



Fungal treatment for liquid waste containing U(VI) and Th(IV)

E.A. Ghoniemy^a, T.F. Mohammaden^b, M. Ramadan El-Shahat^c, M.A. Elkhawaga^a,
M. Mahmoud Rezk^{b,*}, M. Morsi Wessam^b

^a Botany and Microbiology Department, Faculty of Science (Girls), Al-Azhar University, Egypt

^b Isotopes Department, Nuclear Materials Authority, Egypt

^c Faculty of Agriculture, Ain Shams University, Egypt

ARTICLE INFO

Article history:

Received 16 November 2019

Received in revised form 1 March 2020

Accepted 13 May 2020

Keywords:

Fungal

Biosorption

Liquid waste

Radioelements

ABSTRACT

Four fungal and one bacterial isolates were isolated from a liquid waste sample of Nuclear Material Authority. Those dried biomasses were screened for uranium (U) and thorium (Th) adsorption efficiency where the most potent isolate was identified according to sequence similarities and phylogenetic analysis as *Aspergillus niger* LBM 134. Using U or Th synthetic solutions many factors were investigated for controlling the biosorption process to conduct the optimum process conditions (the solution pH, contact time, elemental initial concentration, biomass dosage, and sorption temperature). *A. niger* LBM 134 dried biomass was examined ESEM-EDX and the FTIR techniques before and after the sorption process, also the data were handled by different kinetics and isothermal models. Application on the real liquid waste revealed that the bio-uptake capacities were 18.5 and 11.1 mg/g for U and Th respectively.

© 2020 Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Although the useful and peaceful applications of radioactive elements, if they discharged improperly to the environment, they can be detrimental to the living species (including man). With the progressive using of the radio elements, radioactive pollution became a serious environmental issue and dragged the efforts of many workers [1–4]. Large amounts of wastewater containing uranium (U) and Thorium (Th) result from different nuclear activities e.g. the nuclear power plants, mining of the radioactive-ores, the milling processes and even from the laboratories [5,6]. Disposing of these polluted liquid wastes to the environment causes a potential reaching of uranium and thorium to top of the food chain, hence can be ingested by humans causing several serious health problems such as; severe kidney and/or liver damage, bone marrow cancer, leukemia and even death [7–10].

Many conventional methods were employed to treat the polluted effluents and remove or even minimize the concentration of the included pollutants. Chemical precipitation and ion exchange are the most used treatment technologies, but oxidation/reduction, filtration, electrochemical treatment, reverse osmosis and membrane technologies are also common [2,11,12]. Unfortunately, when the pollutant concentrations are low, these techniques have an excessive cost and are not efficient enough; in addition, they deliver sludge disposal

problems [13]. In this regard, the biological treatment appears the optimal solution overcoming the weak points of the other conventional techniques where it is eco-friendly, cost-effective and high efficient [14,15]. The microorganisms can uptake radioactive and heavy metal ions either actively (bioaccumulation) and/or passively (biosorption). Biosorption refers to the passive metal ions uptake by different forms of biomass, which may be dead or alive.

The dried microorganisms as metal-removal agents have many advantages such as; less sensitive to metal ion concentration (toxicity effects), operate at ambient conditions of pH and temperature, result in controlled chemical or biological sludge volume, supplying of nutrients is not required as well as they can also be procured from industrial sources as a waste product from the fermentation processes [5,16].

The current work was designed to contribute to the environmental protection issue via treating the liquid waste that resulted from the activities of the Egyptian Nuclear Materials Authority's laboratories (NMA). This waste contains U and Th ions (in addition to some heavy metals) concentration levels by which it cannot be discharged to the surroundings without the proper treatment. So, the dried fungal biomass was employed as a sorption agent for U and Th from the concerned liquid waste.

2. Materials and methods

2.1. Sample collection and analysis

The liquid waste sample was gathered in polyvinyl chloride (PVC) containers of 20-liter volume from different uranium (U) and

* Corresponding author.

E-mail address: DDRezk@yahoo.com (M. M. Rezk).

thorium (Th) processing laboratories in the Egyptian Nuclear Material Authority. The collected liquid waste was subjected to chemical analysis before and after its treatment with dried fungal biomass using the inductively coupled plasma emission spectroscopy (ICP-ES) to identify the type and concentrations of the involved metals as well as verify the effect of the used biomass.

2.2. Isolation and purification of metal tolerant microorganisms

2.2.1. Media preparation

The used media in growth and isolation of microorganisms is Czapek-Dox agar media for fungi [17]. This media is composed of NaNO_3 (g/L), KH_2PO_4 (2 g/L), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (0.5 g/L), KCl (0.5 g/L), $\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$ (traces), sucrose (30 g/L) and agar (15 g/L) then, the pH of the medium was adjusted to 4–6. The media was sterilized by autoclaving at 15 psi for 15 min.

2.2.2. Microorganisms isolation and purification

An appropriate amount of the collected liquid waste poured into the prepared Czapek-Dox media spatula spray technique according to Elwan and El-Sayed [17]. The plates were then incubated for 7 days at 30 °C after which colonies of fungi and bacteria were isolated, purified by streaking several times on Dox agar medium until pure cultures obtained then subculture on slants of the same medium for preservation.

2.2.3. Biomass preparation

The microbial isolates inoculated into the Czapek-Dox broth (The same media without agar) medium and incubated for 7 days at 30 ± 2 °C. The mycelial biomass was harvested and dried at 70 °C in the dryness oven.

2.3. Selection of the most effective microorganisms

The dried biomasses were tested for their U or Th adsorption capacities from synthetic solution under the following fixed conditions; 0.5 g of each dried biomass, U or Th standard solution of 100 mg/L, pH 4.5 (similar to the media pH), contact time 30 min at room temperature. The most potent biosorption microorganism was identified.

2.4. Identification of the selected fungus

The most potent tolerant fungus was identified on the basis of macroscopic (colonial morphology, color, texture, shape, diameter and appearance of colony) and microscopic characters (septation in mycelium, presence of specific reproductive structures, shape and structure of conidia) [18–20]. The identification was confirmed through the 18S rRNA gene sequencing and phylogenetic analysis. The fungus was transferred to Czapek Dox media and incubated with shaking (180 revs/min) at 25 ± 2 °C for 7 days. Mycelia were collected by centrifugation and DNA was extracted. Purified DNA was subjected to PCR amplification using primers ITS1 and ITS4. Fungal identification methods were based on their internal transcribed spacer ribosomal DNA (ITS-rDNA) sequences. A pair of primers ITS1 (5'-TCC GTA GGT GAA CCT GCG G-3') and ITS4 (5'-TCC TCC GCT TAT TGA TAT GC-3') was used for ITS-rDNA amplification [21]. Sequence data was analyzed in the Gene Bank database by using the BLAST program available on the National Center for Biotechnology Information website (www.ncbi.nlm.nih.gov). The unknown sequence was compared to all of the sequences in the database to assess the DNA similarities. Alignment and molecular phylogeny were evaluated using Bio Edit software. Purification and sequencing of PCR products for the isolate under study were performed in the Sigma company of scientific service.

2.5. Metals analysis

The uranium content in the liquid waste was chemically determined using the inductively coupled plasma emission spectroscopy (ICP-ES) while the titration technique was used for uranium determination all over the batch experiments according to the method described by Davies and Gray [22]. On the other hand, the thorium content was estimated spectrophotometrically at λ_{max} 654 nm [23].

2.6. Stock solution preparation

For the experimental studies, stock standard solutions (1000 mg/L) of both U and Th were prepared using uranyl acetate and thorium nitrate. A uranium stock solution containing 1000 mg/L of U(VI) was prepared by dissolving 1.782 g of uranyl acetate in 1% nitric acid solution (100 mL) and diluting to 1000 mL. A thorium stock solution containing 1000 mg/L of Th(IV) was prepared by dissolving 2.46 g of thorium nitrate in a 1000 mL solution. The pH values of the working solutions were adjusted using NaOH or HNO_3 (0.01 M). A series of standard solutions of gradual lower concentrations from both elements were prepared. The standard solutions were separately sterilized for 15 min at 110 °C at 21 lbs.

2.7. Factors controlling the biosorption process

2.7.1. Effect of pH

The biosorption experiments were applied at different pH values ranging from 1 to 9 to determine the effect of pH on the sorption process. Under the fixed condition of 0.5 g of dried biomass, U or Th standard solution of 100 mg/L, pH 4.5 and contact time 30 min at room temperature

2.7.2. Effect of contact time

The effect of contact time on the biosorption process was investigated in the range of 5–60 min for both elements. Under the fixed condition of 0.5 g of dried biomass, U or Th standard solution of 100 mg/L, at room temperature and the achieved optimum pH.

2.7.3. Effect of U and Th initial concentration

The effect of the initial concentration of U and Th on the biosorption process was examined in the range of 50 to 350 and 10–200 mg/L for both uranium and thorium respectively. Under optimum values of pH and contact time achieved from the above experiments in parallel with 0.5 g of dried biomass and U or Th standard solution of 100 mg/L.

2.7.4. Effect of biomass dosage

The influence of the dried biomass dosage on the biosorption process was tested using the dosage range of 0.1–1.5 g/100 mL solution.

2.7.5. Effect of temperature

The temperature range of 20–100 °C was applied to investigate the effect of working temperature on uranium and thorium biosorption. The experiment was carried out under optimum conditions of pH, initial U or Th concentrations, time and dosage.

2.8. Batch biosorption procedure

It is worth to mention that for all the experiments; the dried biomass was mixed with the U or Th solutions in the Erlenmeyer flasks of 250 mL volume under the designed experimental conditions. The flasks were inoculated and shacked at 200 rpm using the rotary shaker for the desired times then the mixtures were filtered by Whatman filter paper (18.5 cm Ash 44) where both

U or Th concentrations were chemically measured in the filtrates. The removal percentage of metal ions and the equilibrium uptake of dried biomass were calculated [24–26].

$$q_e = (C_i - C_e) V/m \quad (1)$$

$$E (\%) = ((C_i - C_e)/C_i) * 100 \quad (2)$$

Where q_e = equilibrium uptake of dried biomass

C_i = initial concentration of metallic ions (mg/L);

C_e = final concentration of metal ions (mg/L);

m = dried mass of the bio-sorbent in the reaction (g);

V = volume of the reaction mixture (L).

E = Removal percent

2.9. Kinetic experiments

Kinetic data were obtained at different time points (0–60 min). The adsorption kinetic data were analyzed using pseudo-first and pseudo-second-order kinetic models [27,28] as follow:

$$\text{Pseudo-First-Order: } \log (q_e - q_t) = \log (q_{1st}) - k_1/2.303 t \quad (3)$$

$$\text{Pseudo-Second-Order: } t/q_t = 1/k_2 q_{2nd}^2 + 1/q_{2nd} t \quad (4)$$

Where q_t is the experimental adsorption capacity at the time (t), q_{1st} and q_{2nd} are the calculated adsorption capacity from the Pseudo-First-Order and Pseudo-Second-Order models (mg/g) respectively,

k_1 (min^{-1}) and k_2 (g/mg min) is the rate of Pseudo-First-Order and Pseudo-Second-Order models respectively.

The straight-line plot of $\log (q_e - q_t)$ against t gives $\log (q_e)$ as slope and intercept equal to $k_1/2.303$. Hence the amount of solute sorbed per gram of sorbent at equilibrium (q_e) and the first-order sorption rate constant (k_1) can be evaluated from the slope and the intercept.

2.10. Adsorption isotherm

Adsorption isotherm was carried out with different initial concentrations of U or Th (0–350 mg/L) and (0–200 mg/L) respectively, at room temperature of 25 ± 2 °C. The obtained experimental data were tested with the linearized form of Langmuir (used to describe the solid phase adsorption system) and Freundlich (indicator for multilayer adsorption on a heterogeneous adsorbent surface) isotherm models [29,30]. The linear form of Langmuir adsorption isotherm is expressed by the following equation [31–34]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_L} + \frac{1}{K_L q_L} \quad (5)$$

where q_L is the Langmuir maximum adsorption capacity (mg/g)

K_L is the Langmuir binding constant.

The linear form of the Freundlich model is as follows.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

Where K_F and $1/n$ are constants related to theoretical adsorption capacity and intensity of adsorbent/adsorbate binding, respectively.

2.11. Desorption of loaded metals

Several desorbing agents were individually tested for the efficient elution of the loaded metals from the dried biomass. The employed desorbing materials included; Na_2CO_3 (1 mol/L), NaCl (1 mol/L), H_2SO_4 (1 mol/L) and HCl (1 mol/L). The experiments were carried out

using 0.2 or 0.3 g of the biomass (for U or Th, respectively) and 100 mL of the desorbing solution where the mixture was put into Erlenmeyer flask then shaken for 30 min at room temperature.

The best desorbing material was tested for its most efficient concentration at different molarities (0.5, 1, 1.5, 2 and 2.5 mol/L) under similar conditions as mentioned above.

2.12. Biomass reusability

The dried biomass reusability was tested by successive adsorption and desorption cycles. The desorption process was carried out using the efficient concentration of desorbing material for U and Th, and the adsorption efficiency was estimated at the end of each cycle.

2.13. Environmental scanning electron microscope (ESEM)

The surface features of the dried biomass before and after the adsorption process were investigated using the Environmental Scanning Electron Microscope (ESEM), Philips type model XL30 which attached to Energy Dispersive X-ray unit (EDX) and hold in the Nuclear Materials Authority laboratory.

2.14. FTIR spectroscopy

Fourier transforms infrared (FTIR) spectroscopy was employed to identify the functional groups of the biomass wall that can be involved in the metal ions binding. The unloaded and loaded dried biomass was initially blended with the potassium bromide (KBr) then subjected to the investigation by the FTIR instrument that works in the range of 400 to 4000 cm^{-1} (Thermo scientific type, model NICOLET-iS10, USA). The Fourier transform infrared (FTIR) spectroscopy instruments are held in the NMA laboratory.

2.15. Environmental protection and metal recovery

For environmental, economic and strategic purposes, the adsorbed U or Th were recovered. For uranium recovery, the loaded biomass was burned at 550 °C for 2 h in the muffle furnace. After cooling, the residue was dissolved in conc. H_2SO_4 and the pH was adjusted at 2.5 using 1 M NaOH, then H_2O_2 solution (30 %) was excessively added causing precipitation of the pale-yellow colored product. The precipitated product was filtered, dried and identified using the ESEM-EDX. For thorium recovery, the loaded biomass was burned at 850 °C for 2 h in the muffle furnace and after cooling the residue was directly identified by the ESEM-EDX

3. Results and discussion

3.1. Adsorption capacities of microbial isolates

The microbial isolates were categorized into four fungal types assigned as F1, F2, F3, and F4 in addition to one bacterial species. The dried biomasses of the purified microbial isolates were examined for their U and Th adsorption efficiency under the following fixed conditions; 0.5 g of each dried biomass, U or Th standard solution of 100 mg/L, pH 4.5 (similar to the media pH), contact time 30 min at room temperature. As shown in the Table 1 the dried biomass of fungal isolate (F4) gave the highest adsorption percentage. So, this fungus was selected as the most potent biosorption and be used for further studies.

3.2. Identification of the selected fungus

Micro-morphological studies of fungal isolate, F4 using a light microscope revealed that the fungal isolate grew rapidly on the Czapek Dox medium at 28 ± 2 °C, reaching a size of 5–7 cm in 5–7

Table 1
The adsorption efficiency percentage of microbial isolates dried biomass.

Dried biomass of Microbial	Isolates	F1	F2	F3	F4
Adsorption Efficiency (%)	U	60	64	69	75
	Th	57	56	42.5	60

days. The mycelium surface was velvety and smooth with regular radial ornamentation. The spores had ahead of carbon black color and without any transudate. The reverse of the fungus appeared colorless then yellow to yellow-brownish. The vesicle was globose or subglobose with a diameter of 28 μm . The conidiophore was globular with a diameter of 9.5 μm . The size of Uniseriate Sterigmata was in the range of (7.7 \times 4.5 μm). The spores are subglobose with a diameter of 3.5 μm . To confirm the identification of fungal isolate, the 18S rRNA gene sequencing and phylogenetic analysis were used. The 18S rRNA gene sequencing was compared with the sequence of *Aspergillus* sp. through multiple sequence alignment. Experimental analysis of PCR amplification was studied through agarose gel electrophoresis. Fig. 1 shows the phylogenetic tree of the fungal isolate, which showed that the isolate was closed to *Aspergillus niger* strain LBM 134 by 100 % identity.

3.3. Factors controlling the biosorption process

3.3.1. Effect of different pH

Fig. 2 shows that both uranium or thorium uptake capacities by *A. niger* dried biomass exhibited ascending trend with the pH increasing till they reached their maximum uptake capacities of

both U or Th at pH 4. Uranium mainly present as uranyl cation (UO_2^{2+}) at pH 1–4, over this pH uranium begins to form different anionic and cationic species followed by precipitate [25,27,32,35] Where, thorium present as thorium cation (Th^{4+}) at pH 1–4, over this pH thorium, begins to precipitate [36]. The suggested mechanism of the adsorption process is the interaction between cation species of adsorbate (U or Th) with the active site on the *A. niger* through chelation or electrostatic attractions (the pH influences both U and Th speciation in the aqueous solution and the binding sites present on the biomass surface [2,37,38]. Other workers pointed to that, the pH 4 is the optimum value delivering the favorable sorption of the latter Th species [39] (Fig. 3).

3.3.2. Effect of contact time

The time dependence of the adsorption process is carried out mainly for two purposes; to reveal the applicability of the adsorption process and to predict the adsorption mechanism. So, studying the effect of contact time on the adsorption process is essential to determine the optimum operating conditions for the full-scale batch reactor. The results indicated that the adsorption of both U and Th passed through two successive phases (Fig. 4). The first phase showed a rapid increase in their adsorption by the dried biomass with increasing the contact time till reaching the maximum adsorption capacities at 30 and 20 min for both U and Th respectively. Such behavior can be interpreted due to the dissociation of the metal-ions/hydronium-ions complexes followed by the interaction of metal ions with microbial functional groups [40]. Also, the availability of a large number of vacant surface sites permits rapid adsorption of the metal ions. Other workers believed that since biosorption is a metabolism independent process, it would be expected to be a very fast reaction [41,42]. On the other hand, the second phase revealed decreasing of the

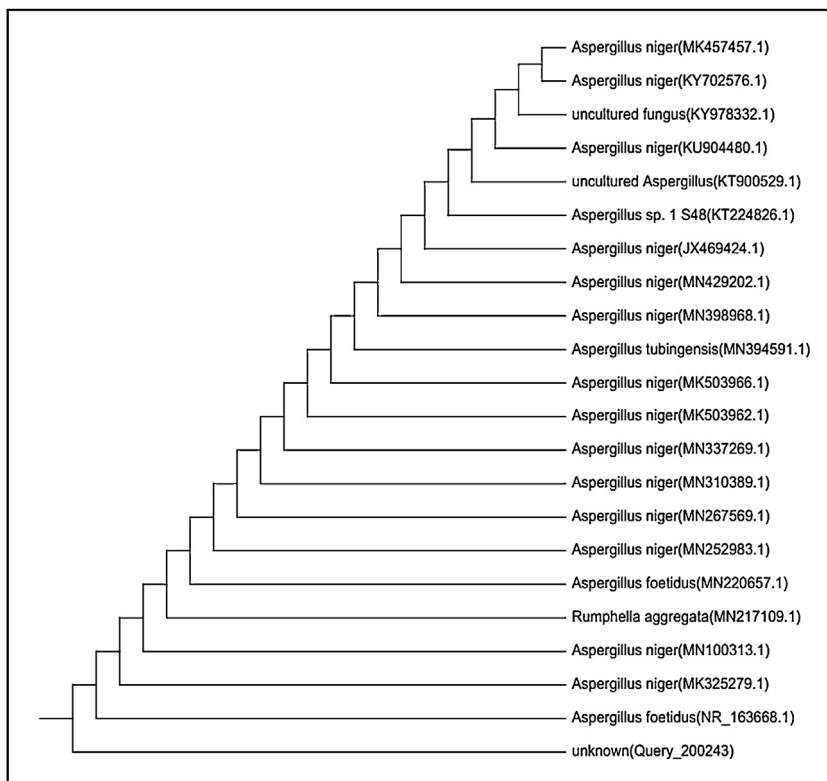


Fig. 1. The phylogenetic tree of the *Aspergillus niger* strain MK457457.1.

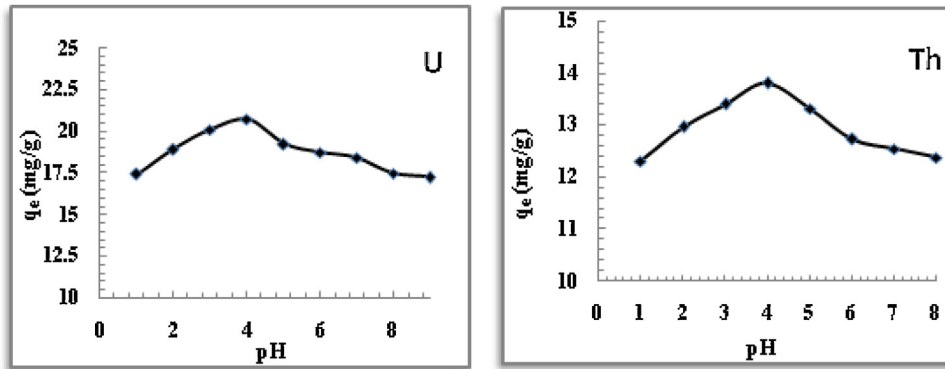


Fig. 2. Effect of different pH values on U or Th adsorption processes onto *A. niger* dried biomass.

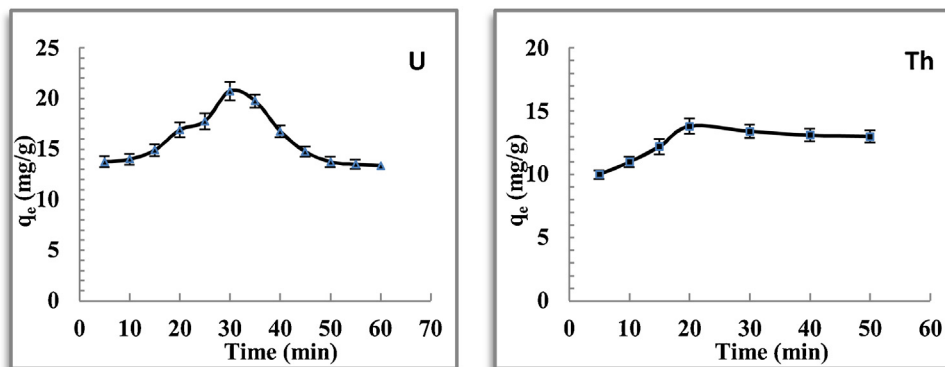


Fig. 3. Effect of different contact times on the U and Th adsorption process onto *A. niger* dried biomass.

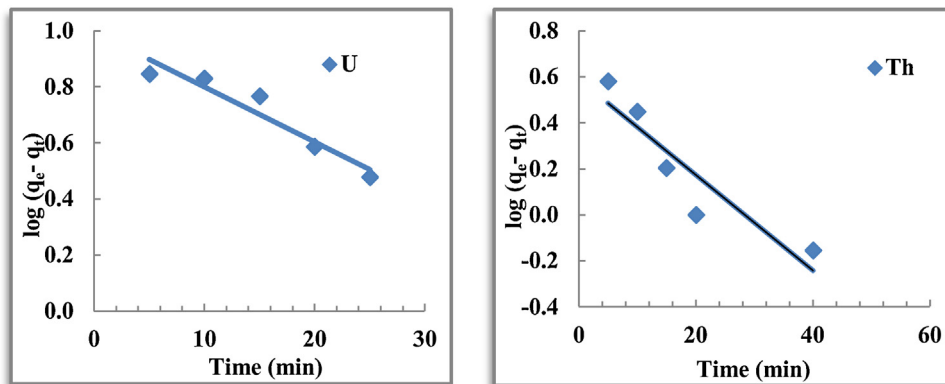


Fig. 4. Pseudo first-order model for U and Th adsorption onto *A. niger* dried biomass.

metals adsorption with increasing of the contact time more than the optimum values which are likely ascribed to the limited number of remaining vacant surface sites as well as the repulsive forces between the adsorbed ions and those ions in the bulk phase.

3.4. Adsorption kinetics

The kinetic studies are of great importance for both gaining insights on the physical chemistry of the adsorption processes and on the design of sorption systems. The kinetics characteristic of the

Table 2

Kinetic data for the adsorption of uranium and thorium ions onto *A. niger* dried biomass.

Kinetic model	Parameters	U	Th
Experimental	q_e (mg/g)	20.75	13.8
Pseudo first order	q_{1st} (mg/g)	9.87	3.61
	k_1 (min^{-1})	0.27	0.046
	R^2	0.91	0.847
Pseudo second order	q_{2nd} (mg/g)	23.26	13.51
	K_2 (g/mg.min)	0.007	0.052
	R^2	0.968	0.997

adsorption process is important to clarify the rate and mechanism of the adsorption reaction. The fast biosorption kinetics observed initially is typical for the biosorption process involving no energy mediated reactions and metal removal from solution are due to purely physicochemical interactions between biomass and metal solution [43,44]. Kinetic models test the experimental data as a function for heterogeneity of the adsorbent surface and the metal removal rate in order to design appropriate sorption processes. The sorption kinetic models used in this study include pseudo-first-order and pseudo-second-order.

The obtained q_e , q_{cal} and R^2 values of both uranium and thorium point to that adsorption of both metals onto the *A. niger* (dried biomass) follow the pseudo-second-order rather than pseudo-first-order that suggests the adsorption rate depends on the properties of both adsorbate and adsorbent (Table 2 and Figs. 5 and 6).

3.4.1. Effect of U or Th initial concentration

Studying the effect of initial metal ion concentration is important to understand and describe the mass transfer resistance of the metal ions between the aqueous and the adsorbent solid

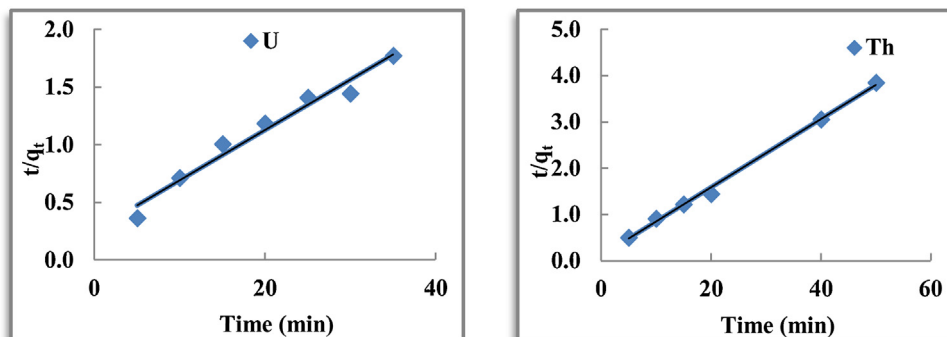


Fig. 5. Pseudo Second-order model for U and Th adsorption onto *A. niger* dried biomass.

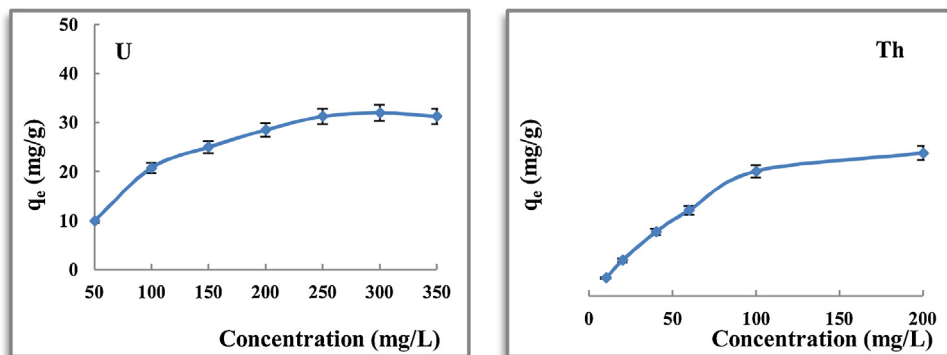


Fig. 6. Effect of U and Th initial concentrations on adsorption process onto *A. niger* dried biomass.

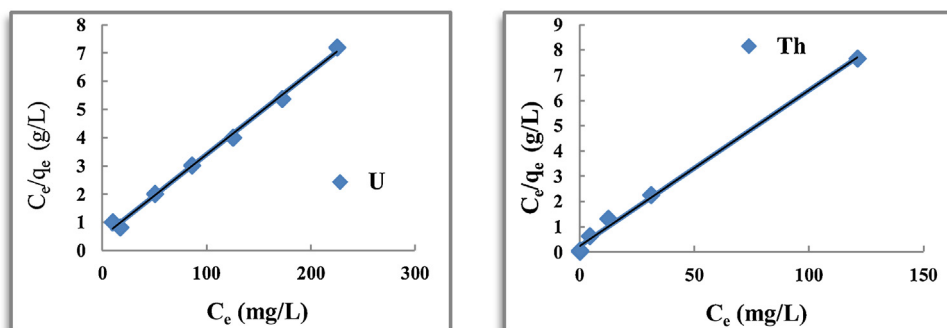


Fig. 7. Langmuir isotherm models for the U or Th adsorption onto *A. niger* dried biomass.

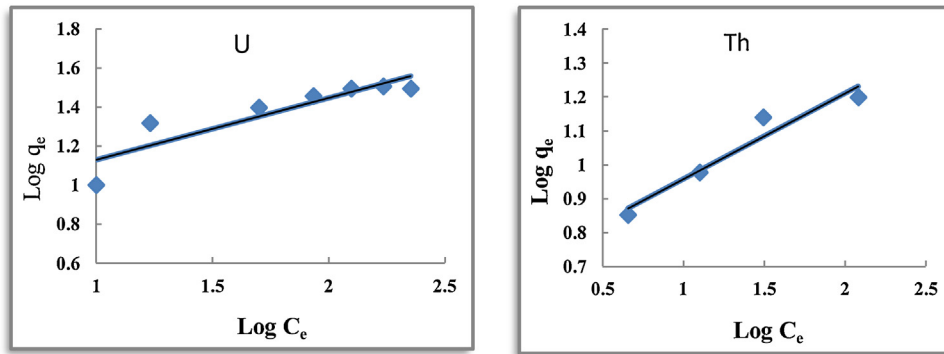


Fig. 8. Freundlich isotherm models for the U or Th adsorption onto *A.niger* dried biomass.

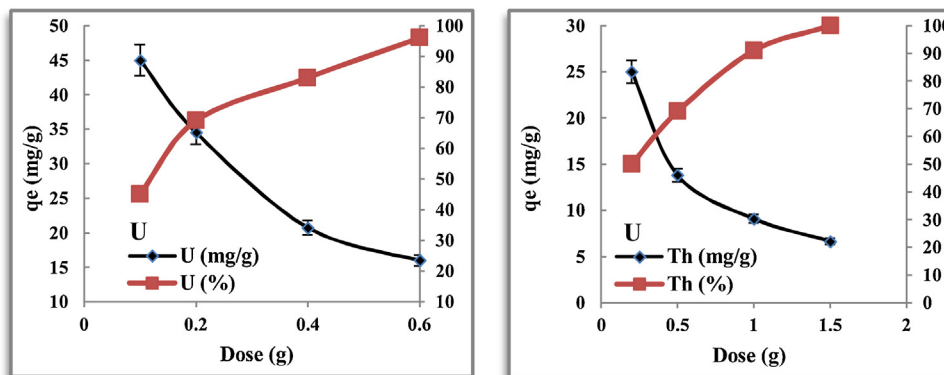


Fig. 9. Effect of *A. niger* dried biomass dosage on the biosorption processes of U and Th.

phases. The adsorption capacity of U or Th ions by the used biomass with the varied ion concentrations showed a proportional trend (Fig. 7) where the maximum uptake capacities were 32 % and 13.8 % at initial concentrations of 300 and 100 ppm for U and Th respectively. Increasing of U and Th uptake with increasing of their initial concentrations could be attributed to enhancing the mass transfer driving force hence, increasing the metal ions adsorbed per unit weight of adsorbent at equilibrium [45]. In addition, increasing initial U and Th concentration permits increasing the number of collisions between these ions and the adsorbent surface which also enhances the adsorption process.

3.5. Adsorption isotherms

The experimental results were treated according to different adsorption models to verify the adsorption parameters that drive the adsorption process. Adsorption isotherms were carried out with different initial concentrations of uranium and thorium ion varying from 10 to 100 mg/L. The obtained experimental data were tested with the linearized form of Langmuir (used to describe the solid phase adsorption systems) and Freundlich (indicator for multilayer adsorption on a heterogeneous adsorbent surface) isotherms models.

The adsorption isotherms of U or Th obtained at 25 °C were plotted according to Langmuir and Freundlich models (Figs. 8 and 9

respectively) while the estimated and calculated parameters from both models were illustrated in the Table 3.

Comparing the experimental adsorption capacities “ q_e ” of both U and Th with the “ q_L ” and “ K_F ” from Langmuir and Freundlich models respectively as well as the regression coefficient “ R^2 ” values obtained from both models, it can be concluded that the adsorption process of both U and Th by the *A. niger* dried biomass follows the Langmuir isotherm model. The better fitting of the Langmuir model for both ions suggests the monolayer U or Th binding onto the employed biomass and no interaction between the sorbed ions. Also, the preferential distribution of U and Th on the solid biomass surface rather than in the liquid sorbate phase is

Table 3

Data estimated from the adsorption isotherms of U or Th biosorption process onto *A. niger* dried biomass.

Isotherms model	Parameters	U	Th	Temp.
Experimental	q_e (mg/g)	32	15.8	298 K
Langmuir	q_L (mg/g)	34.48	16.39	
	K_L (L/mg)	0.058	0.25	
	R^2	1.0	0.99	
Freundlich	K_F (mg/g)	6.472	5.093	298 K
	N	3.15	3.98	
	R^2	0.81	0.94	

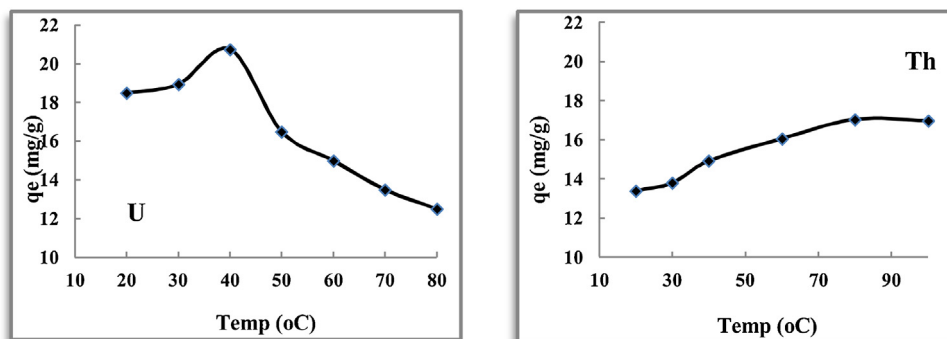


Fig. 10. Effect of temperature on U and Th biosorption process onto *A. niger* dried biomass.

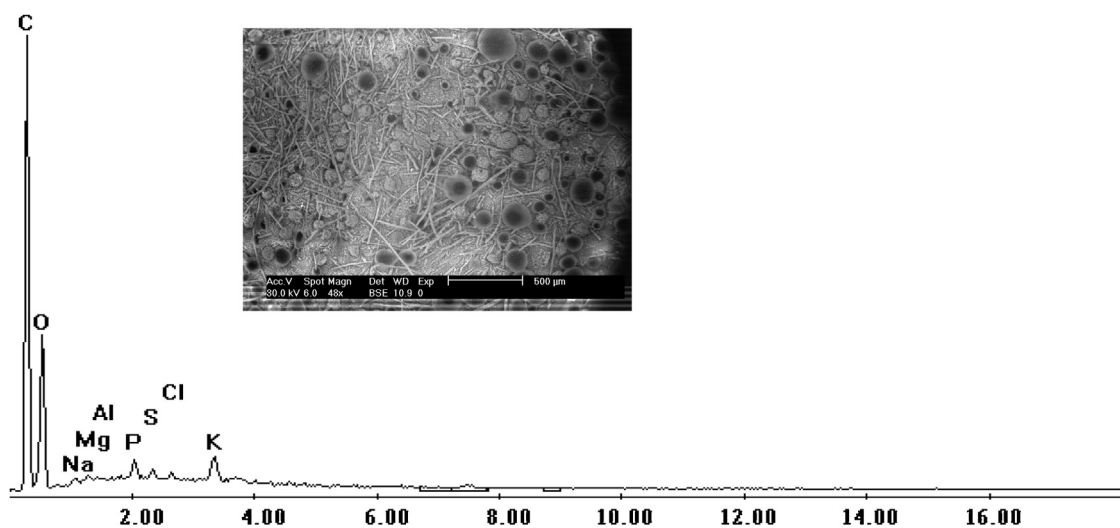


Fig. 11. ESEM-EDX chart showing the surface shape of the *A. niger* before the adsorption process were no signs for bonded metals.

highly suggested and means that the adsorption process is controlled by the monolayer coverage system.

3.6. Effect of dried biomass dosage

As shown in Fig. 10, the binary relation between the uptake capacity (q_e mg/g) of either uranium or thorium and the dried biomass dosage the maximum uptake capacity was obtained at 0.2 and 0.3 g of the biomass dosage with uranium and thorium respectively. Biomass dosage over those values was accompanied by decreasing of the uptake capacity. The dried biomass dosage plays an essential role in the metal ions sorption and it is reasonable as increasing of biomass dose as increasing of the metal removal percentage from the bearing liquid waste or solutions. This relation seems logical due to the more availability of the biomass binding sites with increasing of the adsorbent dosage [46]. However, more important and effective metal-adsorption meaning should be considered during the investigation of this factor, which called the uptake capacity, (mg/L) that refers to the capability of

the adsorbent to be loaded by the adsorbate. Such a phenomenon could be ascribed to that the high biomass dosage causes the formation of cell aggregates, thereby reducing the effective biosorption area, or maybe lead to interference between binding sites [43,47,48].

3.7. Effect of temperature

The results clarified in Fig. 11 indicated that the best uptake capacities of U and Th with the temperature variation were obtained at 40 and 80 °C respectively. Although an increasing of Th-uptake with temperature elevation was observed it was non-significant comparing to the consumed energy while the U-uptake showed marked decreasing with all the tested temperatures above the optimum one.

The reason for decreasing the uptake capacities of both U and Th with temperature above than the optimum degrees may be ascribed to a weak interaction between these ions and the biomass binding sites, these weak interactions might be Vander-Waal's

Table 4Effect of the different eluting agents on desorption of U and Th from *A. niger* dried biomass.

Eluting agents	(1 M)	NaCl	H ₂ SO ₄	HCl	Na ₂ CO ₃	HNO ₃
Metal desorption %	U	60	91.9	84	83.84	90
	Th	50	83	62	73.56	81

Table 5Effect of different sulfuric acid concentrations on desorption of U and Th from *A. niger* dried biomass.

Different concentrations of H ₂ SO ₄ (M)	Metal desorption %	
	U	Th
0.5	83.8	62.8
1	91.9	83
1.5	96.9	75
2	84	76
2.5	83	70

Table 6

Effect of multiple sorption/desorption cycles on the uptake efficiency.

qe (mg/g)	Sorption/desorption cycles				
	1 st	2 nd	3 rd	4 th	5 th
U	20.75	18.25	17.00	11.25	08.13
Th	13.80	13.40	12.60	10.00	08.00

interactions, hydrogen bonding . . . etc., which are broken at high temperatures. Also, some workers pointed to that biosorption of some metals become an energy independent's mechanism at high temperatures and experienced a significant reduction after the optimum temperature was reached.

Expectedly, the temperature increasing usually enhances the biosorption capacity by increasing the surface activity and kinetic

energy of the adsorbate but may damage the physical structure of biosorbent [29]. However, for many biosorption processes, metal uptake is influenced to a limited extent within a certain range of temperature because physicochemical processes such as ion exchange exist largely in biosorption consequently; the temperature was found to have a minor effect on the accumulation of metals.

3.8. Desorption of loaded metals

Under the adsorption optimum conditions, the loaded *A. niger* was subjected to the desorption. The different tested desorbing agents revealed that H₂SO₄ (1 M) is the most efficient one where it gave desorption percent for U and Th reached 91.9 and 83 % respectively (Table 4). On the other hand, testing of various sulfuric acid-concentrations illustrated that 1.5 and 1 M are the optimum concentrations giving desorption efficiencies 96.9 and 83 % for U or Th respectively (Table 5).

3.9. Biomass reusability

The successive adsorption/desorption cycles indicated that the dried *A. niger* behaves as an effective bio-sorbent for the 3rd cycle for both uranium and thorium removal (Table 6). Such results encourage using of the dried *A. niger* to reduce the capital cost accompanying by efficient pollutants removal from the liquid wastes.

3.10. The biomass changes accompanied the adsorption process

Verifying changes of the biomass surface and functional groups due to uranium and thorium adsorption was attained by exposing the dried biomass (before and after adsorption process) for investigation using the environmental scanning electron microscope-energy dispersive X-ray (ESEM-EDX) and the Fourier transform infrared spectroscopy (FTIR).

3.10.1. ESEM-EDX investigation

Changing of *A. niger* surface shape before and after sorption of U and Th and the elemental analysis of the loaded ions were investigated by the ESEM-EDX (Figs. 12–14). Both criteria verified

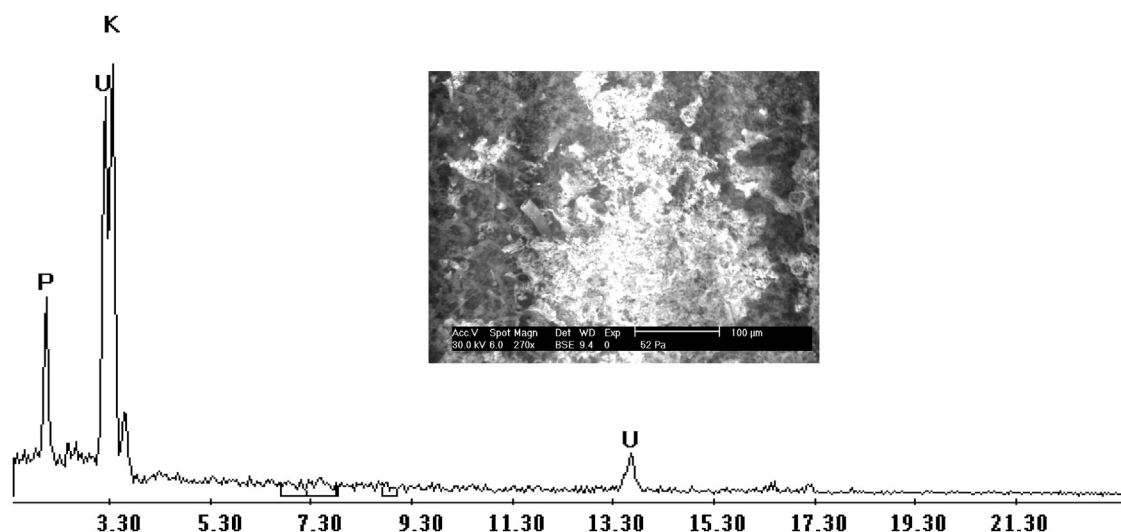


Fig. 12. ESEM-EDX chart showing changes of *A. niger* surface morphology due to adsorption of U ions.

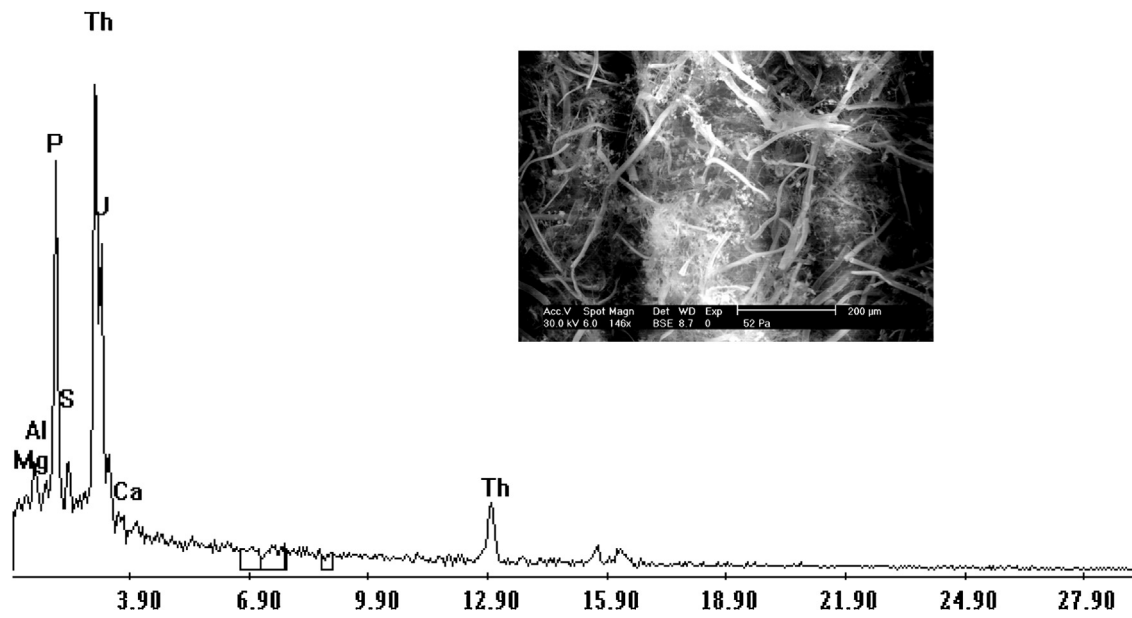


Fig. 13. ESEM-EDX chart showing changes of *A. niger* surface morphology due to adsorption of Th ions.

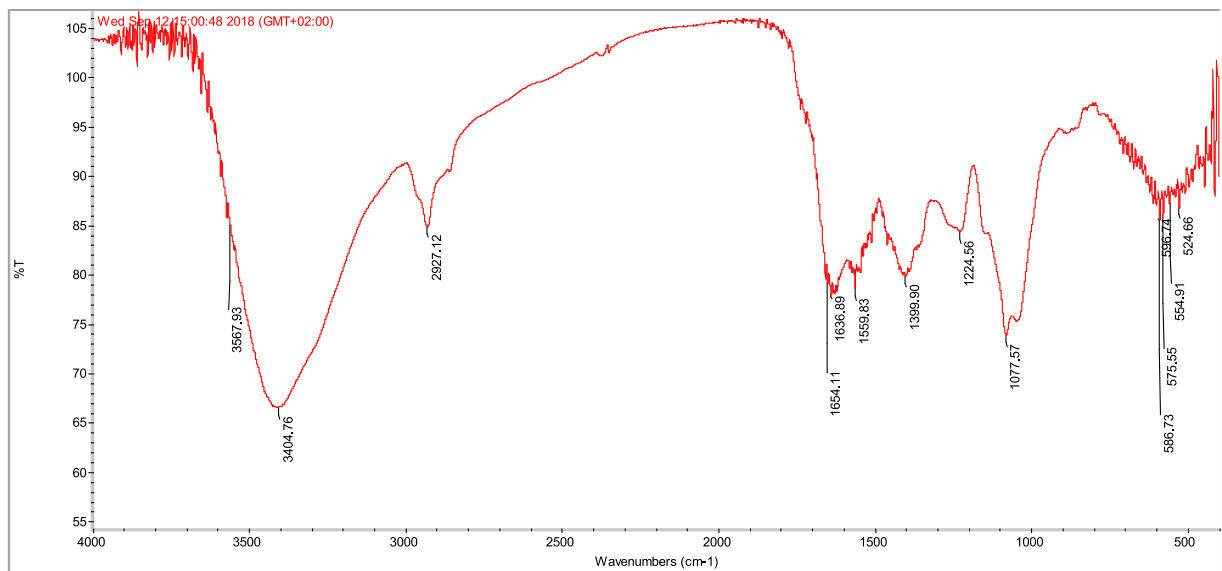


Fig. 14. The FTIR spectra of the unloaded *A. niger*.

Table 7
The functional groups and their wavelengths before and after sorption of U and Th.

Functional group	Wavelength (cm ⁻¹)		
	Before sorption	After U-sorption	After Th-sorption
O H	3567.93	3422.47	3650.26
C H	2927.1	2925.23	2925.38
C=O	1654.11	1745.51	1744.53
C-O	1399.90 - 1077.57	1375.56 - 1034.85	1419.55 - 1034.85

the success sorption process by the used biomass where the morphological changes are attributed to the sorption of both U and Th on the binding sites of the biomass.

3.10.2. FTIR investigation

FTIR is usually used to identify the functional groups in the tested materials [49]. The FTIR spectra illustrated the positions and intensities of the functional group's peaks before and after the sorption processes (Table 7 and Figs. 15–17). The noticed shifting of

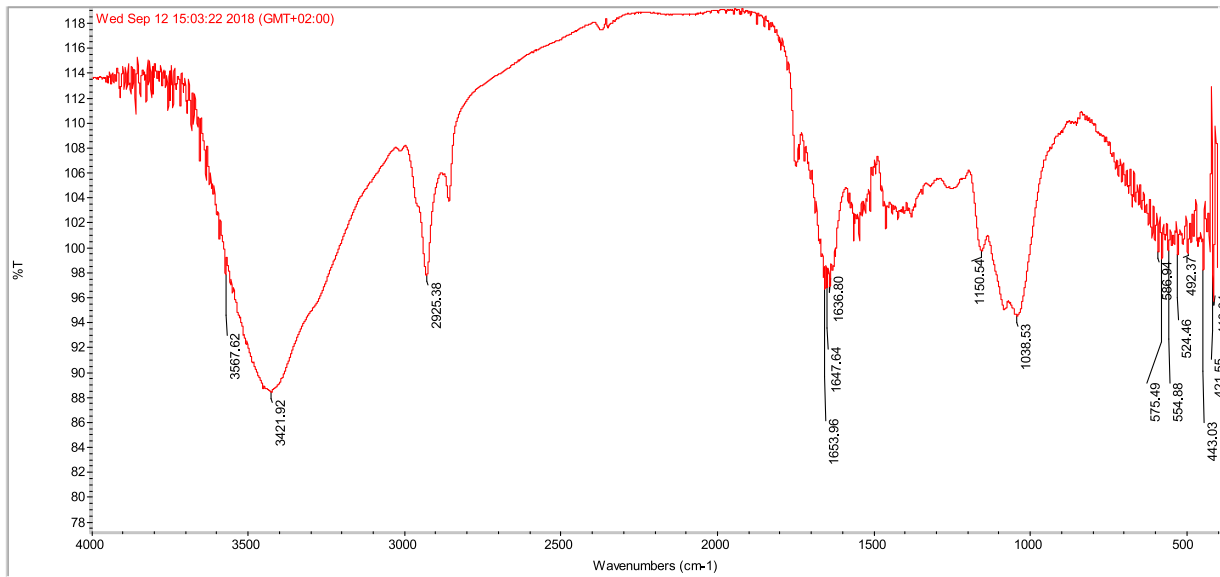


Fig. 15. The FTIR spectra of the *A. niger* loaded by uranium.

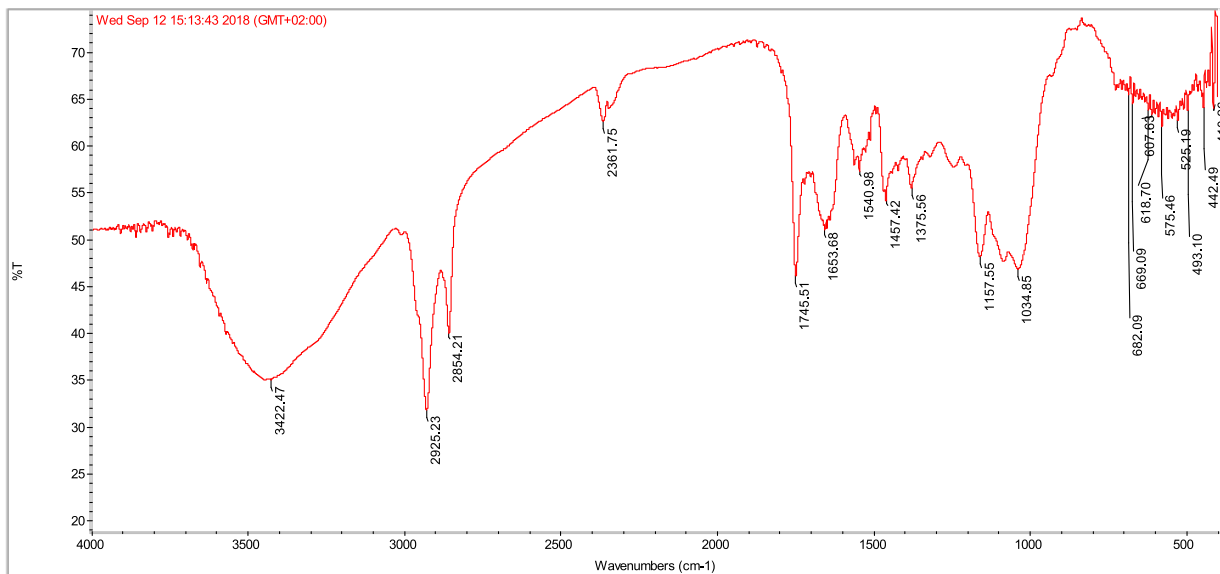


Fig. 16. The FTIR spectra of the *A. niger* loaded by Th.

the peak-bands before and after sorption of U and Th into the *A. niger* is a strong indication for the functional group's participating in the interaction of the ions on the immobilized fungal beads. Moreover, this shifting can be attributed to the surface complication created between metals and the carboxylic functional groups which probably support the chemical complication as one of the available mechanisms drive the biosorption process of U and Th.

3.11. Application on the real liquid waste

As a consequent of the batch experiments, the conducted optimum adsorption conditions were applied together (either for uranium or thorium) on the real liquid waste. Comparing the results of the chemical analysis of the liquid waste before and after

treatment with the dried biomass (Table 8) revealed the efficient adsorption role played by the *A. niger* on both U and Th as well as other metals such as; Fe, Cr, Cu, Zn, Mo, As, Pb, V and REEs. It is worth to notice that the bio-uptake for both elements are lesser values than those obtained from the batch experiments, but such behavior seems reasonable when we consider the competence of the other included ions species in the liquid waste on the binding sites of the bio-adsorbent. However, the results support using *A. niger* as a qualified adsorbent for the treatment of the liquid wastes that could be originated from various activities.

3.12. Environmental protection and metal recovery

The adsorbed U and Th by *A. niger* dried biomass was recovered in the form of pale-yellow colored precipitation product, while the

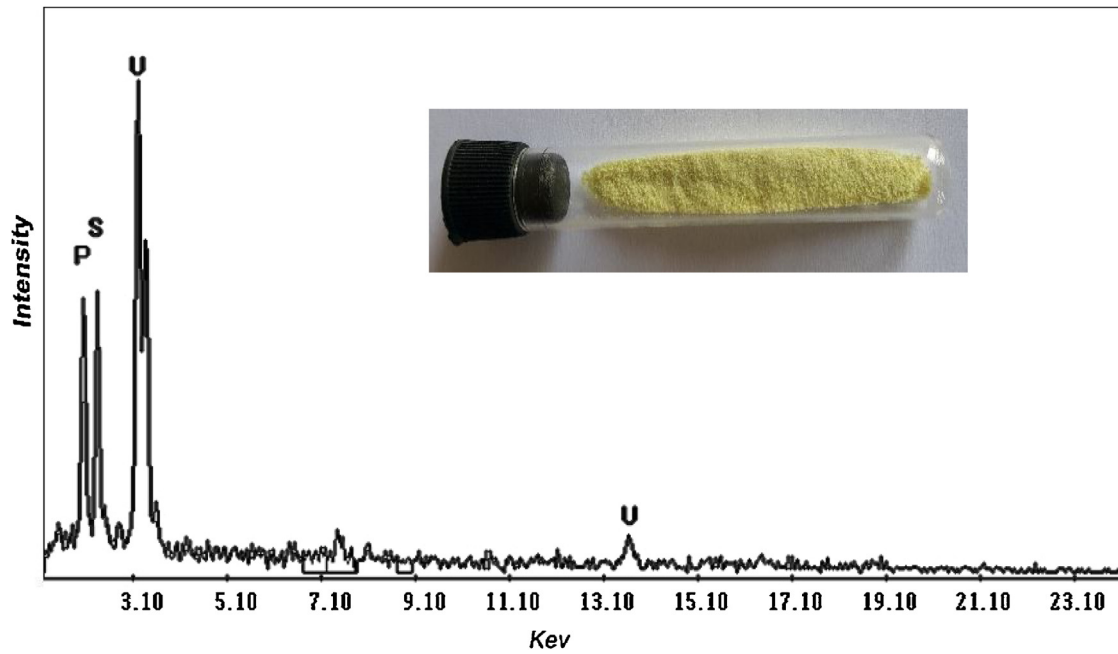


Fig. 17. Pure recovered uranium and its ESEM-EDX chart.

Table 8

The chemical analysis of the liquid waste before and after treatment by *A. niger* dried biomass (n.d = not detected).

Element		Fe	Cr	Cu	Zn	Mo	B	As	Pb	V	REEs	U	Th
Conc. (ppm)	Before	1.59	55.23	0.07	0.48	0.17	0.15	0.23	0.19	0.48	1.11	51.5	43.94
	After	n.d	16.2	n.d.	n.d.	0.05	n.d	0.02	n.d.	0.44	n.d.	13.36	10.74

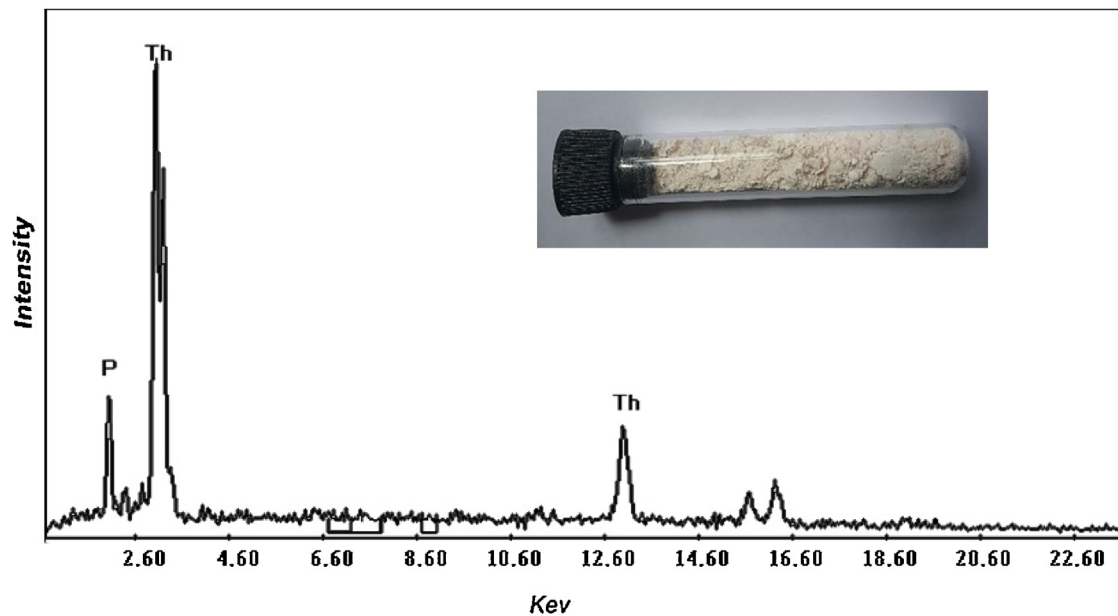


Fig. 18. Recovered thorium and its ESEM-EDX chart.

recovered thorium was in the form of white-colored precipitation products (Figs. 17 and 18).

4. Conclusion

This dried biomass (*A. niger*) behaved as low-cost, environmental friendly and good efficient adsorbent for the treatment of liquid waste containing radioactive elements. The rapid U and Th binding as observed by the present biomass at pH 4 have been suggested to be essential as a good biosorbent allowing short solution-sorbent contact time.

Declaration of Competing Interest

None.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.btre.2020.e00472>.

References

- [1] P.L. Bishop, Pollution Prevention: Fundamentals and Practice, Tsinghua University Press, Beijing, 2002.
- [2] P. Sar, S.F. D'Souza, Biosorption of thorium (IV) by a *Pseudomonas* biomass nuclear agriculture and biotechnology division, bhabha atomic research centre, trombay, Mumbai 400 085, India, *Biotechnol. Lett.* 24 (2002) 239–243.
- [3] J.S. Wang, X. Hu, Y.G. Liu, S.B. Xie, Z.L. Bao, Biosorption of uranium (VI) by immobilized *Aspergillus fumigatus* beads, *J. Environ. Radio.* 10 (2010) 504–508.
- [4] O. Abdia, M. Kazemi, A review study of biosorption of heavy metals and comparison between different biosorbents, *J. Mater. Environ. Sci.* 6 (5) (2015) 1386–1399.
- [5] H.K. Alluri, S.R. Ronda, V.S. Settalluri, J.S. Bondili, V. Suryanarayana, P. Venkateshwar, Biosorption an eco-friendly alternative for heavy metal removal, *Afr. J. Biotechnol.* 6 (25) (2007) 2924–2931.
- [6] C. Kuber, F. D'Souza Bhainsa, Thorium biosorption by *Aspergillus fumigatus*, a filamentous fungal biomass, *J. Hazard. Mater.* 165 (2009) 670–767.
- [7] N. Abalya, T.V. Ramachandra, R.D. Kanamadi, Biosorption of heavy metals, *Res. J. Chem. Environ.* 7 (2003) 71–78.
- [8] K.M. Paknikar, A.V. Pethkar, P.R. Puranik, Bioremediation of metalliferous wastes and products using inactivated microbial biomass, *Indian J. Biotechnol.* 2 (2003) 426–443.
- [9] S. Xie, J. Yang, C. Chen, X. Zhang, Q. Wang, C. Zhang, Study on biosorption kinetics and thermodynamics of uranium by *Citrobacter freundii*, *J. Environ. Radioact.* 99 (2008) 126–133.
- [10] S.A. Ayangbenro, O.O. Babalola, A new strategy for heavy metal polluted environments: a review of microbial biosorbents, *Int. J. Environ. Res.* 14 (2017) 94–115.
- [11] S. Ahluwalia, D. Goyal, Microbial and plant derived biomass for removal of heavy metals from wastewater, *Bioresour. Technol.* 98 (2007) 2243–2257.
- [12] A. San, U. Dogan, M. Tuzen, Equilibrium, thermodynamic and kinetic investigations on biosorption of arsenic from aqueous solution by algae (*Maugeotia genulflexa*) biomass, *Chem. Eng. J.* 167 (1) (2011) 155–161.
- [13] V. Diana, H.C. Ceretti, A.D. Maria, R. Silvana, Z. Anita, Cadmium, zinc and copper biosorption mediated by *Pseudomonas veronii* 2e, *Bioresour. Technol.* 99 (2008) 5574–5581, doi:<http://dx.doi.org/10.1016/j.biortech.2007.10.060>.
- [14] E.N. Bakatula, E.M. Cukrowska, I.M. Weiersbye, L. Mihaly-Cozmuta, A. Peter, H. Tutua, Biosorption of trace elements from aqueous systems in gold mining sites by the filamentous green algae (*Oedogonium* sp.), *J. Geoch. Exp.* 144 (2014) 492–503.
- [15] R.A. Bahobill, H.M. Bayoumi, M.M. El-Sehrawey, Fungal biosorption for cadmium and mercury heavy metal ions isolated from some polluted localities in KSA, *Int. J. Curr. Microbiol. App. Sci.* 6 (6) (2017) 2138–2154.
- [16] T. Barkay, J. Schaefer, Metal and radio nuclide bioremediation: issues, considerations and potentials, *Curr. Opin. Microbiol.* 4 (2001) 318–323.
- [17] S.H. Elwan, M.R. El-Naggar, The growth behavior of *Azotobacter chroococcum* in association with some microorganisms in the soil, *J. Basic Microbiol.* 12 (1) (1972) 7–13.
- [18] K.H. Domsch, W. Gams, T.H. Anderson, Compendium of Soil Fungi, Academic Press, London, England, 1980.
- [19] H.L. Barnett, B.B. Hunter, Illustrated Genera of Imperfect Fungi, fourth edition, Prentice Hall Inc., 1999.
- [20] S. Zafar, F. Aqil, I. Ahmad, Metal tolerance and biosorption potential of filamentous fungi isolated from metal contaminated agricultural soil, *Bioresour. Technol.* 98 (2006) 2557–2561.
- [21] T.J. White, T. Bruns, S. Lee, J.W. Taylor, Amplification and direct sequencing of fungal ribosomal RNA genes for phylogenetic, PCR Protocols: A Guide to Methods and Applications, Academic Press, San Diego, California, USA, 1990, pp. 315–322.
- [22] W. Davies, W.A. Gray, Rapid and specific titrimetric: method for the precise determination of U using FeSO₄ as reductant, *Talanta* 11 (1964) 1203–1211.
- [23] Z. Marcenko, Spectrophotometric Determination of the Elements, Wiley, New York, 1976.
- [24] A.M. Abu El-Soad, M.O. Abd El-Magied, E.G. Kovaleva, G. Lazzara, Synthesis and characterization of modified sulfonated chitosan for beryllium recovery, *Int. J. Biol. Macromol.* 139 (2019) 153–160.
- [25] B.M. Atia, M.A. Gado, M.O. Abd El-Magied, E.A. Elshehy, Highly efficient extraction of uranyl ions from aqueous solutions using multi-chelators functionalized graphene oxide, *Sep. Sci. Technol.* (2019), doi:<http://dx.doi.org/10.1080/01496395.2019.1650769>.
- [26] Mahmoud O. Abd El-Magied, A. Mansour, F.A. Alsayed, M.S. Atrees, S. Abd Eldayem, Biosorption of beryllium from aqueous solutions onto modified chitosan resin: equilibrium, kinetic and thermodynamic study, *J. Dispersion Sci. Technol.* (2018), doi:<http://dx.doi.org/10.1080/01932691.2018.1452757>.
- [27] Sadeek A. Sadeek, Mohamed A. El-Sayed, Maisa M. Amine, Mahmoud O. Abd El-Magied, Selective solid-phase extraction of U(VI) by amine functionalized glycidyl methacrylate, *J. Environ. Chem. Eng.* 2 (2014) 293–303.
- [28] A.F. Tag El-Din, E.A. Elshehy, M.O. Abd El-Magied, A.A. Atia, M.E. El-Khouly, Decontamination of radioactive cesium ions using ordered mesoporous monetite, *RSC Adv.* 8 (2018) 19041–19050.
- [29] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc.* 40 (1918) 1361–1367.
- [30] H.M.F. Freundlich, Über die adsorption in losungen, *Zeitschrift für Physikalische Chemie (Leipzig)* 57 (1906) 385–470.
- [31] A.F. Tag El-Din, E.A. Elshehy, M.O. Abd El-Magied, A.A. Atia, M.E. El-Khouly, Decontamination of radioactive cesium ions using ordered mesoporous monetite, *RSC Adv.* 8 (2018) 19041–19050.
- [32] M.O. Abd El-Magied, Abdelghaffar S. Dhmees, Abd Allah M. Abd El-Hamid, Ekramy M. Eldesouky, Uranium extraction by sulfonated mesoporous silica derived from blast furnace slag, *J. Nucl. Mater.* 509 (2018) 295–304.
- [33] M.O. Abd El-Magied, A. Mansour, F.A. Alsayed, M.S. Atrees, S. Abd Eldayem, Biosorption of beryllium from aqueous solutions onto modified chitosan resin: equilibrium, kinetic and thermodynamic study, *J. Dispers. Sci. Technol.* 39 (2018) 1597–1605.
- [34] M.O. Abd El-Magied, W.M. Salem, A.A. Daher, E.A. Elshehy, Fabrication of silica microspheres (HB/A@Si-MNS) for hafnium and zirconium recovery from zirconyl leach liquor, *Colloids Interfaces* 2 (2018) 1–14.
- [35] M.O. Abd El-Magied, T.F. Mohammed, I.K. El-Aassy, H.M.H. Gad, A.M. Hassan, M.A. Mahmoud, Decontamination of uranium-polluted groundwater by chemically-enhanced, sawdust-activated carbon, *Colloids Interfaces* 1 (2017) 1–17.
- [36] M.O. Abd El-Magied, A.A. Tolba, H.S. El-Gendy, S.A. Zaki, A.A. Ati, Studies on the recovery of Th(IV) ions from nitric acid solutions using amino-magnetic glycidyl methacrylate resins and application to granite leach liquors, *Hydrometallurgy* 1 (69) (2017) 89–98.
- [37] M. Tsezos, B. Volesky, Biosorption of uranium and thorium, *Biotechnol. Bioeng.* 23 (1981) 583–604.
- [38] G. Uslu, M. Tanyol, Equilibrium and thermodynamic parameters of single and binary mixture biosorption of lead (II) and copper (II) ions onto *Pseudomonas putida*: effect of temperature, *J. Hazard. Mater.* 135 (2006) 87–93.
- [39] Y. Andres, H.J. MacCordick, J.C. Hubert, Adsorption of several actinides (Th, U) and lanthanide (La, Eu, Yb) ions by *Mycobacterium smegmatis*, *Appl. Microb. Biotechnol.* 39 (1993) 413–417.
- [40] H.M.H. Gad, T.F. Mohammed, M.A. Mahmoud, Solid phase extractive pre-concentration of uranium (VI) from liquid waste onto peach stone steam pyrolysis activated carbon, *Asian J. Chem.* 28 (4) (2016) 751–760.
- [41] K. Vijayaraghavan, Y.S. Yun, Bacterial biosorbents and biosorption, *Biotechnol. Adv.* 26 (3) (2008) 266–291.
- [42] R. Saravanane, T. Sundarajan, S. Sivamurthyreddy, Efficiency of chemically modified low cost adsorbents for the removal of heavy metals from wastewater: a comparative study, *Indian J. Environ. Health* 44 (2002) 78–81.
- [43] Z. Yi, B. Lian, Adsorption of U(VI) by *Bacillus mucilaginosus*, *J. Radioanal. Nucl. Chem.* 293 (2012) 321–329.
- [44] Y.H. Lee, P.J. Adams, D.T. Shindell, Evaluation of the global aerosol microphysical Model E2-TOMAS model against satellite and ground-based, *Geosci. Model. Dev. Discuss.* 8 (2015) 631–667.
- [45] Z. Aksu, Equilibrium and kinetic modeling of cadmium (II) biosorption by *C. Vulgaris* in a batch system: effect of temperature, *Sep. Purif. Technol.* 21 (2002) 285–294.
- [46] E. Romera, F. González, A. Ballester, M.L. Blázquez, J. Muñoz, Biosorption with algae: a statistical review, *Crit. Rev. Biotechnol.* 26 (2006) 223–235.
- [47] M. Tawfik, H.M. Mohammed, Preliminary screening of bioactive metabolites from three fungal species of *Drechslera* isolated from soil in Basrah, Iraq, *J. Journal of Basrah Researches (Sciences)* 31 (2005) 44–62.
- [48] T. Tsuruta, Removal and recovery of U using microorganisms isolated from North American U deposits, *J. Environ. Sci.* 3 (2007) 60–66.
- [49] M.O. Abd El-Magied, A.M.A. Hassan, H.M.H. Gad, T.F. Mohammed, M.A.M. Youssef, Removal of nickel (II) ions from aqueous solutions using modified activated carbon: a kinetic and equilibrium study, *J. Dispers. Sci. Technol.* 39 (6) (2018) 862–873.