



SORPTION OF URANIUM ON SOME NATURAL MODIFIED CLAY MINERAL DEPOSITS

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ABSTRACT

Bentonite and Kaolinite clay mineral samples- as low cost adsorbents- were prepared, characterized, and tested for uranium removal from U rich-soil of Wadi Um Hamad region, south western Sinai, which have total uranium of 260 mg/ kg and DTPA- extractable U 28 mg/ kg. Modification of clay samples were carried out by acid activation and calcination. An adsorption isotherm model was fitted well with langmuir isotherm with a capacity 18.68 mg/g for modified kaolinite and 27.4 mg/g for modified bentonite. Results showed that the U adsorption was pH dependent. The maximum U adsorption value was at pH 5 and 6 for bentonite and kaolinite, respectively. In addition, results indicated that temperature had not any influence on the adsorption capacity. By increasing U ions concentrations from 50 mg/l to 200 mg/l adsorption was stable for kaolinite while for bentonite there was slight decrease, after that with increasing in the U (VI) ions concentration the adsorption capacity decreased for both adsorbents. Calcination of the kaolinite (heating the clay at 400°C followed by agitating with 1.5 N HCl) increased the adsorption capacity from 42% to 90%. XRD patterns showed the destruction of the characteristic diffraction peaks of the kaolinite (7.15 Å° and 3.15 Å°) at (70°C or 400°C). This is similar to behavior of bentonite, as the acid treatment with HCl has broken its lattice structure more than heating to 400°C. Comparing the adsorption capacity of both minerals, it could be noticed that, it is almost similar 93% and 90% for bentonite and kaolinite, respectively. However, the adsorbed U amounts represented

high amounts of the adsorbed U as 86 and 80 %, for bentonite and kaolinite, respectively. So, the retained U amounts represented 14 and 20%, respectively.

Keywords: Uranium, Adsorption, Bentonite, Kaolinite

INTRODUCTION

During the mining process of uranium in southwestern of Sinai (um bogma area), some particles of uranium escape with wind movement and the rainfalls transferred and precipitated in the surrounded wadies (**Afifi et al 1992**). From such wadies is Wadi Um hamad (**El Aassy et al 1986**). The studied uranium rich-soil lies between longitudes 33° 16' - 33° 28' East and latitudes 28° 52' - 29° 00' North, where uranium concentration in those soils reaches 260 ppm.

Uranium as radionuclides is considered from hazardous materials due to its high chemical toxicity and its radioactivity, even at trace level. The environment is affected greatly by uranium as it could reach food chain of humans, causing liver damage or severe kidney and it could even cause death (**Xie et al 2008**).

In this study, Modified clay samples of kaolinite and bentonite were tested for uranium adsorption. Factors that influence the uranium removal efficiency onto clay samples: initial U concentrations, contact time and pH were also studied in detail. Modification of clay samples were carried out by acid activation (**Christidis et al 1997**) and calcination (**Zareh et al 2012**).

MATERIALS AND METHODS

1. Identification of the studied clay samples (adsorbents)

In the present study, kaolinite and bentonite were tested as the raw materials for uranium adsorption. The used clay samples (kaolinite and bentonite)- obtained from Al Amier Ceramic Co. Cairo- were subjected to different chemical and physical analyses, **Table (1)** and mineralogical analyses, **Fig. (1)** (**Jackson, 1976; Brown, 1961; Black, 1965 and Gjems, 1967**).

Table 1 Some characteristics of the used clay samples

Characteristics	Bentonite	Kaolinite
Clay, %	73.5	69
Silt, %	20.5	23
Sand, %	6	8
CEC, meq/100g	83	15.5
EC _e , dS.m ⁻¹	2.03	0.86
Soluble ions meq/l (clay: water extract 1: 2.5)		
Ca ²⁺	12.0	2.30
Mg ²⁺	4.60	1.88
Na ⁺	5.00	2.16
K ⁺	1.27	2.24
Cl ⁻	5.40	2.76
HCO ₃ ⁻	3.70	2.95
CO ₃ ²⁻	-	-
SO ₄ ²⁻	13.8	2.82

Uranium-rich soil (260 ppm U) of Wadi Um Hamad (southwestern of Sinai) was sampled and prepared for different analyses (**Cottenie et al 1982**). Total uranium was determined volumetrically using an oxidimetric titration (**Davies and Gray, 1964**), while DTPA-extractable U was determined according to **Lindsay and Norvell (1978), Table (2)**.

X-ray diffraction patterns of the mineralogical composition of the studied bentonite and kaolinite clay samples before treatments are shown in **Fig. (1)**. Kaolinite sample consists mainly of kaolinite as detected from the presence of 7.15 Å° diffraction peak (first order) and 3.57 Å° (second order) which disappeared upon heating to 550°C for 4 hours. Quartz and feldspar are also present as detected from the presence of (3.57- 3.34 Å°) and (4.47- 4.25 Å°) diffraction in almost all treatments. Calcite was also detected from presence of 3.03 Å° diffraction peak. The three minerals are present in the following order: kaolinite> quartz> calcite. Semectite mineral was identified from the presence of 15.5 Å° diffraction peak which expanded to 18 Å° upon glycerol solvation and collapsed to 10.1 Å° peak upon heating to 550°C for 4 hours.

2. Preparation of the studied clay samples

Bentonite and kaolinite clay samples were modified by a series of pretreatments (**Christidis et al 1997; Zareh et al 2013**) to improve their removal efficiencies. Those pretreatments are: (1) Acid activation of clay samples which was done by treating 0.5 g clay with 25 ml 1.5 N HCl at 70 °C on water bath for 8 hours. (2) Calcinations of the clay which was done by heating samples at 400 °C for one hour then, agitating with 25 ml 1.5 N HCl for 1 hour. Finally, the mixture filtered then the solid part washed by deionized water and dried at room temp. The effect of each pretreatment was studied solely.

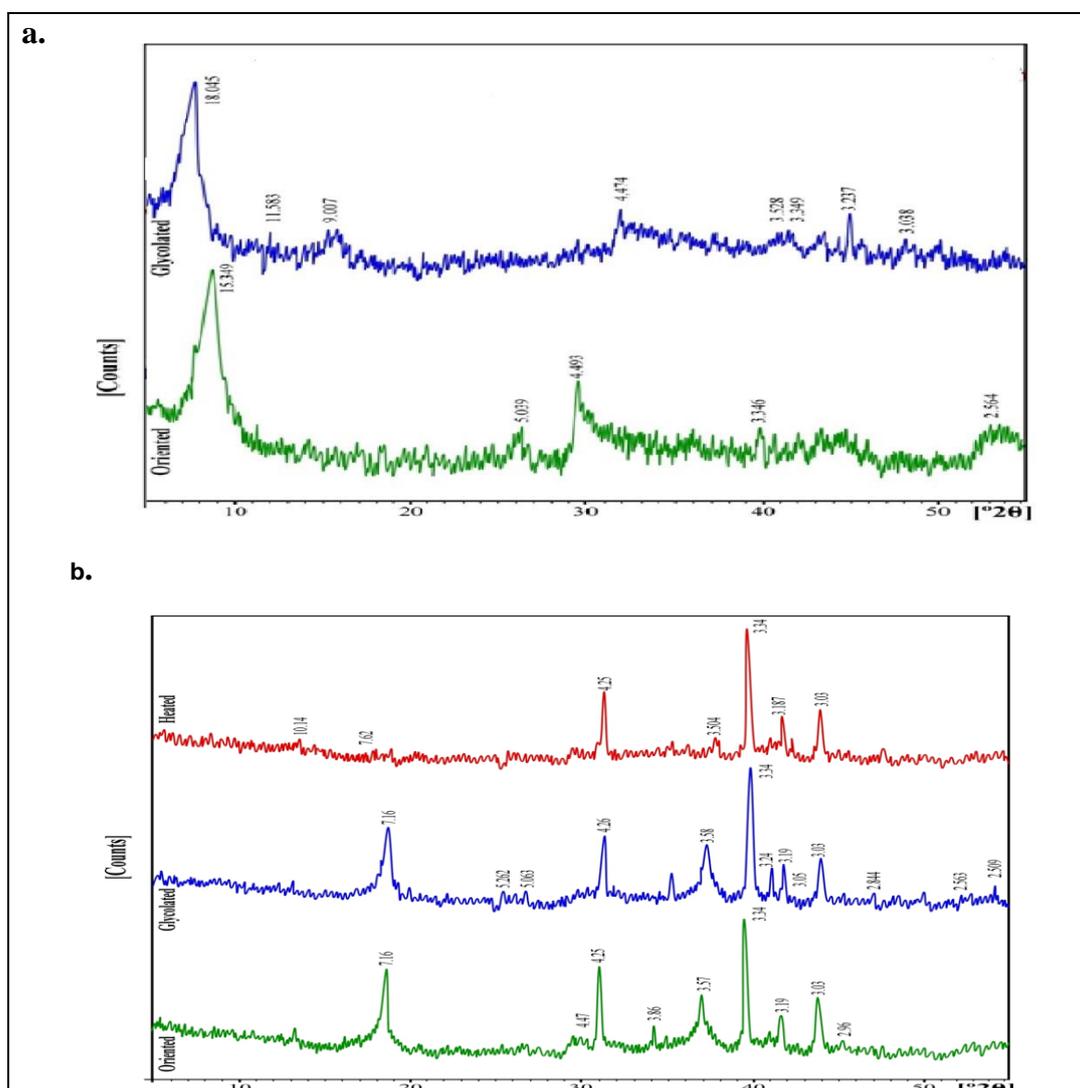


Fig. 1. XRD pattern of the used bentonite (a) and kaolinite sample (b) before pretreatment

Table 2. Some physical and chemical characteristics of Um Hamad soil

pH	EC _e (dS/m)	OM %	CaCO ₃ %	CEC (meq/100g soil)	Particle size distribution, %			
					Sand	Silt	Clay	Texture class
8.01	3.73	1.21	2.36	7.8	56.6	35.6	7.8	Loamy sand

Table 2. Cont.

Soluble cations				Soluble anions				Total U concentration	DTPA- extractable U ($\mu\text{g/g}$)
meq/l *									
Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	HCO ₃ ⁻	CO ₃ ²⁻	SO ₄ ²⁻	260	28
1.76	4.91	27.68	0.38	29.82	0.82	-	4.09		

* (soil: water extract 1: 2.5)

3. Adsorption experiment

The uranium adsorption experiments were performed in Erlenmeyer flasks, where about 0.5g from the modified clays contacted with 25 ml of the uranium prepared solution $UO_2(NO_3)_2 \cdot 6H_2O$ using a mechanical shaker. Each controlling factor studied alone, while all other factors kept constant. The applied ranges of the controlling factors were as follow: pH from 2 to 9, contact time: from 15 to -120 min, U (VI) concentration: from 50 to 600, mg/l and temperature: 25 to 75 °C.

In each experiment, solution pH was adjusted using 0.1 N HCl and/or 0.1 N NaOH. The flasks were gently shaken and the samples obtained after different time intervals were centrifuged and uranium was determined in the filtrate. Adsorption capacity (q_e) and removal efficiency (%) are obtained using Eqs. (1) and (2), respectively (Aytas et al 2009):

$$\text{Adsorption capacity, } q_e \text{ (mg/g)} = (C_i - C_e) * V/m \dots (1)$$

$$\text{Removal efficiency (\%)} = [(C_i - C_e)/C_i] * 100 \dots (2)$$

Where q_e was the equilibrium concentration of U (VI) adsorbed on modified clays at equilibrium, C_i was the initial concentration of the U (VI) solution (mg/l) and C_e was the equilibrium concentration of the U(VI) solution (mg/l), V was the volume of the U (VI) solution (L) and m was the weight of modified clay (g). The adsorption percentage (removal efficiency from U(VI) solutions) was calculated by the difference of initial and final concentration using the equation expressed as removal efficiency (%). The data obtained were fitted to the Langmuir adsorption equation in the straight line form:

$$C_e/q_e = C_e/Q_m + 1/Qmb$$

Where Q_m was the saturated monolayer adsorption (mg/g), b was the Langmuir constant sites and was a measure of the adsorption energy (ml/mg).

4. Uranium desorption

Elution process of uranium from the loaded bentonite and kaolinite was investigated with solution of 1.0 M CH_3COONa solution by shaking each of the loaded bentonite (0.5 g) and kaolinite (0.5 g) with the 25 ml solution. A systematic calculation of the eluted uranium amounts carried out after each analysis for the collected eluent as described by (Zareh et al 2013).

5. Chemicals and reagents

A stock solution of U (VI) (1000 mg l^{-1}) was prepared by dissolving accurately weighted amount (2.109 g) of uranyl nitrate $UO_2(NO_3)_2 \cdot 6H_2O$ in deionized water and then diluted to appropriate concentrations for each test.

RESULTS AND DISCUSSION

1. Effects of acid activation and calcination of clays on U adsorption

Results in Table (3) and Fig. (2) revealed the effect of clay modification on uranium adsorption. Acid activation treatment of bentonite increased the removal efficiency of the mineral from 61% to 75%, (with 14% increase) while bentonite calcination increased removal efficiency of the mineral to 93%.

Table 3. Effect of clay modification on U adsorption

Treatments	C_i (initial)	C_e (mg/l)	adsorbed ($\mu\text{g/g}$)	q_e (mg/g)	U removal efficiency (%)
Natural bentonite	200	78	122	6.1	61
Acid activated bentonite	200	50	150	7.5	75
Calcinated bentonite	200	14	186	9.3	93
Natural kaolinite	200	116	84	4.2	42
Acid activated kaolinite	200	60	140	7.0	70
Calcinated kaolinite	200	20	180	9.0	90

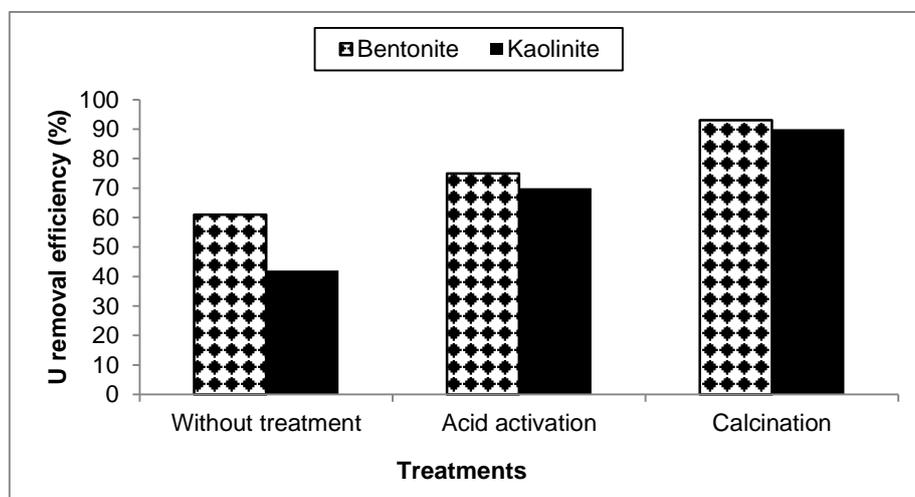


Fig. 2. Effect of different clay modification treatments on U removal efficiency

Data in the same table also show that U removal efficiency of kaolinite increased from 42% to 70% upon activating the mineral with 1.5 N HCl at 70 °C on water bath for 8 hours. Calcination of the kaolinite increased the removal efficiency from 42% to 90%. XRD pattern (Fig. 3) show the destruction of the characteristic diffraction peaks of the kaolinite (7.15 Å and 3.15 Å) at (70°C or 400°C). This is similar to behavior of bentonite, as the acid treatment with HCl has broken its lattice structure more than heating to 400°C. In other words calcination is more effective in increasing the removal efficiency of bentonite than acid activation. Fig. (4) reveals the destruction of bentonite in both treatments (acid activation and calcination). This could be due to that calcination, which include heating the mineral at 400°C for one hour, facilitates the solubility of the increasing its surface area.

2. Effect of controlling factors

2.1. pH effect

The increase in the uranium adsorption until pH 6 and 5 respectively may be caused by the both minerals surface properties in term of surface dissociation of function groups. This means that at pH value below 4, the removal efficiency was low due to the competition between U (VI) ions and H⁺ for the same adsorption site and the protonization of residual oxygen containing groups on both kaolinite and bentonite such as hydroxyl group (Wang et

al 2013). However, after pH 5 and 6 hydrolysis start as a result of the formation of complexes in aqueous solution Fig. (5). The obtained results agreed with Roberto and Davide (1997) who mentioned that uranium sorption on montmorillonite clay is a strong function of solution pH.

2.2. Influence of contact time

Contact time affected the adsorption of uranium ions by both modified clay minerals and the results are presented in Fig. (6). Through the adsorption of uranium on bentonite and kaolinite, it go by three stages. The first stage of dsorption of U increased rapidly in the first 45 min almost for bentonite and kaolinite then it slowed down next until ≈ 60 min where equilibrium stage was attained after that. Uranium adsorption became almost constant after 60 min, till the rest of experiments. It is worth to mention that the adsorption capacities of the two minerals after 90 min are almost similar.

2.3. Initial uranium concentration effect

Influence of uranium ions concentrations onto U removal efficiencies are shown in Fig. (7). Our obtained results revealed that by increasing U ions concentrations from 50 mg/l to 200 mg/l adsorption was stable for kaolinite while for bentonite there was slight decrease, after that with increasing in the U (VI) ions concentration the efficiency decreased for both adsorbents.

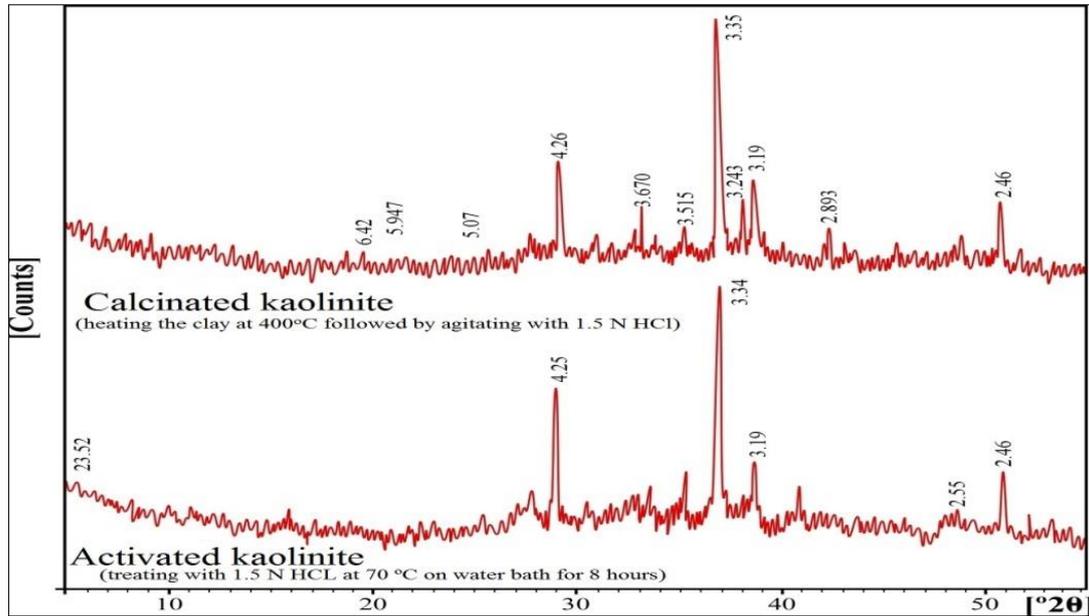


Fig. 3. XRD pattern showing the effect of the different pretreatment on the kaolinite sediments

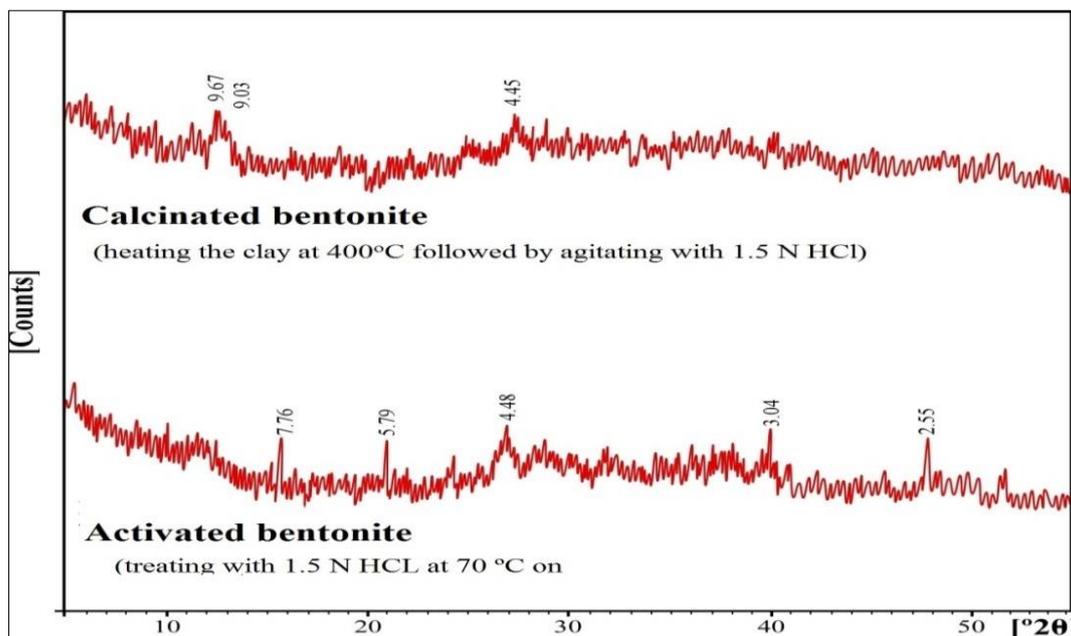


Fig. 4. XRD pattern showing the effect of the different pretreatment on the bentonite sediments

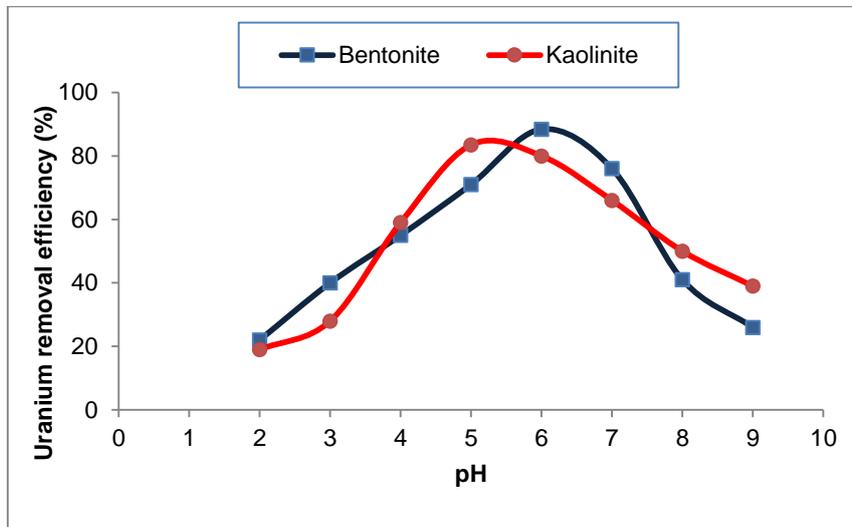


Fig. 5. Effect of solution pH upon uranium removal efficiency of modified bentonite and modified kaolinite

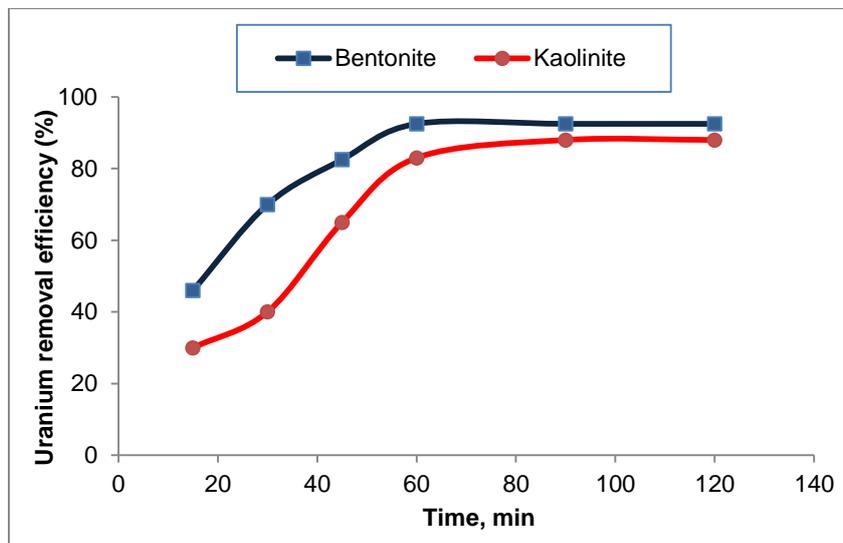


Fig. 6. Effect of contact time on U removal efficiency of the modified bentonite and kaolinite

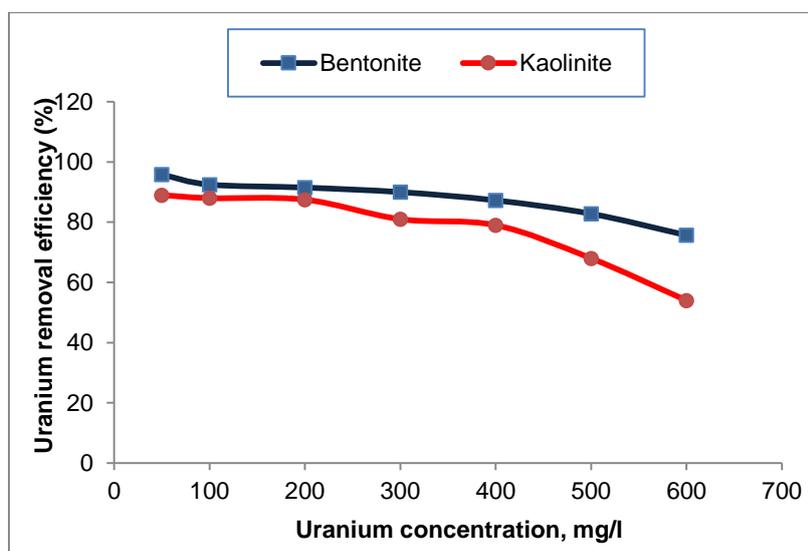


Fig. 7. Influence of initial U concentrations on uranium removal efficiency of the modified bentonite and kaolinite

2.4. Effect of adsorption temperature

The influence of adsorption temperature where examined and the results are plotted in **Fig. (8)**. It is noticeable that U removal efficiency is constant with increasing the temperature. For that, room temperature ($\approx 25^\circ\text{C}$) was chosen as the optimum temperature.

3- Uranium adsorption process mechanism

The availability of heavy metal depends on the retention capacity of adsorbents to which the metal associate. Metal availability is governed by sorption-desorption reactions particularly with clay surfaces.

The mechanism of uranium adsorption process by modified bentonite and modified kaolinite can be explained according to the data obtained by **Mohamed (2016)** and **Youssef (2017)**, where they stated that when the clays of kaolinite and bentonite get activated by acid and calcinated with heating, the clay's physical and chemical properties are changed but keeps its layer structure. The U (VI) adsorption phenomenon on clay mineral (kaolinite) is due to more aluminol sites available (**Bachmaf et al 2010**).

3.1. Adsorption Isotherms

The obtained data were fitted to the Langmuir adsorption equation. Results of the adsorption of U by bentonite and kaolinite illustrated in **Table (4)** and **Fig. (9)**. The maximum adsorption value obtained in accordance to Langmuir isotherm was 27.4 mg/g for bentonite and 18.68 mg/g for kaolinite. The values of correlation coefficient (R^2) were 0.99 and 0.98 for bentonite and kaolinite, respectively, which indicated that adsorption of U (VI) onto Modified clays was more favorable at higher initial U concentrations than at lower concentrations (**Youssef, 2017**).

Table 4. Langmuir adsorption isotherm of U^{+6} ions on bentonite and Kaolinite

Langmuir Parameters		
	bentonite	Kaolinite
$q_{\max}(\text{mgg}^{-1})$	27.4	18.68
$B (\text{Lmg}^{-1})$	1.034	0.031
R^2	0.98	0.983

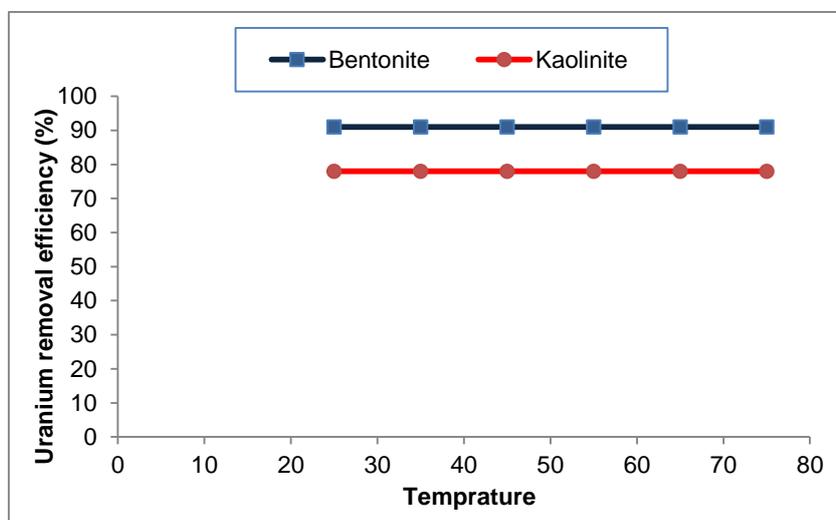


Fig. 8. Temperature effect on uranium removal efficiency by the modified bentonite and kaolinite

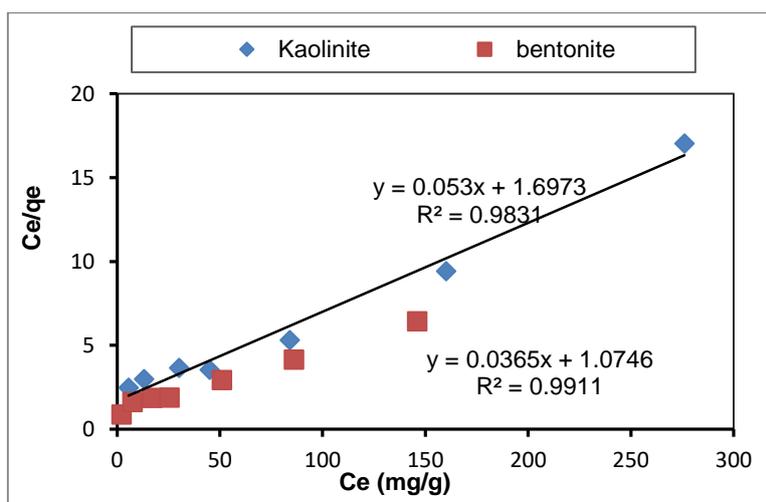


Fig. 9. Plot of adsorption isotherm for uranium (VI) on the modified bentonite and kaolinite

According to the Langmuir isotherm model, U 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 (Zareh, 2012). In fact, it is useful to evaluate the sorptive capacity of the used clay deposits for specific ion; in the present investigation, the adsorbed U saturated 93% and 90% of bentonite CEC and kaolinite CEC, respectively. However, heavy metal adsorption is basically adsorbed via two different mechanisms, namely specific adsorption, chemisorptions of inner-sphere complexes

and non-specific adsorption outer-sphere complexes (Sposito, 1984).

4- Uranium desorption

Table (5) summarized the obtained results of recovery percentage (desorbed %). Uranium desorption from loaded adsorbent were 86% and 80% for bentonite and kaolinite, respectively. The non extractable U was considered retained and represents 14 and 20% from the adsorbed U.

Table 5. Amounts of desorbed and retained U

Eluent Type	Desorbed Uranium %		Retained U %	
	Bentonite	Kaolinite	Bentonite	Kaolinite
1.0 M CH ₃ COONa	86	80	14	20

5. CONCLUSION

Both bentonite and kaolinite minerals behaved similarly concerning U adsorption. The increase noticed in adsorption capacities was due to increase in surface area of both minerals due to their breakdown by acid treatment. The uranium adsorption follow Langmuir isotherm with a capacity 18.68 mg/g for modified kaolinite and 27.4 mg/g for modified bentonite. However, the adsorbed U amounts represented high amounts of the adsorbed U as 86 and 80 %, for bentonite and kaolinite, respectively. So, the retained U amounts represented 14 and 20%, respectively.

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ادمصاص اليورانيوم على بعض رواسب معادن طينية معدلة

[186]

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متساوي الحرارة Langmuir مع 18.68 مجم / جم
للكاؤولينيت و 27.4 ملجم / جرام للبتونيت كقدرة
نظرية.

سجلت قيم اليورانيوم المنطلقة من معدني الطين
المستخدمين 86 و 80 % من قيمة الكمية الكلية التي
سبق ادمصاصها على سطح المعدن وبالتالي تعتبر
الكمية المتبقية (لم يتم انطلاقها) تعتبر محتجزة
(14% و 20%) من لكلا المعدنين البنتونيت
والكاؤولينيت، على التوالي.

الكلمات الدالة: اليورانيوم، الإدمصاص، البنتونيت،
الكاؤولينيت

الموجز

تم استخدام رواسب معادن طين البنتونيت
والكاؤولينيت كمواضع منخفضة التكلفة وتمت توصيفها
واختبارها لإزالة اليورانيوم من تربة غنية باليورانيوم -
بمنطقة وادي أم حمد - جنوب غرب سيناء. أظهرت
النتائج أن ادمصاص اليورانيوم كان يعتمد على الرقم
الهيدروجيني. الحد الأقصى للادمصاص حدث عند
الرقم الهيدروجيني 5 و 6 للبتونيت والكاؤولينيت، على
التوالي. أيضا، أظهرت النتائج أن درجة الحرارة ليس
لها تأثير على كفاءة الإدمصاص. أظهر اختبار
اختلاف درجة الحرارة بالادمصاص أن البيانات
التجريبية المحققة تم تركيبها بشكل جيد مع نموذج