



Evaluation Study for Uranium Adsorption from Gattar Pilot Plant Pregnant Solution by Egyptian Bentonite Sediments

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Bentonite deposits have a great potential for using an engineering barrier in the multicarrier system of deep geological repository. In this paper, Egyptian clay sediments of bentonite collected from El Sahel EL Shamally (North Coast-H) West Alexandria, Egypt. Firstly, complete characterizations of the bentonite clay sediments such as complete chemical analysis of major oxides and trace elements, XRD and IR spectroscopy were performed. The bentonite clay sediment adsorption factors for anionic uranium species were also investigated. This included the ratio of the clay sediment to the pregnant uranium solution (S/L ratio), the uranium pregnant solution initial concentrations and its pH and the agitation time ranging from 30 to 240 min. The uranium adsorption optimum conditions by bentonite sediments are as follow: S/l 1:2, pH=6, agitation time 120min., temperature 30 °C and uranium concentration 70 ppm giving about 70% adsorption efficiency. On the other hand, the uranium desorption efficiency percent obtained was 78% using 1M HCl for 3 cycles and 69% using 1 M NaCl for 3 cycle.

Keywords: Clay sediments, Egyptian bentonite, Uranium, pregnant solution

Introduction

UO_2^{+2} ions represent the uranium (VI) state and are known to form compounds such as uranyl carbonate, uranyl chloride and uranyl sulfate. Several methods are available for removing uranium from aqueous solution, such as chemical precipitation, reverse osmosis, solvent extraction, micelles ultrafiltration, and adsorption. Amongst these methods, adsorption is an attractive method due to its high efficiency, ease of handling, and availability of different adsorbents. Various kinds of new adsorbents for removing and recovering uranium have been reported among which natural clays and their composites are considered as particularly effective, of low-cost, and of chemical stability. Bentonite is a well-defined naturally occurring 2:1 aluminum silicate mineral consisting of one alumina octahedral layer sandwiched between two silica tetrahedral layers [1].

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. 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 desirability 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 minerals content affects uranium leaching efficiency. Ores having higher clay minerals content are lower in uranium extraction efficiency because they 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 absorbability and immobilization and in the same time which one have high affinity with uranium to prevent its losses. 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. This is because clay minerals are mostly present in the clayey or silty size and hence block the filter pores. Determination of uranium absorbability 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 [2].

Due to the increasing concern to guarantee a safe environment by avoiding the environmental pollution problems, it is very important to achieve an effective exploration of geological barriers for suitable disposal sites, especially in radionuclide waste disposal management. Thus, clay sediments represent very good adsorbents having both geological and technical convenience to be landfill barriers. These sediments account an excellent natural barrier due to their ability to close fissures and cracks, their chemical reactivity to immobilize important contaminants like heavy metals and nuclear elements. This target is completely correct with the increasing applications of heap leaching technology in the extractive metallurgy of elements.

Mahdy (2004), [3] Studied the amount of adsorbed uranium on kaolinite and bentonite and vermiculite sediments from Kalabsha (Aswan), Abu Tartur (Western Desert) and El Hafafite (Eastern Desert) localities. The author proved that the U adsorption increased by

increasing the initial concentration of such elements, and proved that U adsorptions is basically depends upon the clay type and the initial concentration of the adsorbed elements. The optimum adsorption conditions in this study were: solid/liquid ratio 1:100, pH 6-8, while adsorption time ranged from 3-4 hours giving U adsorption maxima 10.52, 14.08 and 11.90 respectively. The obtained adsorption data were found to fit Langmuir isotherm. The aim of the present work is to evaluate the potentiality of Egyptian bentonite clay sediments for uranium adsorption and desorption and to determine their optimum conditions

Experimental

Material and methods

Mechanical and chemical analysis including major and trace elements concentration of a representative technological sample (natural bentonite) collected from EL Sahel El Shamally (North Coast –H) West Alexandria, Egypt is in Tables(1&2), according to Black *et al.*, (1985) [4], Wilson, (2004) [5], While uranium solution was kindly received from Gattar pilot plant, Egyptian Nuclear Materials Authority and its complete chemical analysis including major and trace elements was represented in Table(3).

For mineralogical investigation of the study sample, thin slurry of the separated clays placed on a glass slide was air dried at room temperature and subjected to XRD analysis. In the present study, Philips XRD unit (PW3710) with a generator model PW 1830 fitted with a scintillation counter model PW 3020 was used. The XRD tube used was a Cu target model PW22 33 attached with a Ni –filter. The tube operated at 40 kV and mA. XRD analysis carried out on their clay fraction (<2 microns). The identification of the clay minerals was achieved through the XRD pattern using the American Standards and Testing Materials (ASTM) Cards, Index to XRD Powdered Data Files. Scanning Electron Microscope was also used with magnification ranges from 100 x to 1000x in the ESEM mode. The operating conditions were as follow: resolution equals to 3.5 nm at 30 KV, 25 nm at 1 KV BSE equals 10.0.

In the Infrared analysis, study samples were prepared as pellets using KBr binding material and subjected to a Bruker vector spectrophotometer

model FT-IR-22 Germany, in region of 4000-250 cm^{-1} was used according to Mahdy(2004).[3].

Uranium analysis

Uranium was determined in the pregnant leach solution, the crude uranium concentrate and in the adsorption experiments using the oxidimetric titration procedure with a standard solution of NH_4VO_3 till the appearance of a purplish red color represents the end point [6]. Uranium concentration in the working sample solution was calculated according to the following equation:

$$U \text{ (g/L)} = T.V1.1000/V$$

T: titration intensity of NH_4VO_3

V1: consumed NH_4VO_3 (ml)

V: Volume of sample (ml)

Uranium adsorption process

Bentonite technological sample prepared for adsorption experiments which crashed and sieved it (2mm), after that some experiments for uranium adsorption were carried out where certain weights of the prepared bentonite sample were agitated with certain volumes of uranium solution. Through these experiments, most factors affecting the adsorption efficiency percent were studied such as (solid/liquid ratio, contact time, pH, temperature and concentration). All uranium adsorption experiments were carried out using 5 g of the bentonite sample by mixing with 25 mL of uranium solution and stirring for 2 h using a mechanical shaker at 175 rpm in the room temperature. After filtration and analysis of uranium adsorption efficiency was determined.

Uranium desorption process

For this process 5g portions of the study sample loaded with uranium were equilibrated with 10 mL aliquots of HCl and NaCl at different concentrations (0.25, 0.5 and 1M). The suspended materials were shaken for 2 h at room temperature. After filtration and analysis, uranium desorption efficiency was determined.

Results and Discussion

Mechanical and chemical characteristics

Table (1) represents the mechanical analysis while Table (2a, b) shows the chemical characteristics of the studied bentonite sediments and chemical characteristics of the pregnant solution.

Table (1): Physical and Chemical characteristics of the study EL Sahel EL Shamally (North Coast H) sediments, Mahdy (2004).[3]

| Sample Textural | EC | AEC** | CEC* | pH* |
|-----------------|------|-------|-------|-----|
| Clay | 2.85 | 8.53 | 86.67 | 6.7 |

♦ Soil extract 1:5 **AEC for kaolinite, montmorillonite = 7-20, 20-30 Meq/100g respectively

* CEC for kaolinite, montmorillonite = 3-15, 60-150 Meq/100g respectively

From this table it could be concluded that:

(1) The textural classes of bentonite sediment belong to clay

(2) Chemical analyses of the extract (1:5) indicated that the study sediments are around neutral, non-saline and the values of CEC, AEC are within the range of published data [5].

On the other hand, the mineralogical analysis of EL Sahel EL Shamally (H) bentonite sediments shown in XRD pattern, Figure (1) and SEM- EDAX chart Figure(2) reveals that bentonite sample is composed of 48% Quartz, 11% kaolinite and 41% Montmorillonite.

Table (2a): Chemical composition EL Sahel EL Shamally (H) sediments bentonite sample

| Major Oxides (%) | | Trace Elements (ppm) | |
|--------------------------------|--------|-----------------------------|------|
| SiO ₂ | 51.2 | V | 268 |
| Al ₂ O ₃ | 17.30 | Cr | 115 |
| TiO ₂ | 0.93 | Co | 31 |
| P ₂ O ₅ | 0.55 | Ni | 48 |
| FeO | 0.12 | Cu | 33 |
| Fe ₂ O ₃ | 4.74 | Zn | 63 |
| Na ₂ O | 2.70 | Ga | 33 |
| K ₂ O | 0.67 | Rb | 111 |
| CaO | 1.40 | Sr | 254 |
| MgO | 1.20 | Y | 37 |
| L.O.I | 18.64 | Zr | 295 |
| Total | 100.45 | Nb | 12 |
| | | Ba | 3483 |

Table (2b): Chemical composition of Gattar pilot plant Pregnant sulfate solution

| Elements | Conc. ppm | Elements | Conc. ppm |
|-----------------|------------------|-----------------|------------------|
| Si | 67 | Gd | 16 |
| Al | 19 | Ba | 2 |
| P | 89 | Sr | 16 |
| Fe | 2311 | Th | 59 |
| Ca | 139 | U | 180 |
| Mg | 234 | V | 8.5 |
| Na | 165 | As | 44 |
| K | 139 | Zr | 1 |
| Cu | 20 | Y | 21 |
| Mn | 408 | La | 15 |
| Zn | 129 | Ce | 87 |
| Pb | 4 | Pr | 16 |
| Mo | 15 | Nd | 48 |
| Co | 2 | Sm | 16 |
| Cr | 89 | Tb | 33 |

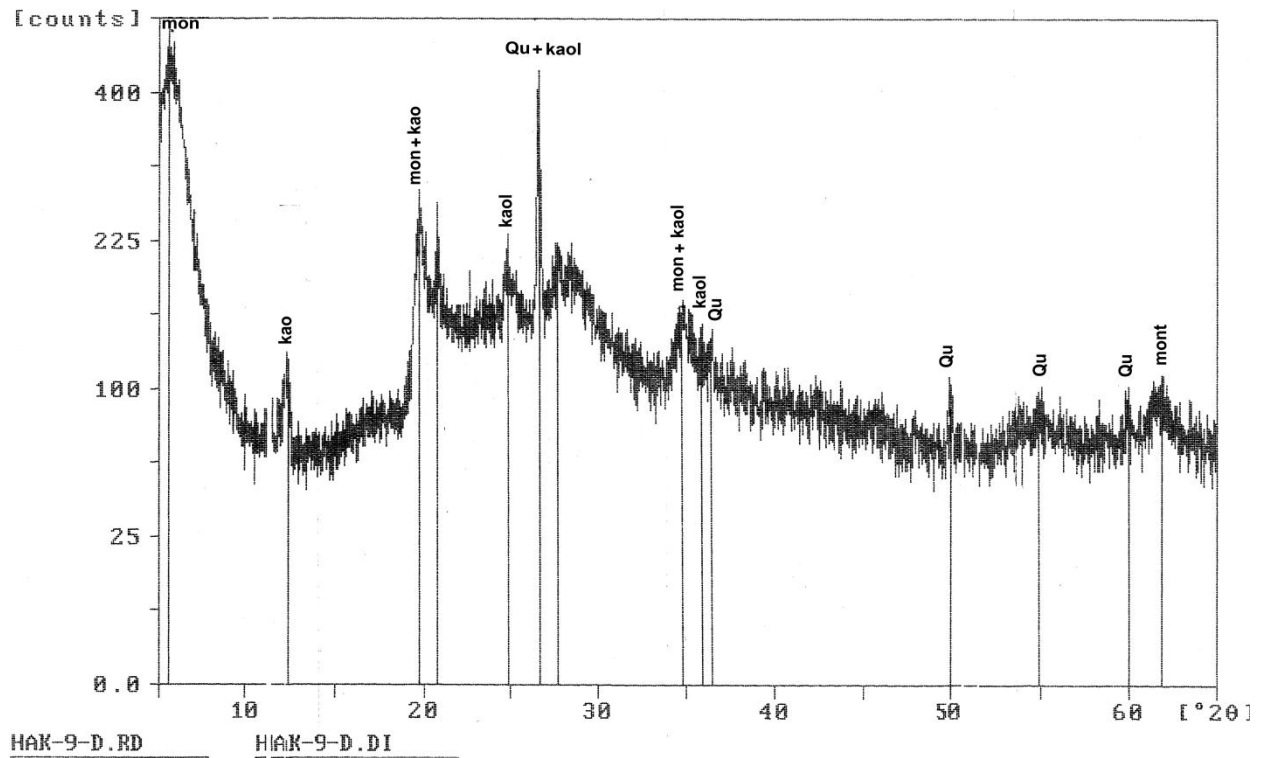


Figure (1): XRD pattern of El Sahel el Shamally (H) bentonite sediments

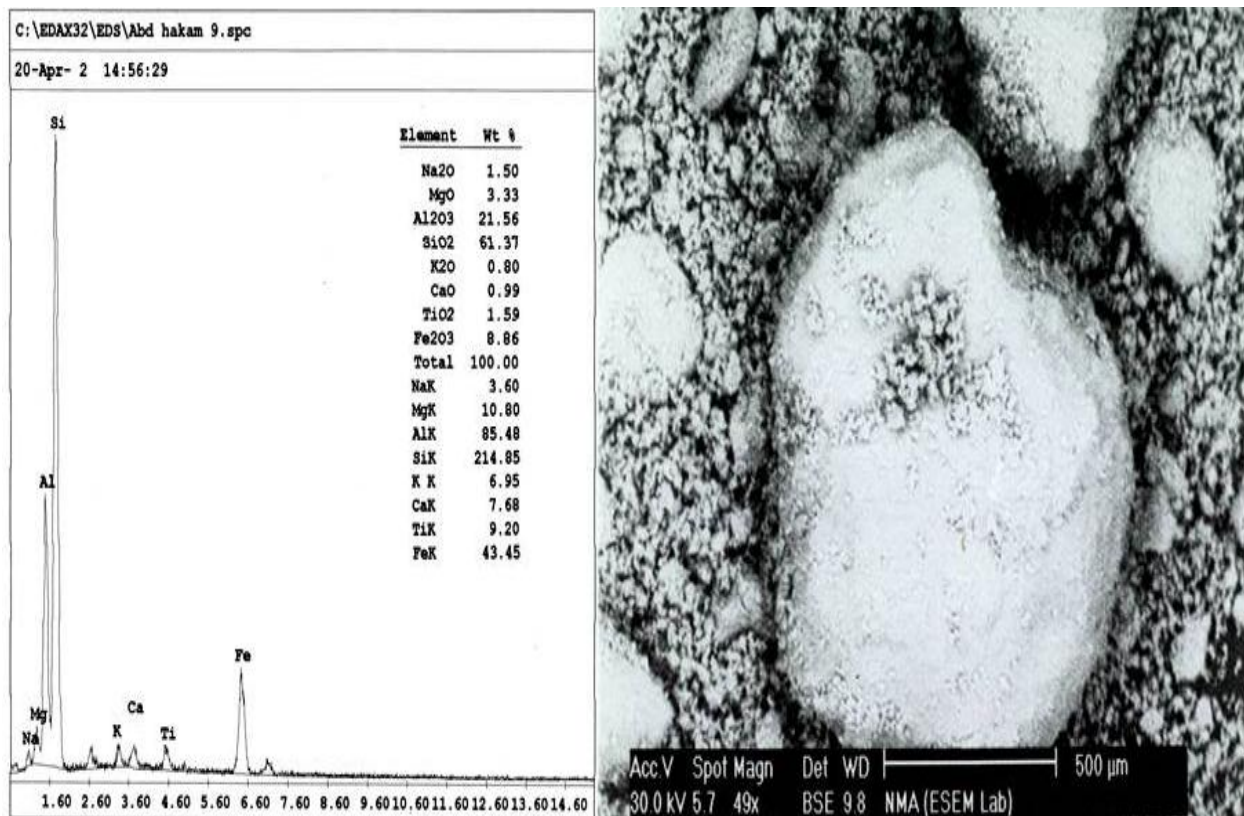


Figure (2): SEM- EDAX of El Sahel El Shamally bentonite sediments

Uranium adsorption process

The following effective parameters were studied for achieving the maximum U adsorption efficiency using natural bentonite

Effect of solid/liquid ratio

The effect of soiled/liquid ratio (bentonite dose) upon U adsorption using EL Sahel-EL Shamally H bentonite sediments is shown in Figure (3) which indicates that increasing the solid/liquid ratio from 1:1 to 1:2 led to increase uranium adsorption efficiency up to 55.1%. Further increasing

Of S:L ratio to 1:3, 1:5 and 1:10 has an opposite effect where uranium adsorption efficiency decreased down to 21%. The other experimental conditions were fixed at uranium concentration 180 ppm, at room temperature; 120min contact time and initial pH. This may be due to increasing the adsorbent amount which may cause aggregation of adsorbent. Consequently, the adsorptive capacity of the available adsorbent was not fully employed at a higher adsorbent amount.

Effect of agitation time

This effect was already studied in the time range from 30 to 240 min where the other experimental conditions were fixed at S/L ratio of 1:2, uranium concentration of 180 ppm at room temperature and the initial solution pH value. From the obtained data in Figure (4), it can be noticed that

the uranium adsorption efficiency increased gradually by increasing the stirring time from 30 to 120 min and then gradually decreased down to the minimum value at 240min stirring time.

Effect of pH value on uranium adsorption

The effect of pH upon uranium adsorption on EL Sahel – El Shamally (H) bentonite was studied at different pH values ranging from 1 to 8 of pregnant solution. The other experimental conditions were fixed at the S/L ratio of 1:2, the uranium concentration of 180 ppm at room temperature and the contact time 120 min. Figure (5) reveals that, uranium adsorption depends mainly on the acidity of the sulfate solution (pH value). Where at low $\text{pH} \leq 4.2$, the number of H_3O^+ ions exceeds that of the UO_2^{2+} several times and the surface is most likely covered with H_3O^+ ions, reducing the number of binding sites for the adsorption of UO_2^{2+} . At a pH value greater than 4.2, more H_3O^+ ions leave the clay mineral surface making the sites available to the cation exchange with the UO_2^{2+} ions and hydrolysis precipitation starts due to the formation of complexes in aqueous solution, i.e., $\text{UO}_2(\text{OH})^+$, $(\text{UO}_2)_2(\text{OH})_2^{2+}$, $(\text{UO}_2)_3(\text{OH})_5^{3+}$, $(\text{UO}_2)(\text{OH})_2$, which increase uranium (VI) adsorption [7]. But when applied at the real pregnant sample the authors applied the pH of 4 due prevention of uranium precipitation.

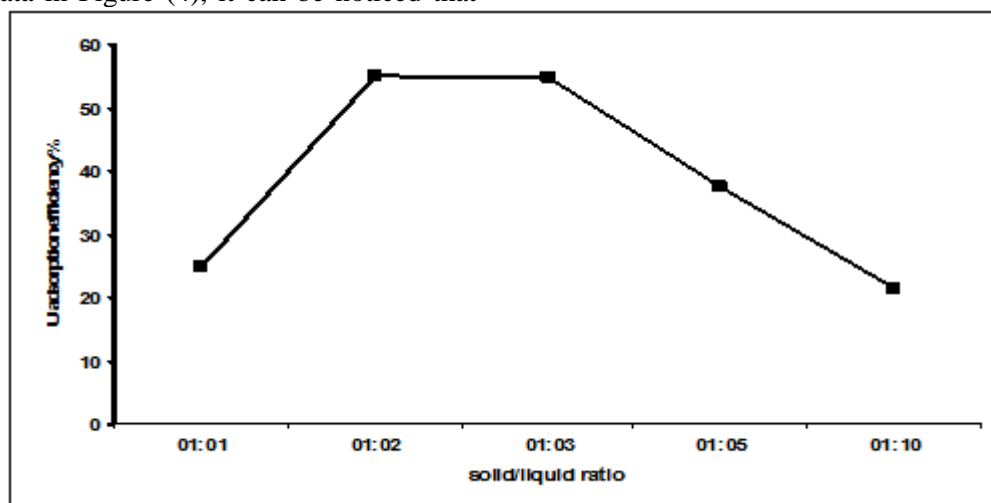


Figure (3): Effect of solid/liquid ratio upon U adsorption by bentonite sediments

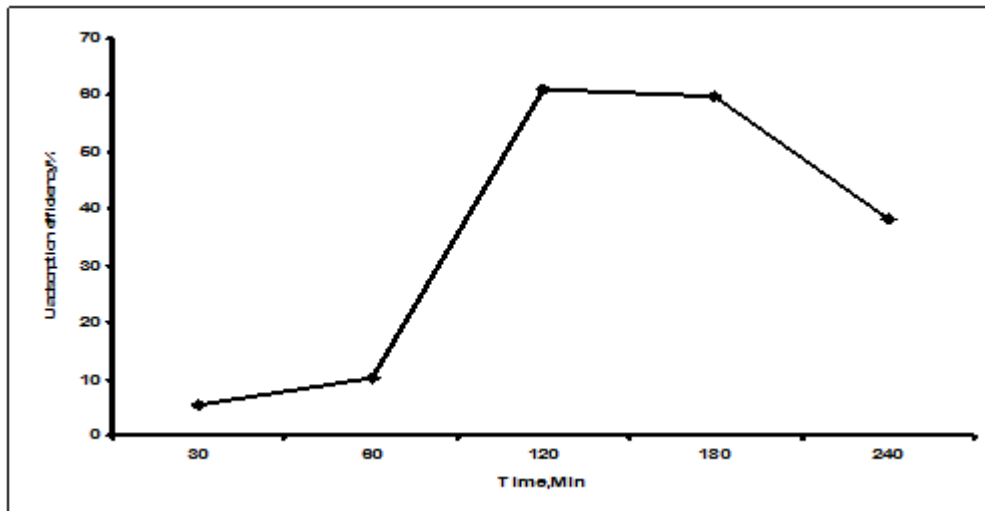


Figure (4): Effect of agitation time upon U adsorption by bentonite sediments

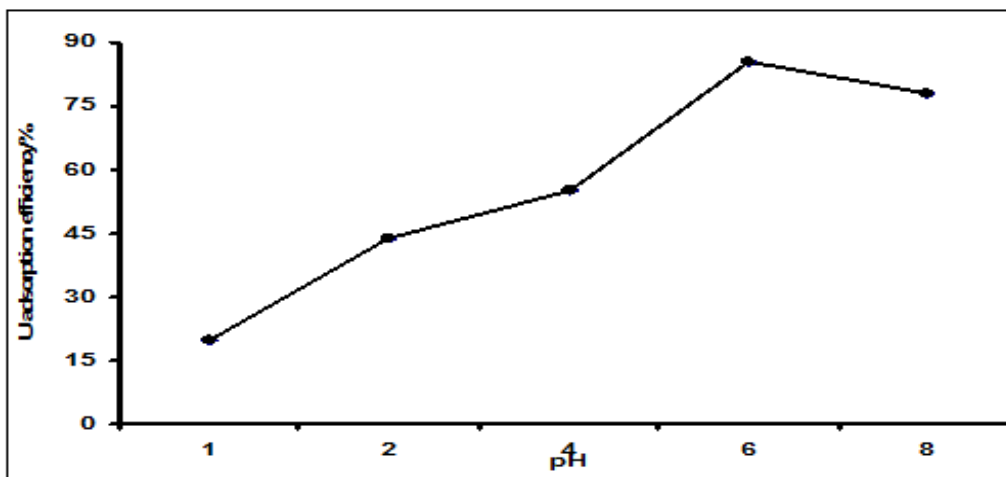


Figure (5): Effect of pH upon U adsorption by bentonite sediment

Effect of temperature

This parameter was performed at different temperatures (30, 50, 70, 100, 120°C) where the other experimental conditions were fixed at S/L ratio of 1:2, uranium concentration of 180 ppm, the contact time 120 min and pH 4. Data presented in Figure (6) emphasizes that increasing temperature from 30 to 120°C has an opposite effect on the uranium adsorption efficiency which decreased down to its minimum value. This may be attributed to the breakdown of the formed U complexes by increasing temperature.

Effect of uranium concentrations

Results obtained from studying this effect at different concentrations (50, 70, 100, 120, 150

and 180 ppm) are shown in Figure (7). Other experimental conditions were fixed at the solid/liquid ratio 1:2, the equilibrium time 120 min, pH 4 and 30°C. These results show that uranium adsorption increases by increasing concentration then decreased.

The increasing trend of sorption at low concentration range in set-1 might be due to strong bonding energies of U with the surface functional groups at sorption sites of soil. On the contrary, when the specific bonding sites become increasingly occupied, sorption becomes unspecific at high concentrations [8].

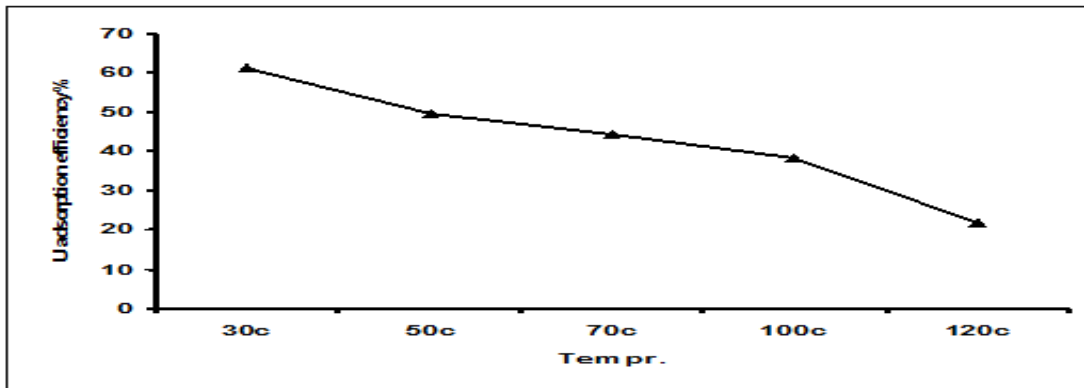


Figure (6): Effect of temperate upon U adsorption by bentonite sediment

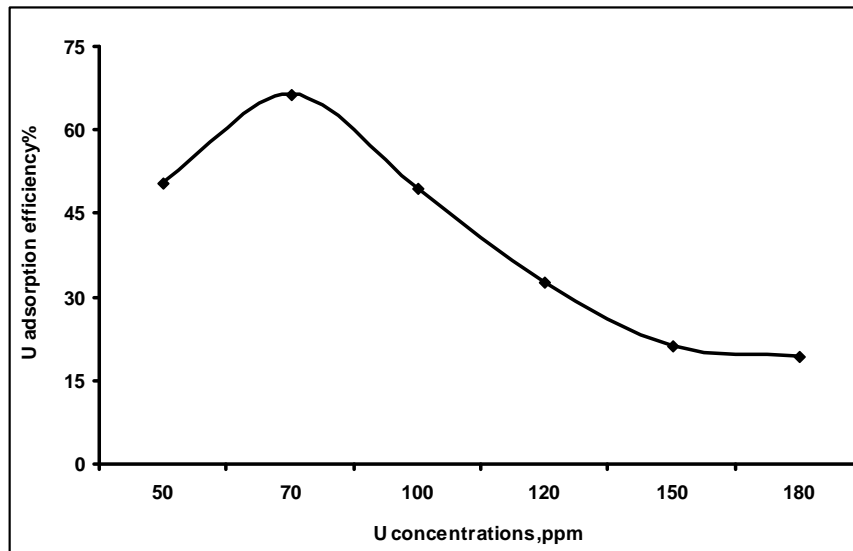


Figure (7): Effect of U concentrations upon adsorption by bentonite sediments

Uranium desorption process

Desorption of uranium from the loaded bentonite was applied where different concentrations of NaCl (0.25, 0.5 and 1M) and 1M HCl were used. Table (3) shows the uranium desorption efficiency percent at different NaCl concentrations. These experiments were performed at solid/liquid ratio $\frac{1}{2}$ for 2 hours and recycled 3 times and HCl 1M 3 cycle. This results was agreement with R. Donat and S. Aytas2 (2005). [9].

Table (3): Uranium desorption efficiency from loaded bentonite sediments by NaCl and HCl

| Sample | 0.25 M NaCl | 0.5 M NaCl | 1M NaCl | 1M HCl |
|-----------|-------------|------------|---------|--------|
| Bentonite | 51% | 75% | 69% | 78% |

IR change after adsorption

IR spectroscopy of EL Sahel EL Shamally H sediments sample spectra is illustrated in Figure(8) which reveals that the bentonite sample is characterized by vibrational frequency at 4320 cm^{-1} and 422 cm^{-1} , which are related to the non-crystalline hydrated Al silicate variable composition [10]. The changes after uranium adsorption on bentonite sediments are shown in Figure (9) and the main absorption bands are summarized, Table (4).

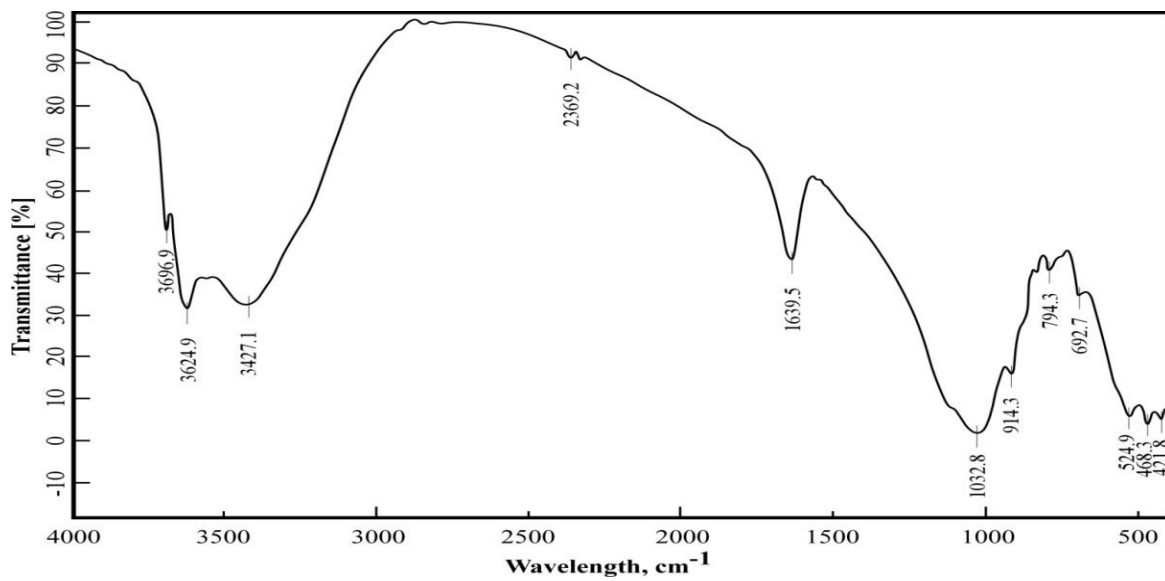


Figure (8): IR spectroscopy of El Sahel El Shamally Bentonite sample

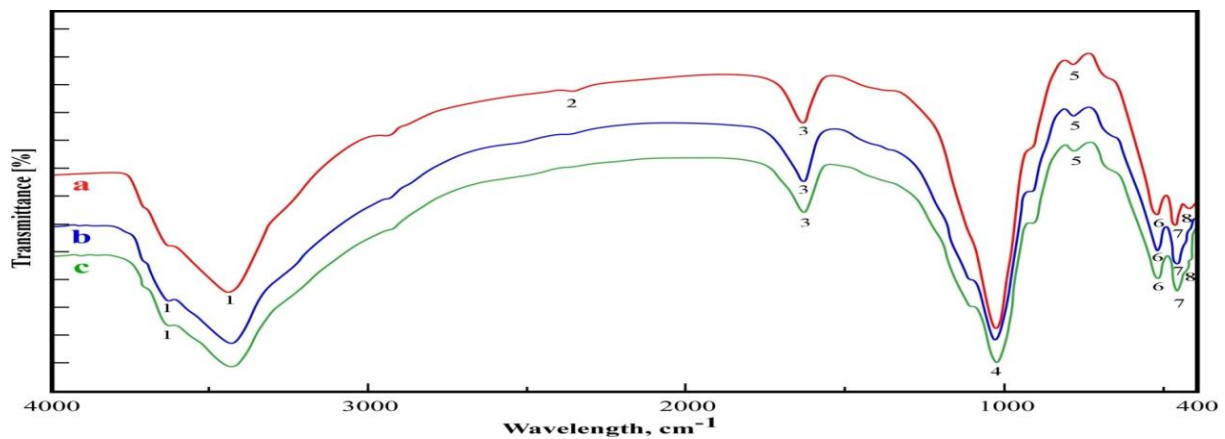


Figure (9): IR spectroscopy of El Sahel El Shamally Bentonite sample after adsorption (1: First adsorption cycle, 2: Second adsorption cycle, 3: Third adsorption cycle)

Table: (4): Mineralogical Changes before and after adsorption of uranium upon bentonite sediments

| Bands of bentonite before adsorption | Bands of bentonite after Adsorption (1, 2,3) | Functional Group |
|--------------------------------------|--|---|
| 3696 | - | OH stretching |
| 3624.9 | - | International Montmorillonite, Muscovite [10] |
| 3427.1 | 3423-3427 | Non crystalline hydrate Al-Silicate[10] |
| 2369.2 | 2925 | May be Uranium adsorption.[10] |
| 1639 | 1632-1634 | H ₂ O bend |
| 1032.8 | 1032.6-1034 | C-O stretching. |
| 794 | 788-787 | May be(UO ₂) ₂ [11] |
| 457 - 461 | 464-466 | May be Si – O or Montmorillonite |
| - | 525 | May be U-O group[10] |

Conclusion

It is proved that the studied Egyptian clay sediments of bentonite can be used as a geologic barrier suitable for uranium adsorption from its solution. The maximum uranium adsorption efficiency percent was about 70% while that of desorption was 78%. The use of this clay can possibly guarantee a safe environment and minimize the environmental pollution problems.

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