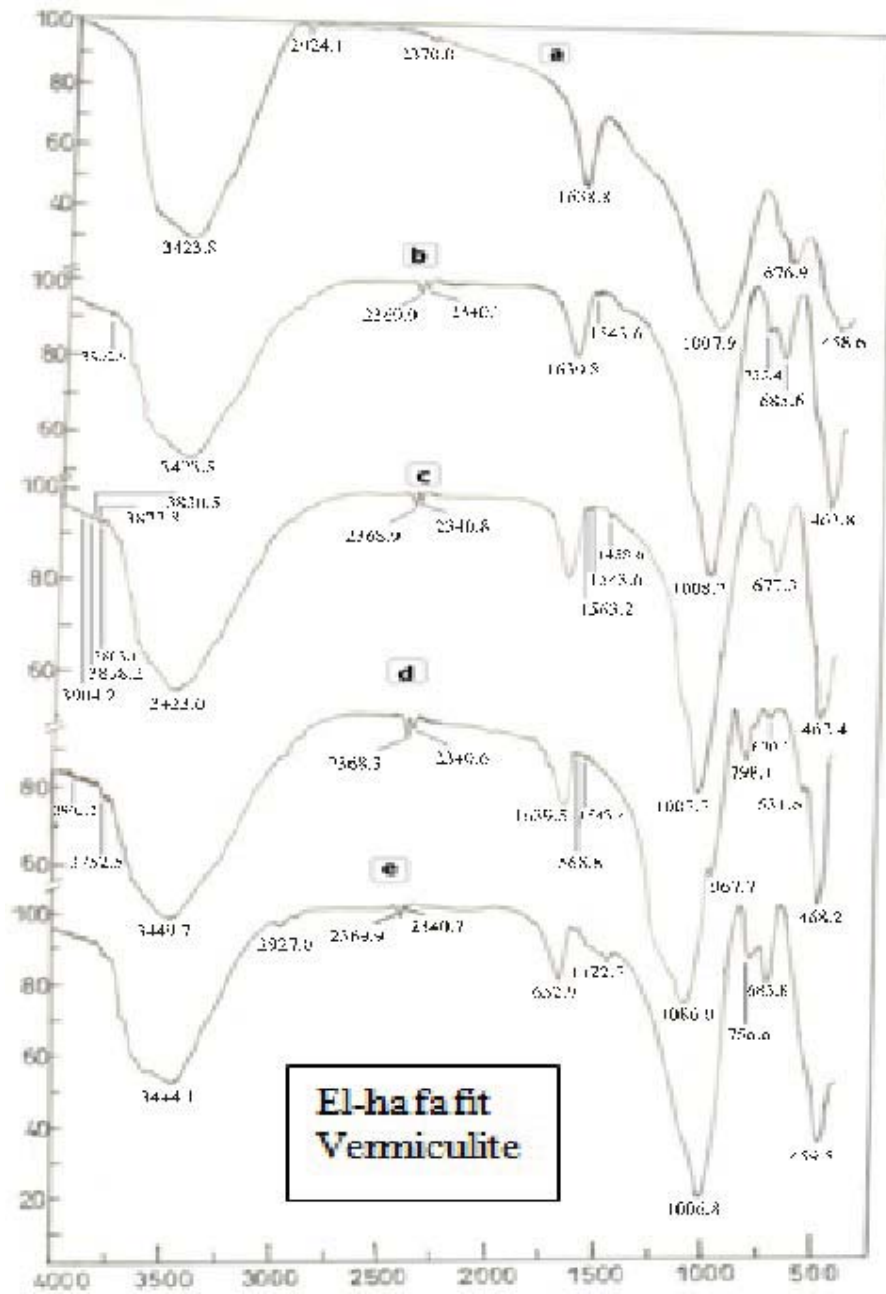


Fig. 6: (a)

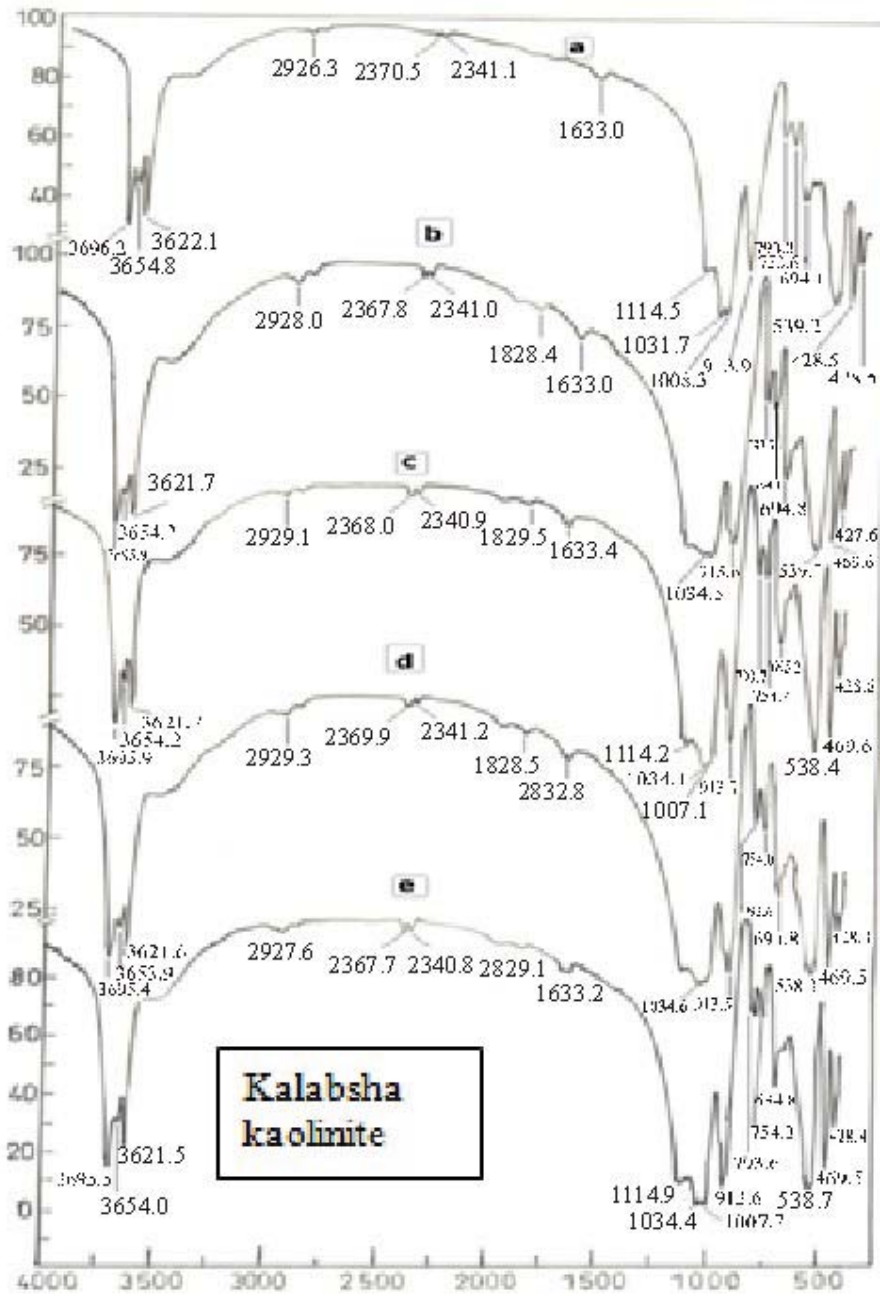


Fig. 6: (b)

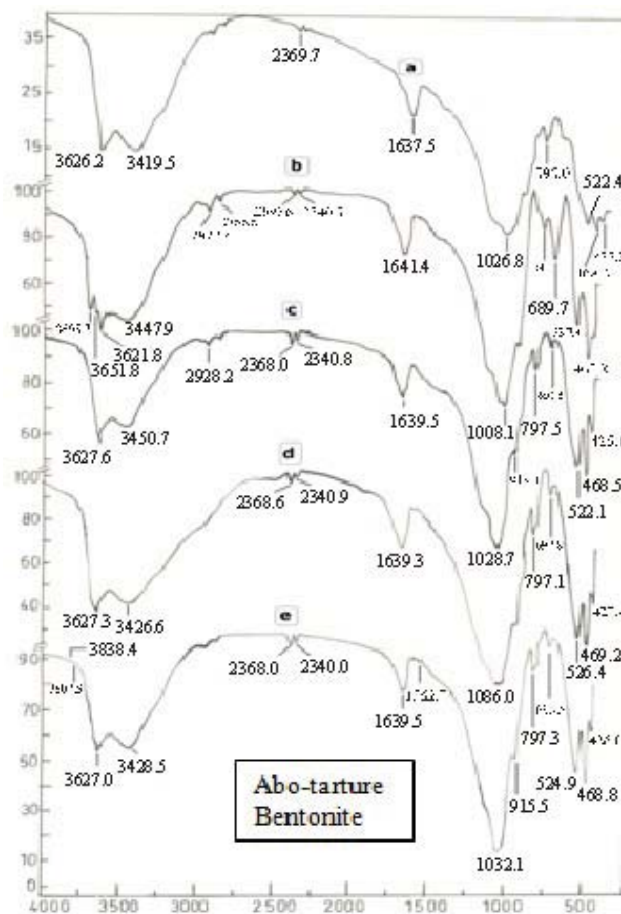


Fig. 6: (c)

Fig. 6: I.R spectra of U sorption by studied clay sediments : (a) before adsorption (b) after adsorption (c) after desorption by H₂O (d) after desorption by HCl (e) after desorption by NaOH

Kalabsha Kaolinite:

After uranium adsorption by Kalabsha kaolinite sample, it exhibited only one additional vibrational frequency at 1828.4 cm⁻¹. This exhibition may be due to the clay hydrolysis by the aqueous U solution that caused H₂O stretching and presence of O-H group.

After desorbing the Kalabsha kaolinite sample by water, this vibration frequency still existed. However, two additional recorded vibration frequencies at 1114.2 and 1007.6 cm⁻¹ have appeared. This appearance may be interpreted as to fundamental vibration frequencies of the Kalabsha kaolinite regenerated either by water washing or to uranyl ion adsorption. It is worthy to mention that Farmer, (1974) reported that the vibration frequency for the uranyl ion in the autunite [Ca (UO₂)₂ (PO₄)₂ · 8-12 H₂O], uranocircite [B(UO₂)₂ (PO₄)₂·2-8 H₂O], torbernite [Cu (UO₂)₂ ·8-12 H₂O], meta-zeunerite [Cu (UO₂)₂ (AsO₄)₂ and carnotite [K₂(UO₂)₂ (VO₄)₂ ·3 H₂O] occurs in the same vibration region, i.e. at (1123, 1023 cm⁻¹), (1115, 1023 cm⁻¹), (1115, 1013 cm⁻¹), (1028, 1505 cm⁻¹) and (1030, 988 cm⁻¹), respectively.

When desorbing Kalabsha kaolinite sample by 0.1 M HCl the vibration frequency at 1828.5 cm⁻¹ still reported, however, the two-vibration frequencies at 1114.2 and 1007.6 cm⁻¹ disappeared due to U leaching from the kaolinite. On the other hand, when performing the desorption experiment by 0.1 M NaOH, the vibration frequency at 1829.1 cm⁻¹ continued to exist. Also, the two other vibration frequencies at 1114.2 and 1007.6 cm⁻¹ reappeared again may be due to the re-precipitation of U in-between the clay mineral layers after its desorption by Na OH.

Abu Tartur Bentonite:

The uranium adsorption by Abu Tartur bentonite was demonstrated by nine additional vibration frequencies at 3695.7, 3651.4, 2927.4, 2856.5, 2340.7, 1008.1, 754.7, 689.2 and 537.4 cm^{-1} . From the first to the third vibration frequencies as well as the fifth one are fundamental frequencies characterizing the kaolinite calys. This may refer to the kaolinitic content of the bentonite sample. While, the vibration frequency at 2856.5 cm^{-1} can be interpreted as due to the clay hydrolysis by the aqueous U solution (H_2O stretching and O-H group presence). The vibration frequency at 1008.1 cm^{-1} may be interpreted as due to the adsorption of uranyl group. The last three vibration frequencies at 754.7, 689.2 and 537.4 cm^{-1} are also attributed to uranium adsorption as stretching modes. Farmer (1974) supported the obtained results and added that a band at 520 cm^{-1} assigned to a stretching mode involving the U-O group, moreover, the vibration frequencies at 545 and 550 cm^{-1} for the uranium mineral related to autunite, uranocircite and torbernite.

After conducting the desorption experiment by water the vibration frequencies at 3695.7, 3651.4, 2856.5 and 1008.1 cm^{-1} have disappeared. However, those ones at 2928.2 and 2340 cm^{-1} still existed. Considering the three vibrational frequencies, which attributed to the adsorbed uranium, two of them at 754.7 and 537.4 cm^{-1} have disappeared probably because they are easily washable by tap water. The third vibration frequency at 693.3 cm^{-1} is still present. Five additional vibration frequencies were recorded at 1028.7, 915.3, 797.5, 522.1 and 425.1 cm^{-1} . Some of these frequencies are originally present in the bentonite but became more sharp after desorption by water. The other mentioned frequencies may be attributed to U adsorption as has been mentioned before, but became more activated after water washing or else may be attributed to the fundamental vibration frequencies of the kaolinite content in the bentonitic sample.

After performing the desorption experiment by 0.1 M HCl bentonite sample, two vibration frequencies at 2928.2 and 915.3 cm^{-1} have disappeared. However, six vibrational frequencies at 2340.7, 1031.3, 792.1, 692.8, 526.4 and 427.4 cm^{-1} still existed. This means that at least some of the adsorbed U can be leached by 0.1 M HCl, while the rest resist leaching by acidic desorbate.

When applying 0.1 M NaOH as desorbing agent for the adsorbed U the six vibration frequencies, at 2340.4, 1032.1, 797.3, 693.5, 524.9 and 426.0 cm^{-1} are still existed. Those related to U adsorption that still resists leaching by Na OH or else re-precipitated under high pH values. The evidence for the latter assumption is the re-appearance of the vibration frequency at 915.3 cm^{-1} . Five vibration frequencies are newly appeared at 3904.7, 3858.0, 3838.0, 3802.9 and 1562.7 cm^{-1} . These interpreted as due to water held in the structure as OH group. The adsorption of the IR spectra may be due to the stretching occurred at 3904.7 cm^{-1} and overtones and combination seen at 3858.0, 3838.0, 3802.9 and 1562.7 cm^{-1} .

El Hafafit Vermiculite:

The U adsorption upon El Hafafit vermiculite sample has demonstrated in the appearance of five additional recorded vibration frequencies at 3802.9, 2340.4, 1543.5, 755.4 and 685.6 cm^{-1} . The first three vibration frequencies could attributed to the water held in the structure as OH group and the adsorption due to their stretching occurred at 3802.9, 2340.4 and 1543.5 cm^{-1} . Indeed, the water interred the system when treating the vermiculite samples by the U adsorbing solution. On the other hand, the other two vibration frequencies at 755.4 and 686 cm^{-1} could related to the fixation of the uranyl group upon the vermiculite sample. Farmer (1974) has assigned the stretching modes for the bands at 745 and 705 cm^{-1} and that at 280 cm^{-1} to the bending modes of the UO_2 group. In addition, the same author has given the frequencies of the uranyl groups at 665 cm^{-1} (stretching) and 265 cm^{-1} (bending).

When performing the desorbing experiment by tap water upon the adsorbed U on El Hafafit vermiculite, the above mentioned vibration frequencies at 3803.1, 2340.6 and 1543.6 cm^{-1} are still existed. However, those at 755.4 and 685.6 cm^{-1} have disappeared may be because the detected frequencies are due the capture of some U drops in the clay particles which are easily washable by tap water. Five additional vibration frequencies have newly recorded at 3904.2, 3858.2, 3838.0, 3822.8 and 1563.2 cm^{-1} . Their presence may attribute to the water held in the structure of the clay mineral as OH group. Accordingly, the adsorption of the IR spectra could be due to the stretching occurred at 3904.7 cm^{-1} and overtones and combination seen at 3858.2, 3838.5, 3822.8 and 1563.2 cm^{-1} . Moreover, a new vibration frequency appears at 1458.6 cm^{-1} , which possibly due to traces of carbonate content of additional vibration frequency at 677.3 cm^{-1} . This is a very common impurity in KBr. After applying the desorption experiment by 0.1 M HCl upon the loaded U of El Hafafit vermiculite, all the vibration frequencies attributed to water held still present in addition to a new one at 3752.5 cm^{-1} . It is noticed that the vibration frequency at 1458.6 cm^{-1} has disappeared, may be due to the dissolution of the carbonate traces by HCl. Four new vibration frequencies at 967.7, 796.8, 690.1 and 531.6 cm^{-1} have appeared. These frequencies may be due to the U adsorption (Farmer, 1974).

Finally, when trying the desorption of the loaded U of El Hafafit vermiculite by 0.1 M Na OH, eight vibration frequencies at 3905.2, 3858.7, 3839.0, 3822.5, 3803.5, 3752.5, 1562.8 and 1543.4, cm^{-1} , in addition to three vibration frequencies at 967.7, 796.8 and 531.6 cm^{-1} have disappeared. This may be attributed to the returning of the vermiculite sample to its nature. Two vibration frequencies still existed at 2340.7 and 685.8 cm^{-1} . Three frequencies have been newly existed at 2927.0, 1422.7 and 758.6 cm^{-1} . The first frequency is actually characterize El Hafafit vermiculite before performing U adsorption and desorption tests. While, the second frequency may be attributed to the presence of carbonate impurity as has been mentioned before. The last two frequencies can attribute to the resistant adsorbed U to leach with Na OH, or else to the newly precipitated U by the alkaline agent.

Conclusions:

Uranium can be sorbed upon Kalabsha kaolinite, Abu Tartur bentonite and El-Hafafit vermiculite. The amount of adsorbed uranium increases with the increase of U concentration, pH and equilibration time till 3 hrs. It decreases with the increase of the solid/liquid ratio. Pretreatment of the clay sediments by roasting, HCl and NaOH proved to increase the U adsorption efficiency. Release of U from the loaded clay sediments was possible to different extents depending upon clay type and desorbing agent. The IR analyses proved that considerable mineralogical changes occurred after U adsorption and desorption. This study may contribute to U recovery from clay sediments. In addition, the U desorption data would be useful in improving the uranium extraction technology. The study also proved that the clay sediments could be utilized as suitable geological barrier for immobilizing elements involved in the nuclear industry waste disposal.

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