

Removal and recovery of Th^{4+} and UO_2^{2+} ions from aqueous solutions by adsorption onto glauconite (dark green color)

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Abstract

As a natural and low-cost material, glauconite is applied as an adsorbent to remove Th^{4+} and UO_2^{2+} ions from aqueous solutions by a batch system. Two different samples of glauconite (dark green and light green color) are delivered from Baharia Oases, Egypt. The effects of analytical parameters such as pH, contact time, concentration of metal ion, mass adsorbent, interfering ions, and temperature on adsorption on glauconite (dark green) are investigated. The similar uptake percentage of the two different glauconite samples (dark green and light green) at certain condition verify the role of Si-OH in the proposed adsorption mechanism. Isotherm studies of the adsorption are also carried out to understand the nature of adsorption of Th^{4+} and UO_2^{2+} ions on glauconite (dark green). Equilibrium data are best fitted with Langmuir model. The adsorption capacity of Th^{4+} and UO_2^{2+} ions is found to be 50 and 40 mgg^{-1} , respectively. Thermodynamic parameters ΔH° , ΔS° and ΔG° values showed that the sorption process was endothermic ($\Delta H^\circ > 0$), had increased entropy ($\Delta S^\circ > 0$) and spontaneous ($\Delta G^\circ < 0$). The retained metals are eluted by using different reagents. The preconcentration could be made selective to UO_2^{2+} ions by using HNO_3 0.1 M, NaCl 0.9 M and oxalic acid 0.1 M rather than Th^{4+} ions.

Keywords: Removal; Uranium; Thorium; Glauconite; Sorption isotherms

1. Introduction

Long lived radionuclides in radioactive waste are considered to be dangerous pollutants and their migration by ground water is strongly affected by their adsorption on the geologic materials. Presence of radionuclides and toxic metals in wastes is a major environmental concern. Such wastes arise from technologies producing nuclear fuels, and from laboratories working with radioactive materials (Yusan et al., 2012).

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Higher level of uranium and thorium concentrations are considered as health hazard due to its natural radioactivity and chemical toxicity, which may cause damage to the health of human beings such as severe liver damage, kidney damage, its accumulation in bones and eventually death (**Ilaiyaraja et al., 2013**).

Uranium and thorium are very essential elements in nuclear and atomic energy program. Their recovery is essential to minimize their discharge into the environment from the point of view of safety and economy (**Seyhan et al., 2008**). Although a variety of methods such as precipitation, solvent extraction, electrolysis and ion exchange can be used to remove dissolved metals from aqueous samples, most of them have disadvantages of non economic, poor removal efficiency, high cost, generation of secondary pollution and ineffectiveness for low metal concentrations. Solid phase extraction has commonly been used as a technique for preconcentration/separation of various inorganic and organic species. This technique has advantages of higher enrichment factor, safety with respect to hazardous samples, minimal costs due to low consumption of reagent, environment friendly, flexibility and easier incorporation into automated analytical techniques (**Sadeghi and Sheikhzadeh, 2009**).

During the last decade, research efforts have been directed towards using low cost alternative techniques or development of low cost sorbents applicable for the removal and separation of undesirable metal ions from an aqueous phase (**Ali et al., 2011**). A variety of low cost sorbents such as sludge (**Santos and Boaventura, 2015**), loofah fibers (**Tang et al., 2014**), Dry desulfurization slag (FDG ash) (**Wu et al., 2014**) and fly ash (**Mishra and Patel, 2009**) have been tried as sorbent materials.

Sorption of heavy metals on clay surfaces is important for economic reasons because most natural clays are low-cost and readily available. Glauconite is one of them, This mineral has been widely used for geochronological analysis (**Franus and Bandura, 2014**). Glauconite is a natural three-layer sheet aluminosilicate occurring primarily in marine sediments. It contains multivalent iron, aluminum and magnesium ions secured between two flat silicate layers that also contain OH⁻ groups; the triple layers alternating with a layer of water molecules and alkaline earth metals, most notably potassium (**Mith et al., 1996**). Glauconite used to describe predominantly sand-size, generally greenish aggregates found in

unconsolidated deposits and sedimentary rocks and also as an iron-rich, mica-like mineral analogous of an illite. The mineral is rich in iron and consists of various colors: green, yellow, blueish, red, or black. Some glauconite may be nearly colorless (**Tedrow, 2002**). Maturation produces dark green (bluish) glauconite formed from Fe-rich smectite by increasing the content of Fe²⁺ together with K. The change from light green to dark green color in progressively more mature glauconite is explained by light absorption induced by enrichment in octahedrally coordinated Fe²⁺ relative to the total Fe, associated with the progressive decrease in the proportion of Fe³⁺ rich smectite interleaved with glauconite (**Sánchez-Navas et al., 2008**).

In continuation of our work on application of clays as low cost adsorbents in wastewater treatment, herein we report the influence of various experimental parameters on sorption of Th⁴⁺ and UO₂²⁺ ions on glauconite (dark green). A less interfering ions (HCl, NaOH) media was applied to adjust the pH. Isotherms, thermodynamics, and desorption studies were investigated. Moreover, a comparison between the uptake percentage of glauconite (dark green) and glauconite (light green) at certain condition was presented.

2. Materials and Methods

2.1. Instrumentation

Brucker X-ray diffraction (Axs D8 advance Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) with a typical scanning begin at 2θ equal to 20° to 80° and scan rate of 20 min^{-1} , Germany) is used for the identification of different phases that composed the adsorbent materials used. Panalytical Axios Advanced X-Ray Fluorescence, Netherland was used. All spectrophotometric determinations are carried out using UV-vis spectrophotometer 160A Shimadzu, Japan ($\pm 0.005 \text{ A}$). The pH meter measurements are made by Jenco 6173 model.

2.2. Chemicals and reagents

All the chemicals used are of analytical reagent grade (Sigma-Aldrich, Riedel-de Haen AG, Germany) are used for preparation of thorium and uranium. The stock solutions (1000 mgL^{-1}) for UO₂²⁺ and Th⁴⁺ ions are prepared from UO₂(NO₃)₂·6H₂O and Th(NO₃)₄·5H₂O by dissolving 2.11 and 2.48 gm,

respectively, in 1L of double distilled water. Arsenazo-III is obtained from Aldrich Co, Germany.

Two different samples of glauconite (dark green and light green color) are delivered from Baharia Oases, Egypt. These samples are washed with water for several times. Thermally treated glauconite (dark green and light green color) is prepared by ignition at 900 °C for three hours. The weight loss percentage of thermally treated samples was 9%.

2.3. Sorption experiments

The sorption experiments are studied by a batch technique. The effects of analytical parameters such as pH, contact time, concentration of metal ion, mass of adsorbent, interfering ions and temperature on glauconite (dark green) are investigated and uptake efficiency is mutually compared with glauconite (light green) at a certain condition. In all experiments, glauconite was separately shaken with each metal ion at various experimental conditions. The pH of the solutions is maintained in the range $(1.5-9) \pm 0.1$ by NaOH 1 M and HCl 1 M. Separating of solid phase from liquid is done by centrifuging at 4000 rpm for 15 min. After equilibration, the uranium and thorium concentrations are determined spectrophotometrically using Arsenazo-III (0.05%, w/v) as a complexing agent at 653 and 659 nm, respectively against reagent blank. Uptake percentage (%E) and amount of metal ions adsorbed at equilibrium, q_e (mg/g) are calculated from the equations (Wu et al., 2014):

$$\% E = (C_o - C_e) / C_o \times 100 \quad (1)$$

$$q_e = (C_o - C_e) V / m \quad (2)$$

where C_o and C_e are the initial and equilibrium metal ion concentrations in the solution (mg/L), respectively. V is the volume of the aqueous solution (mL) contacted with glauconite and m is the mass of glauconite in grams.

2.4. Sorption isotherms

The adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among the liquid and the adsorbent based on a set of assumptions that are mainly related to the heterogeneity/homogeneity of

adsorbents, the type of coverage, and the possibility of interaction between the adsorbate species. The most common types of models describing the sorption process are the Langmuir and Freundlich models. Total sorption capacity of the adsorbent material is determined by shaking 50 mL containing different concentrations of metal ion from 50 to 250 mgL⁻¹, 0.1 g glauconite, pH 3 ± 0.1 for both metals at 70 ± 1°C.

2.4.1. Langmuir isotherm

Langmuir isotherm describes monolayer adsorption based on the assumption that all the adsorption sites have equal adsorption affinity. The linear form of Langmuir isotherm is given as the following equation (**Bhattacharya et al., 2008**).

$$C_e/q_e = 1/(Q_e b) + C_e/Q_e \quad (3)$$

where q_e is the amount of metal ion sorbed per unit weight of adsorbent material (mg/g), C_e the equilibrium concentration of the metal ion in the equilibrium solution (mg/L), Q_e the monolayer adsorption capacity (mg/g) and b is Langmuir constant. The graphic presentation of (C_e/q_e) versus C_e gives straight line, the numerical value of constants Q_e and b evaluated from the slope and intercept of this line. One of the essential characteristics of the Langmuir model could be expressed by dimensionless constant called equilibrium parameters R_L (**Bhattacharya et al., 2008**).

$$R_L = 1 / (1 + bC_0) \quad (4)$$

where C_0 is the highest initial metal ion concentration (mg/L). The value of R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$).

2.4.2. Freundlich isotherm

Freundlich isotherm can be applied for the adsorption on heterogeneous surfaces and multilayer adsorption. The linear form of Freundlich isotherm can be expressed as the following equation (**Abdel Salam et al., 2011**).

$$\log q_e = \log k + (1/n) \log C_e \quad (5)$$

where q_e is the amount of metal ion sorbed per unit weight of adsorbent material (mg/g), k is constant indicative of the relative sorption capacity of adsorbent material (mg/g) and $1/n$ is the constant indicative of the intensity of the sorption process and C_e the equilibrium concentration of the metal ion in the equilibrium solution (mg/L). The numerical values of the constants k and n are computed from the slope and the intercept of the straight line when a plot of $\log q_e$ versus $\log C_e$ is constructed.

2.5. Thermodynamics studies

The thermodynamic parameters of the adsorption process are obtained from sorption experiments at various temperatures. It is essential to examine the influence of the sorption on glauconite with the change of thermodynamic parameters. The influence of temperature variation on the sorption of UO_2^{2+} and Th^{4+} ions on glauconite from aqueous solution is examined using 0.1 g glauconite in 50 mL of 100 mg/L metal ion from 303 to 343 K at $\text{pH } 3 \pm 0.1$.

2.6. Desorption studies

From the regeneration point of view, the stability of adsorbent is of crucial importance and the adsorbed metal ions should be easily desorbed without destroying the adsorbent under the operation conditions. Various types of reagents including nitric acid, hydrochloric acid, sulfuric acid, oxalic acid and sodium chloride are examined as stripping agent. 50 mL of stripping agent acids are shaken with certain amount of adsorbent material loaded with metal ion. The stripping percentage is calculated as follows (Ilaiyaraja et al., 2013):

$$\text{Stripping\%} = (C/C_o) \times 100 \quad (6)$$

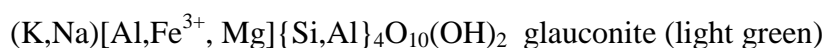
where C_o is the concentration of the metal ion on the adsorbent material surface and C is the concentration of the metal ion in the desorptive reagent after definite time.

3. Results and Miscussion

3.1. Glauconite characterization

3.1.1. X-ray study

The chemical analysis of two samples of glauconite (dark green and light green color) are listed in Table 1. The chemical analysis showed that the main constituents of glauconite are silica, alumina and iron oxides. The X-ray diffraction studies are carried out for two samples of glauconite (dark green and light green color) as shown in Fig. 1 which indicate that the glauconite (dark green and light green color) mineral is defined as an illite type of a clay mineral. Glauconite is dioctahedral mica with the chemical formula.



where ions within [] and { } brackets are located in octahedral and tetrahedral sites, respectively, whereas ions within () brackets are found in the interlayer sites. A fundamental characteristic of glauconite is that the unit cell is composed of a single silicate layer rather than the double layer of most other dioctahedral micas (Mashlan et al., 2012).

Table 1

Major chemical constituents of glauconite samples

Constituents	Mass%	
	Glauconite (dark green)	Glauconite (light green)
<i>SiO₂</i>	27.584	42.277
<i>Al₂O₃</i>	3.567	7.200
<i>Fe₂O₃^{tot}</i>	47.730	27.101
<i>V₂O₅</i>	0.050	---
<i>CaO</i>	0.610	0.335
<i>MgO</i>	2.120	3.321
<i>K₂O</i>	7.010	7.011
<i>TiO₂</i>	0.070	0.456
<i>P₂O₅</i>	0.073	0.045
<i>SO₃</i>	0.045	0.115
<i>Cr₂O₇</i>	0.027	0.014
<i>MnO</i>	0.046	0.079
<i>CuO</i>	0.025	---
<i>ZnO</i>	0.083	0.028
<i>ZrO₂</i>	0.048	0.022
<i>SrO</i>	0.012	0.005
<i>Nb₂O₅</i>	----	0.003
<i>PbO</i>	---	0.006
<i>F</i>	---	0.235
<i>Cl</i>	---	0.327
<i>LOI</i>	10.900	11.100
<i>Total</i>	99.800	99.680

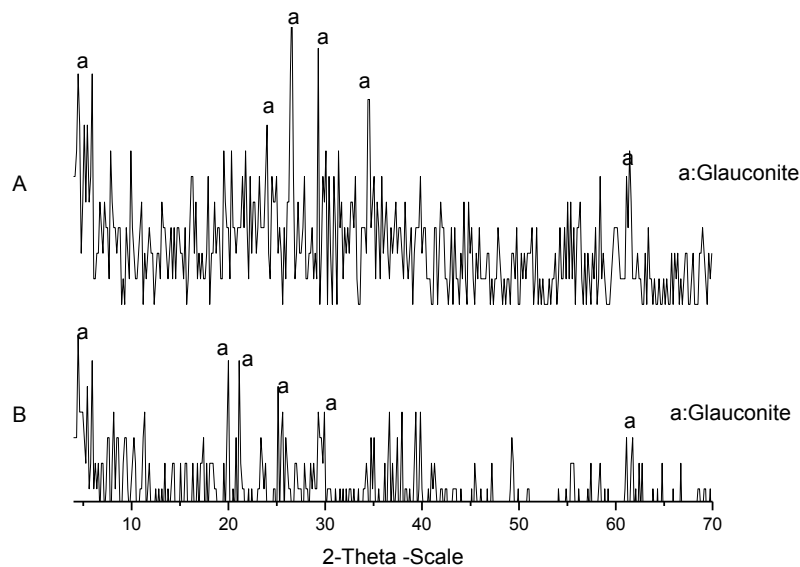


Fig. 1. X-ray diffraction of glauconite (light green A), and glauconite (dark green B)

3.2. Sorption parameters

The parameters which may affect the uptake of UO_2^{2+} and Th^{4+} ions by glauconite (dark green), such as pH, shaking time, initial concentration of metal ion, sorbent mass, interfering ions, and temperature are investigated.

3.2.1. Effect of initial pH

The pH of the aqueous solution is an important parameter that influences the metal ion speciation and total surface charge on adsorbents (**Ilaiyaraja et al., 2013**). The effect of pH on the sorption process of uranium and thorium on glauconite is studied by contacting 0.1 g glauconite with 50 mL containing 100 mg/L of the metal ion adjusted at different pH values and shaken for 10 min at room temperature. The results of the influence of uptake as a function of pH on the sorption of uranium and thorium on glauconite are shown in Fig. 2. Adsorption of UO_2^{2+} ions increased sharply with increase of pH up to 4.0 and then started decreasing. Hydrolysis of the uranyl ion practically begins at pH 3.0 (**Anirudhan and Jalajamony, 2013**). At pH 4.0 – 8.0 mononuclear $[\text{UO}_2(\text{OH})]^+$ as well as polynuclear $[(\text{UO}_2)_2(\text{OH})_2]^{2+}$, $[(\text{UO}_2)_3(\text{OH})_5]^+$ products of the general type $[(\text{UO}_2)_x(\text{OH})_y]^{(2x-y)+}$ becomes the dominant species; when the pH values rise to more than 8.0 $[(\text{UO}_2)_3(\text{OH})_7]^-$ anions increases (**Liu et al., 2013; Tan et al., 2015**). At $\text{pH} \leq 4.0$, the uranium removal is mainly due to the predominant species, UO_2^{2+}

of U(VI). However at very low pH, since H_3O^+ is predominant, its competition towards the adsorption site controls the metal ions adsorption efficiency. Stable soluble uranyl ions complexes, with lower adsorption affinities, are formed above pH 4.0, so that uranium adsorption decreased after this pH (Zhang et al., 2012). Also, Fig. 4 shows that the adsorption of Th^{4+} ions is increased with increasing of pH up to 4.0 and then constant. It is well known that Th^{4+} ions can exist in various chemical forms in solution as a function of pH such as Th^{4+} (major species), $[\text{Th}(\text{OH})_3]^+$ (minor species) at $\text{pH} \leq 3$. At $\text{pH} > 4.0$ the hydrolysis products and the precipitation begin to play role in the adsorption of Th(IV), so the uptake percentage maintain constancy with increasing pH (Cheng et al., 2014).

So, The pH dependence of metal adsorption can largely be related to the type and ionic state of the functional group present in the adsorbent and also to the metal chemistry of the solution. The negative surface charge of glauconite samples increased with increase in pH. The variation of surface charge density of glauconite samples with increasing pH can be a result of the ionization of surface silanol groups (Talip et al., 2009). With increasing adsorption density hydrogen ions pass from surface to solution, and thus change the pH of the bulk solution. The process can be written as follows:

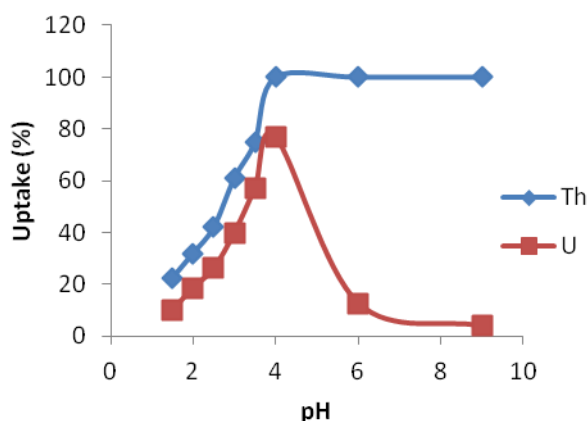
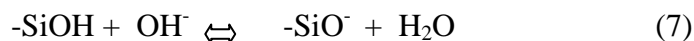


Fig. 2. Variation of the uptake percentage with pH for UO_2^{2+} and Th^{4+} ions sorption on glauconite.

3.2.2. Effect of shaking time

The effect of shaking time on the sorption process is studied using 0.1 g glauconite with a 50 mL containing 100 mg/L of the metal ion adjusted to pH 3 ± 0.1 and shaken at room temperature for different times ranging from 1 to 30 min. The results obtained are represented in Fig. 3. which reveal that the uptake percentage increased with time till the equilibrium is reached. The equilibrium time was 5 min for both elements.

3.2.3. Effect of initial concentration of ion

The effect of the initial concentration of uranium and thorium on the sorption equilibrium rate is studied by contacting a fixed weight of glauconite 0.1 g at room temperature and initial pH 3 ± 0.1 with initial concentrations ranging from 50 to 250 mg/L in 50 mL of UO_2^{2+} or Th^{4+} ions aqueous solutions and shaken for 5 min. From the obtained results shown in Fig. 4. it was observed that by increasing the initial metal ion concentration the uptake percentage of both elements decreased. The poorer uptake at higher metal concentration is resulted due to the increased ratio of initial number of moles of metal ions to the vacant sites available. For a given adsorbent dose the total number of adsorbent sites available is fixed thus adsorbing almost the equal amount of adsorbate, which resulting in a decrease in the removal of adsorbate, consequent to an increase in the initial metal ion concentration. The higher uptake percentage of thorium compared with that of uranium is due to ion diameter influenced the sorption efficiency as it appeared that uranium binding was lower than that of thorium probably because of the steric hindrance caused by two oxygen atoms bound to uranium. Steric hindrance could result from the ionic charge (radii/ionic charge; UO_2^{2+} : 253 pm/2, Th^{4+} : 94 pm/4) (Akkaya, 2013).

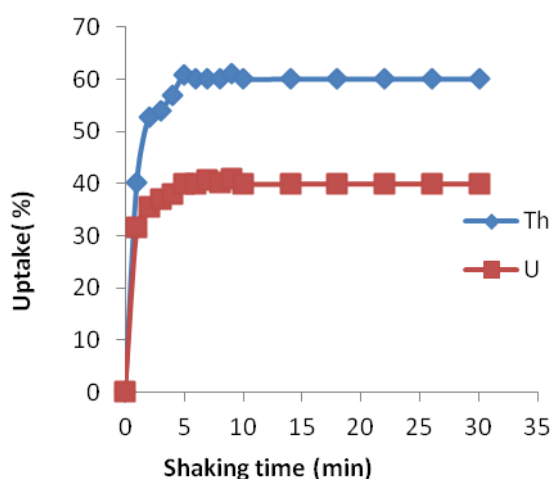


Fig. 3. Variation of the uptake with the shaking time for UO_2^{2+} and Th^{4+} ions sorption on glauconite.

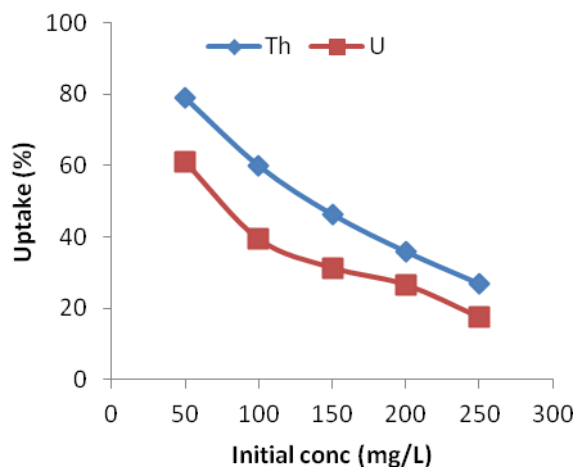


Fig. 4. Variation of the uptake percentage with the metal ions initial concentration for UO_2^{2+} and Th^{4+} ions sorption on glauconite.

3.2.4. Effect of adsorbent mass

Effect of adsorbent mass on the sorption process of the investigated metal ions is studied. The results obtained are represented in Fig. 5. This is studied by taking 50 mL containing 100 mg/L of metal ion adjusted at $\text{pH } 3 \pm 0.1$ for each element and shaken for 5 min at room temperature with different amounts of glauconite ranging from 0.02 to 0.8 g. It is clear that the uptake percentage of both metal ions increased with increasing the amount of adsorbent due to increasing number of sorbent particles in the solution that allows more metal ions to interact with more binding sites till constant at 0.3 g for Th^{4+} ions and 0.6 g for UO_2^{2+} ions.

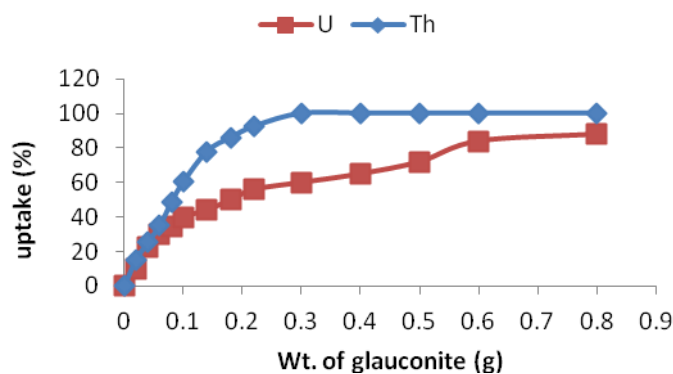


Fig. 5. Variation of the uptake percentage with the adsorbent mass for UO_2^{2+} and Th^{4+} ions sorption on glauconite.

3.2.5. Effect of temperature

Effect of temperature on the sorption process of the investigated metal ions is shown in Fig. 6. This effect is carried out using 0.1 g of glauconite with 50 ml of metal ion concentration of 100 mg/L at $\text{pH } 3 \pm 0.1$ for both elements and 5 min shaking time, the temperature is varied from 30 to 70 °C. It is found that the uptake percentage of both metal ions increased with increasing temperature.

The increase of uptake percentage with rise of temperature may be due to the increase of number of reacting moles having excess of energy which leads to the increase of sorption rate, also the rise of temperature leads to an increase of the rate of mass transfer of the diffusion and ratio of sorption.

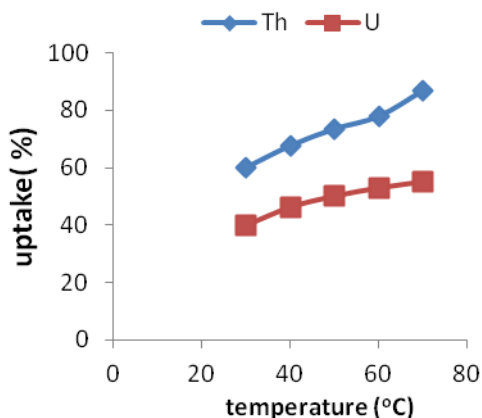


Fig. 6. Variation of the uptake percentage with temperature for UO_2^{2+} and Th^{4+} ions sorption on glauconite.

3.2.6. Effect of interfering ions

Effect of interfering ions such as calcium chloride, sodium chloride, sodium acetate, and oxalic acid on the sorption process of the investigated metal ions are shown in Figs. 7, 8, 9, and 10, respectively. This effect was carried out using 0.1 g of glauconite with 50 mL of metal ion concentration of 100 mg/L at $\text{pH } 3 \pm 0.1$ for both elements with different concentration of interfering ions, 5 min shaking time at room temperature.

Interfering anions e.g Cl^- , $[\text{CH}_3\text{COO}]^-$, $[\text{C}_2\text{O}_4]^{2-}$ had significant effect on sorption of UO_2^{2+} ions at the studied concentrations, but $[\text{C}_2\text{O}_4]^{2-}$ ions only affected on sorption of Th^{4+} ions. The effective anions on sorption of UO_2^{2+} and Th^{4+} ions might be related to complex formation between metal ion and anions, so the mechanism of sorption changed.

Interfering cation e.g Ca^{2+} had significant effect on sorption of UO_2^{2+} and Th^{4+} ions due to competition of these ions with the tested ions for sorption sites, but Na^+ did not affect on Th^{4+} ions sorption due to the change in ionic radii (Shannon, 1976).

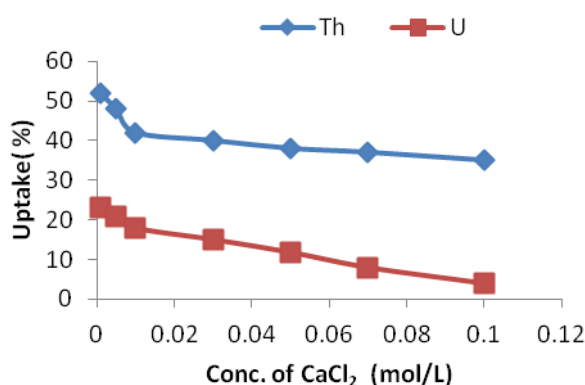


Fig. 7. Variation of the uptake percentage with CaCl_2 concentrations for UO_2^{2+} and Th^{4+} ions sorption on glauconite.

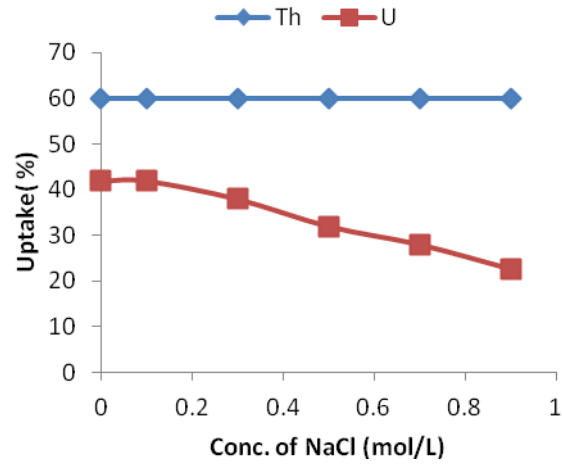


Fig. 8. Variation of the uptake percentage with NaCl concentrations for UO_2^{2+} and Th^{4+} ions sorption on glauconite.

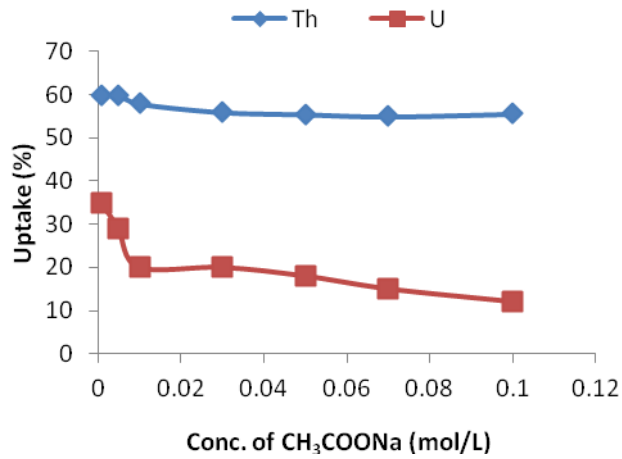


Fig. 9. Variation of the uptake percentage with CH_3COONa concentrations for UO_2^{2+} and Th^{4+} ions sorption on glauconite.

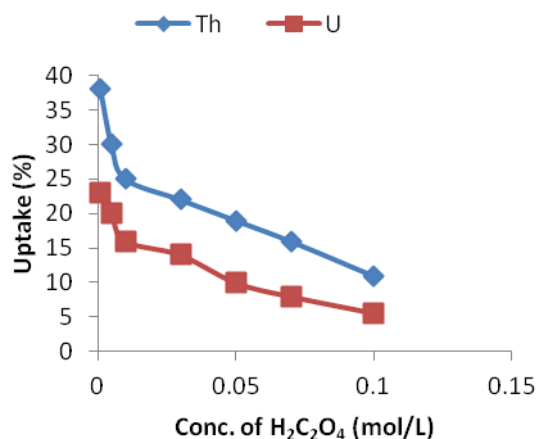


Fig. 10. Variation of the uptake percentage with H₂C₂O₄ concentrations for UO₂²⁺ and Th⁴⁺ ions sorption on glauconite.

3.2.7. Comparison between glauconite (dark green and light green color) and their thermally treated for UO₂²⁺ and Th⁴⁺ ions sorption

The effect of adsorbents employed on the sorption process of the investigated metal ions is studied by taking 50 mL containing 100 mg/L of metal ion adjusted at pH 3.0 ± 0.1 value for each element and shaken for 5 min at room temperature with 0.1 g of adsorbents employed. It is clear that the uptake percentage of Th⁴⁺ ions for glauconite (dark green), glauconite (light green), thermally treated glauconite (dark green) and thermally treated glauconite (light green) was 61.6%, 59.5%, 32% and 33%, respectively. While, it was 40%, 39%, 29.8% and 29% for UO₂²⁺ ions, respectively. The similarity in the uptake percentage of the two different glauconite samples before thermal treatment, verify the dominant role of the Si-OH in adsorption mechanism. The decrease in the uptake percentage after thermal treatment at 900 °C is due to destruction of glauconite samples (Mashlan et al., 2012).

3.3. Sorption isotherms

The parameters and correlation coefficient of Langmuir and Freundlich equations obtained from the plot in the Fig. 11 and Fig. 12 are displayed in the Table 2. It can be seen from the Table 2 that the values of the correlation coefficients of Langmuir equation of thorium and uranium (R²= 0.997, 0.998) were higher than that of Freundlich equation (R²= 0.974, 0.985), indicating that the Langmuir equation

was more correctly fitted the experiments data in the whole range of Th^{4+} and UO_2^{2+} concentrations tested, which represents the presence of monolayer adsorption. All the R_L values are found to be less than 1 and greater than 0 indicating the sorption isotherms of all metal ions, were favorable (**Bhattacharya et al., 2008; Hosseini and Hosseini-Bandegharai, 2011**).

The adsorption capacity (Q_e) is higher for Th^{4+} than UO_2^{2+} ions so, the adsorption of Th^{4+} is more favourable than UO_2^{2+} ions onto glauconite at the same temperature. Smaller ion is hydrated easily and it has got greater hydrated ionic radius whereas ion with greater ionic radius has smaller hydrated ionic radius. Since adsorptive power depends inversely on the size of the species, smaller hydrated ions are adsorbed readily. Ionic radii of Th^{4+} and UO_2^{2+} are 1.19 and 0.97 Å, respectively, and it agrees with the greater adsorption of Th^{4+} over UO_2^{2+} ions (**Anirudhan and Jalajamony, 2013**).

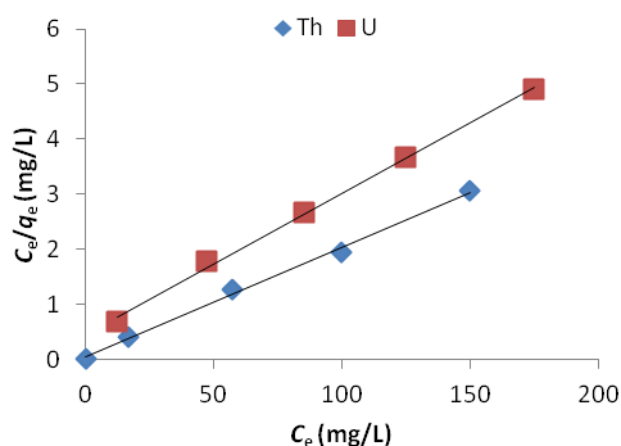


Fig. 11. Langmuir sorption isotherm of UO_2^{2+} and Th^{4+} ions sorption on glauconite.

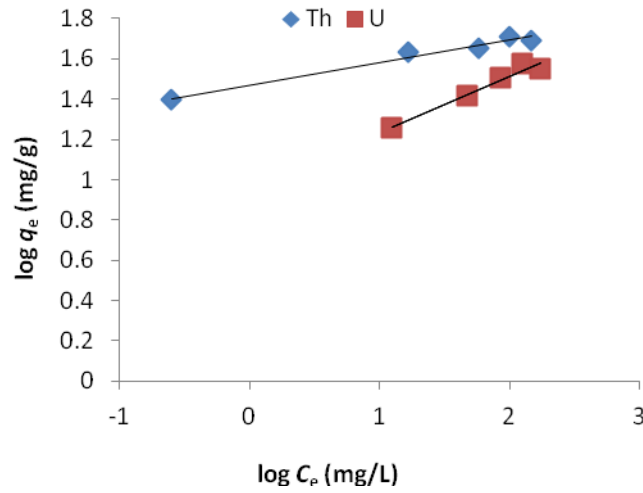


Fig. 12. Freundlich sorption isotherm of UO_2^{2+} and Th^{4+} ions sorption on glauconite.

Table 2

Isotherms constants and values of correlation factors (R^2) for sorption of Th^{4+} and UO_2^{2+} ions on glauconite.

Metal ion	Freundlich isotherm			Langmuir isotherm			
	$1/n$	$\log k$	R^2	Q_e (mg/g)	b (l/mg)	R^2	R_L
Th^{4+}	0.111	1.469	0.974	50	0.470	0.997	0.008
UO_2^{2+}	0.278	0.985	0.965	40	0.055	0.998	0.068

3.4. Thermodynamics studies

Thermodynamic parameters are calculated for this system using the following equations (Satpati et al., 2014; Ilaiyaraja et al., 2013).

$$\ln (K_d) = (\Delta S^0/R) - (\Delta H^0/RT) \quad (9)$$

$$K_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{m} \quad (10)$$

Where, K_d is distribution constant, ΔS^0 , ΔH^0 , R , and T are the entropy, enthalpy, gas constant, and temperature (K), respectively. C_0 and C_e are the initial and equilibrium concentrations (mg L^{-1}) respectively, V is the volume of the solution (mL) and m is the mass of glauconite (g).

The plot of $\ln K_d$ against $1/T$ is shown in Fig. 13. The values of enthalpy (ΔH°) and entropy (ΔS°) are obtained from the slope and intercept of the plot. The entropy and enthalpy values are used to calculate the Gibbs free energy (ΔG°) by using equation (11) (Satpati et al., 2014). The values of ΔH° , ΔS° and ΔG° are presented in Table 3.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (11)$$

In fact, the positive value of enthalpy change ΔH° for the processes further confirms the endothermic nature of the process, the positive entropy of sorption ΔS° reflects the affinity of the adsorbent material towards both elements. It is clear that the free energy for both elements adsorptions is negative indicating the feasibility of the process and its spontaneous nature without an induction period.

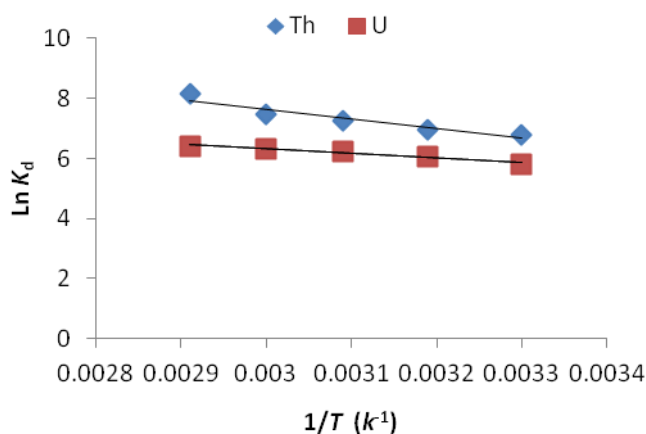


Fig. 13. Variation of $\ln K_d$ with $1/T$ for Th^{4+} and UO_2^{2+} ions sorption on glauconite.

Table 3

Thermodynamic parameters for sorption of Th^{4+} and UO_2^{2+} ions on glauconite.

Metal ion	ΔH° (kJ/mol)	ΔS° (kJ/mol.K)	ΔG° (kJ/mol)				
			303 K	313 K	323 K	333 K	343 K
Th^{4+}	27.230	0.145	-16.700	-18.160	-19.610	-21.100	-22.510
UO_2^{2+}	12.720	0.090	-14.550	-15.450	-16.350	-17.250	-18.150

3.5. Desorption studies

Desorption studies are conducted mainly for regenerating and reusing the adsorbent materials over a number of cycles. In the present study, different reagents

with different concentration from 0.1 to 4 M such as HCl, HNO₃, H₂SO₄, 0.1 M for oxalic acid and 0.9 M for NaCl are used as desorbing agents. At low concentration of acids, there wasn't loss in adsorbent material but, increasing the concentration of acid at 4 M may lead to dissolve the adsorbent material to 4%.

The metal ion loaded glauconite (dark green) is placed in the desorbing solution and is kept shaking for 10 min, as an equilibrium time. After the experiment, the suspension is filtered and analyzed to estimate the metal ion concentration. Figs. 14, 15 and 16 show the dependence of desorption on acid concentration. When the conc. of acids increased, the stripping percentage increased till constant at 1.5 M for HCl and 3 M for HNO₃ and H₂SO₄ which might be due to the exchange of sorbed metal ion with acidic proton.

Desorption is found to be changed from 0.00% for Th⁴⁺ ions to 53.3% for UO₂²⁺ ions loaded adsorbent when the concentration of oxalic acid was 0.1 M, and desorption is found to be changed from 0.00% for Th⁴⁺ ions to 38% for UO₂²⁺ ions loaded adsorbent when the concentration of NaCl was 0.9 M.

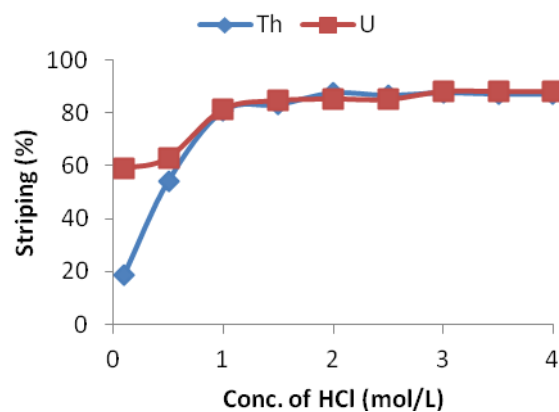


Fig. 14. Effect of HCl on stripping percentage of UO₂²⁺ and Th⁴⁺ ions from glauconite.

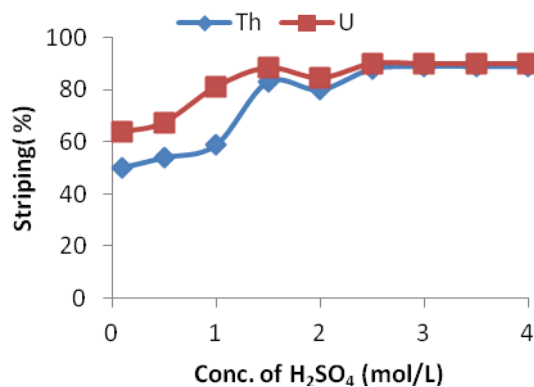


Fig. 15. Effect of H₂SO₄ on stripping percentage of UO₂²⁺ and Th⁴⁺ ions from glauconite.

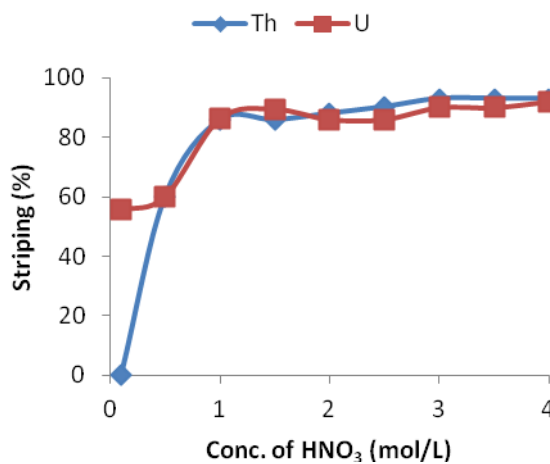


Fig. 16. Effect of HNO₃ on stripping percentage of UO₂²⁺ and Th⁴⁺ ions from glauconite.

4. Conclusions

- (I) Glauconite can be used as a highly effective low-cost adsorbent for the removal of Th⁴⁺ and UO₂²⁺ ions.
- (II) The adsorption of Th⁴⁺ and UO₂²⁺ ions on glauconite (dark green) depended on pH, contact time, concentration of metal ion, mass of adsorbent, interfering ions, and temperature.
- (III) The equilibrium reached to its maximum within 5 min of shaking.
- (IV) Equilibrium data are best fitted with Langmuir model.
- (V) Thermodynamic parameters indicated the present sorption process was endothermic and spontaneous.
- (VI) The Si-OH plays a dominant role in the adsorption process.

hermal treatment of glauconite (dark green & light green color) at 900 °C decreased its sorption efficiency.

(VIII) The adsorbed metal ions can be eluted using HCl, H₂SO₄, and HNO₃.

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الملخص العربي

إزالة واستعادة أيونات Th^{4+} و UO_2^{2+} من المحاليل المائية عن طريق الامتزاز على

الجلوكونيت (الأخضر الداكن)

بهاء أحمد صلاح- أحمد عزام- سعيد أنور سيد

كمادة طبيعية ومنخفضة التكلفة، تم تطبيق الجلوكونيت كمادة مازة لإزالة بعض من عناصر الأكتينيدات مثل UO_2^{2+} و Th^{4+} من محاليلها المائية. أحضرت عينتين مختلفتين من الجلوكونيت (أخضر داكن وأخضر الفاتح) من الواحات البحرية المصرية. ولقد تم دراسة العوامل المؤثرة على عملية الامتزاز للوصول إلى أفضل الظروف وهي الأس الهيدروجيني، وقت الرج، تركيز العنصر الأولى، جرعة المادة الممتزة، أيونات التداخل وأخيراً درجة الحرارة على الجلوكونيت (أخضر داكن) حيث أوضحت النتائج أن الاتزان وصل في خلال 5 دقائق عند pH 3. ولقد تم عمل مقارنة الامتصاص بين عينتان من الجلوكونيت (أخضر فاتح وأخضر داكن) ومعالجتهم حرارياً حيث أوضحت النتائج نقص في كفاءة الامتصاص في العينات المعالجة

حراريا وتشابهاً في كفاءة امتصاص الجلوكونيت الغير معالج حراريا لذلك حققت عينتان مختلفتان من الجلوكونيت (أخضر داكن وأخضر الفاتح) دور Si-OH في ميكانيكية الامتصاص. كذلك تم دراسة منحنيات الامتزاز لكل عنصر "Langmuir" أو "Freundlich". وجد ايضا أن عملية الامتزاز ملائمة لمنحنى "Langmuir" وأن سعة الامتصاص لعناصر UO_2^{2+} و Th^{4+} كانت 50 و 40 مجم/جم على التوالي وكذلك عوامل الديناميكية الحرارية لعناصر الأكتينيدات ومنها وجد أن جميع عمليات الامتزاز كانت ماصة للحرارة اي انها تزيد بزيادة درجة الحرارة. وتم دراسة عملية استرجاع هذه العناصر من على سطح المواد الممتازة باستخدام المحاليل المختلفة HCl , H_2SO_4 , $H_2C_2O_4$, HNO_3 . أوضحت النتائج العملية أن الجلوكونيت (أخضر داكن) يمكن تطبيقه بطريقة فعالة في تركيز و فصل ايونات UO_2^{2+} و Th^{4+} من محاليلهم المائية كما يمكن استخدامه كبديل للمواد الممتازة غالية الثمن.