

Original research

Date seed as an efficient, eco-friendly, and cost-effective bio-adsorbent for removal of thorium ions from acidic solutions

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Received: 27/8/2020

Accepted: 23/9/2020

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Abstract:

Removal of thorium ions from acidic media using high effective bio-adsorbent is a very convenient viewpoint for the management of environmental pollutants. With this respect, this study is aimed to synthesize bio-adsorbent derived from date palm seed (DS bio-adsorbent) for adsorption of Th(IV) from acidic media. The studied bio-adsorbent was characterized by FTIR, SEM, and XRD techniques. The effective experimental parameters on the adsorption performance such as pH, bio-adsorbent dose, contact time, solution temperature, thorium initial concentration, and interfering ions were investigated. Furthermore, adsorption isotherm and kinetic studies were explored to describe the mechanism of thorium adsorption using the proposed bio-adsorbent. The Langmuir model result showed that the DS removal adsorption capacity was 43 mg.g⁻¹ at optimized batch conditions. The kinetic findings indicated that the adsorption mechanism was in an agreement with the pseudo-second-order model. Additionally, the regeneration of the spent bio-adsorbent was studied using 0.3 mol.L⁻¹ HNO₃ as an eluent agent. This research suggested that the date palm seed bio-adsorbent could be evaluated as a beneficial adsorbent for the adsorption of thorium from aquatic and acidic media due to its selectivity and capacity.

Keywords: Date seed bio-adsorbent; thorium ions; elution; isotherm; kinetic; recyclability

1- INTRODUCTION

Recently, the scientific importance and commercial value of thorium has received much research attention because of its extensive use in various areas, including optics, radios, aeronautics, aerospace, metallurgy, chemical and nuclear industries, materials science and nuclear medicine (Liu et al., 2014; Mastren et al., 2017; Mastren et al., 2018). In particular, thorium is considered as a promising (neutron irradiation) fertile material for producing nuclear fuel because it is associated with fewer radioactive fission products and produces lower quantities of highly radio toxic actinides (Cheira et al., 2018; Li et al., 2017).

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The nuclear power production at present is based broadly on the uranium fuel cycle (Banerjee and Gupta 2019; Gupta et al., 2008; Sundararajan et al., 1998). By using thorium instead of uranium as fuel, nuclear power could be safer and more sustainable, according to new research. Also, there is a worldwide belief that thorium fuel will be one of the most important fuels for the world in the future. Thus, purity requirements for thorium and its compounds, especially in nuclear technology, have much significance. However, excessive amounts of thorium have entered the environment due to these activities (Oyewo et al., 2016; Yaftian et al., 2003). Thorium released into the environment can reach the top of the food chain and be ingested by humans, causing irreversible damage to multiple organs and even death (Baybaş and Ulusoy, 2011; Keshtkar and Hassani, 2014).

Furthermore, thorium is naturally present in soil, rocks, surface water, groundwater, plants, and animals at low concentrations, on the order of ten parts per million. Essentially all naturally occurring thorium is present as thorium-232. According to the World Health Organization (WHO), concentration of Th(IV) in drinking water should be below $20 \mu\text{g}\cdot\text{L}^{-1}$. The concentration of thorium in plants is typically about 0.0042 (or 0.42%) of that in soil (Rastegarzadeh et al., 2010; Safavi and Sadeghi, 2006). Conventional methods of Th(IV) detection are complicated and costly (Sadeghi and Davami, 2019). However, at present, consumption of thorium in this direction is restricted owing to sufficient resources of uranium (Neikov et al., 2019).

Several techniques including chemical precipitation, solvent extraction, electro floatation, ion exchange, reverse osmosis and adsorption have been developed to recover thorium from aqueous solutions (Gado et al., 2019; Orabi et al., 2017). At low concentrations, separation/preconcentration through adsorption of long-lived radioactive radionuclides such as thorium from aqueous solution is important in nuclear/radiation chemistry and environmental/waste treatment chemistry (Anirudhan et al., 2010). Adsorption, defined as the concentration of ions or molecules from one phase to the surface of another phase, is important in that it is capable of separating trace elements from large volume solutions. Many inorganic and organic adsorbents such as activated carbons, algae, composites, modified nanoparticles, silica gel, resins, etc., are used for the remediation of radioactive waste. Today's trend is to synthesize new bio-adsorbent materials with high efficiency and stability. In recent years, bio-adsorbent have attracted great interest due to their remarkable potential field of applications (Yılmaz et al., 2020).

This study is aimed at investigating the possibility of using date palm seed as efficient alternative adsorbent materials for the adsorptive removal of thorium ions from acidic solution. The behavior of thorium ions adsorption onto the studied bio-adsorbent were studied with the effect of pH, DS-dosage, contact time, initial thorium concentration, and temperature. Finally, we investigated the isotherm and kinetic parameters for the extractive processes, and assessed the reusability of the bio-adsorbent material.

2- MATERIALS AND METHODS

This section summarizes the experimental procedures and analytical methods that have utilized in the extraction, stripping, recovery, and determination of Th(IV) ions from its solutions. It is also signed in details, the specification of chemicals, reagents and descriptions of the instruments have been used in this work. Bidistilled water has also been used for preparation of the used solutions. All glassware has perfectly been cleaned by their washing several times.

2.1. Instrumentation

Generally, chemicals and samples used in this work are weighed by Sartorius balance. The samples are dried by BMT drying oven. All pH measurements are carried out using Misura Line 1010 pH meter (Romania). The set is calibrated using standard buffer solutions pH 4.01, pH 7.0 and pH 10.0. All samples are stirred and heated by multiple Heating Magnetic Stirrer (VELP Scientifica) during experimental procedures as well as micropipette (100-1000 μ L) is also used. The Perkin Elmer lambda 3b (USA) double-beam UV-Visible programmable spectrophotometer equipped with 1 cm quartz cells controlled by PC running the spectrophotometric software PECSS software program used for spectrophotometric determination of thorium of the samples and standard solutions. The Scanning electron microscopy (SEM) images are taken using a Jeol (Tokyo, Japan) JSM 5600 LV scanning electron microscope equipped with an Oxford Instruments 6587 EDX microanalysis detector. The images have been taken under low vacuum conditions where samples do not show charging effects; in this way, it is possible to avoid the coating of the samples with a high conductance thin film (gold or graphite films). Absorption spectra in the IR region are collected using a Fourier Transform Infrared spectrometer (FT-IR) (Thermo Scientific - NICOLET iS10 USA) spectrometer. This technique is used to characterize the major functional groups of date seed with solvents. Samples are mixed with KBr and the mixture was ground and then pressed with a special press to give a disc of standard diameter in KBr pellet (IR grade, Merck). X-Ray Diffraction technique (XRD) is used to identify the unknown minerals using PHILIPS PW 3710/31 diffractometer, scintillation counter, Cu-target tube and Ni filter at 40 kV and 30 mA.

2.2. Preparation of pure date seed (DS)

Assiut date seeds were collected, washed, dried by air oven, then wetted by water covered by a wet cloth and then left at ambient temperature for 40 days keeping the cloth in wet nature. The germinated seeds with the same characteristics were washed, dried by fan oven, then crushed and ground to powder sample and then, it is washed by bidistilled water and it dried at 110 °C for 6 h.

2.3. Control chemical analysis of thorium ions

Among the many spectrophotometric methods for determining thorium, those based on azo compounds containing arsenic acid groups are of considerable importance. Although the Thoron I method is still employed, it is much less sensitive and less selective than the newer Arsenazo III method. Thoron (I) gives with Th(IV) a coloured complex which is also used for determination of thorium.

2.3.1. Reagents

- 1- Thoron I, 0.1% aqueous solution. It is prepared by dissolving 50 mg of Thoron I in bidistilled water and the solution is diluted to 50 mL in a volumetric flask and then transferred to a dark bottle, where it is stable for at least seven days.
- 2- Ascorbic acid solution, 1% aqueous solution. This solution is prepared by dissolving 1 g of ascorbic acid in bidistilled water and the volume is completed to 100 mL in a volumetric flask.
- 3- Standard thorium solution from 1 to 10 mg/L.

- 4- Tartaric acid solution, 5% aqueous solution. This solution is prepared by dissolving 5 g of tartaric acid in bidistilled water and the volume is completed to 100 mL in a volumetric flask.

2.3.2. Procedure:

Place the sulfate-free sample solution, containing Th(IV) in dilute HCl in a 25 mL standard flask. 1 mL of 1% ascorbic acid solution was added, followed by 1 mL 5% tartaric acid. 2 mL of the Thoron I solution was added, and sufficient HCl to make its concentration 0.25 M after dilution to the mark with bidistilled water.

The absorbance of the solution was measured at 540 nm, using a reagent blank solution as a reference.

2.4. Adsorption studies

Batch adsorption tests are conducted by mixing of 0.05 g of date seed (DS) bio-adsorbent with 20 ml of the different working prepared solutions of thorium ion concentration in the range 1–700 mg.L⁻¹ in proper glass beakers. The prepared mixture is shaken in a mechanical shaker (150 rpm) and 20 mL sample solution is periodically withdrawn from the beaker at known time intervals. Preliminary experiments have shown that adsorption is adequately fast, and the removal rate is found to be negligible after 60 min. Therefore, 60 min is used as the contact time for almost batch tests except in the experiment of the effect of the initial thorium concentration. At the end of each experiment, used bio-adsorbent was filtered to remove any fine particles before being analyzed for the adsorbed metal ions. Several series of experiments are conducted to determine the optimum conditions of the relevant factors controlling the adsorption process such as pH, contact time, amount of DS, initial thorium concentration and solution temperature. All the experiments are carried out in duplicate and the mean value was used in all cases.

On the other hand, for the determination of thorium equilibrium isotherm, the corresponding experiments are conducted by mixing 0.05g of date seed bio-adsorbent with 20 mL of thorium solution using an initial thorium concentration ranging from 1 to 700 mg.L⁻¹. In these experiments, the mixture is shaken for a contact time up to 3h to reach equilibrium. From each adsorption experiment the amount of Th(IV) adsorbed by DS bio-adsorbent was calculated using the following equation:

$$q_e = (C_0 - C_e) \left(\frac{V}{M} \right)$$

Where q_e is the metal uptake (mg/g), C_0 and C_e are the initial and equilibrium Th(IV) concentrations in the solution (mg.L⁻¹), respectively, V is the solution volume (L), and M is the mass of DS bio-adsorbent (g).

2.5. Desorption Studies

To study the desorption characteristics, interest has been restricted to metal ions. The loaded DS bio-adsorbent obtained from the previously mentioned prepared solution of the studied element is thus subjected to desorption. In this process nitric acid is used as eluant. Each experiment is performed by shaking 0.05 g of bio-adsorbent impregnated by thorium with 20 mL of different concentrations of nitric acid at room temperature for 60 min, the solution is then filtered and the concentration of thorium is spectrophotometrically determined with thoron (I). In this study, we have investigated the parameters which affect thorium desorption such as, concentration of eluent, contact time, and temperature.

3- RESULTS AND DISCUSSION

3.1. Characterization of date seed (DS) bio-adsorbent

The chemical composition of the date palm seeds was established according to standard methods and the results were summarized in Table 1. This Table presents the chemical compositions of date seed obtained from Aswan City.

The X-ray diffraction patterns of the DS, and Th-loaded DS are displayed in Figure 1A&B. The X-ray spectra of DS bio-adsorbent do not exhibit a horizontal basic line. These display that the major portions of substances are amorphous. Nevertheless, a few diffraction peaks emerge from the basic line, demonstrating the attendance of a small quantity of crystalline substances. The presence of peaks corresponding to thorium ions adsorption on DS reflects the crystalline nature of date seeds and its impregnation. The peaks at $2\theta = 20.4^\circ$, 23.2° , and 33° could be attributed to the presence of cellulose (Abed et al., 2012; Zhao et al., 2018), (Figure 1A). The peak at $2\theta = 26.4^\circ$ could be assigned to the crystalline carbon (Hamada et al., 2013). While the peaks at $2\theta = 32.3^\circ$, 39.6° , 41.3° and 45° could be assigned to the presence of hemicellulose (Abu-Thabit et al., 2020). Also, the occurrence of thorium adsorption on DS is confirmed with the appearance of new peaks at $2\theta = 14.9^\circ$, and 16.6° , as shown in Figure 1B.

FTIR spectroscopy has been used as a simple technique for obtaining rapid information about the chemical structures and their functional groups. The FTIR spectra of DS, and DS-Th, are presented in Figure 1C&D. The FTIR spectrum for DS displayed a peak at 3387 cm^{-1} attributed to O–H stretching vibrations in hydroxyl groups. The band detected at 2945 cm^{-1} assigned to asymmetric C–H bands in $-\text{CH}_3$ and $-\text{CH}_2$ groups. Commonly, these absorption bands illustrated contributions of carbohydrate, and lignin. The peak at 2865 cm^{-1} is assigned to symmetric C–H bands in $-\text{CH}_3$ and $-\text{CH}_2$ groups, attributed to fats. The peak at 1734 cm^{-1} is assigned to carbonyl C=O, due to either the acetyl, and ester groups of carbohydrates or the ester linkage of carboxylic groups of acids of lignin and fatty acids. The band at 1624 cm^{-1} may represent C=C or C=N vibrations in the aromatic region. The peaks at 1525 and 1445 cm^{-1} may be ascribed to C=C stretching of the aromatic skeletal mode. The peak at 1382 cm^{-1} is due to the C–H stretching of carbohydrates. The band at 1253 cm^{-1} is attributed to C–O–H deformation and C–O stretching of phenolic. The band at 1061 cm^{-1} describes the C–O stretching vibration of carbohydrate. The absorption at 873 cm^{-1} is related to the C–H rocking vibrations of carbohydrate. Moreover, after Th(IV) adsorption as shown in the DS-Th spectra, the –OH, and C=O stretching vibration bands for the bio-adsorbent condensed and shifted to redshift with $10\text{--}15\text{ cm}^{-1}$, which may be due to the linkage of Th(IV) to the bio-adsorbent surfaces. Moreover, sharp peaks were detected at 1365 cm^{-1} and 1044 cm^{-1} for Th-loaded DS, and at 1375 cm^{-1} , these peaks corresponded to the Th–O vibration band of thorium ions, providing direct evidence for thorium ions adsorption on the DS bio-adsorbent (Cheira, 2020; Pool et al., 2005). These results designated the adsorption of thorium ions on the DS bio-adsorbent surfaces.

Figure 2A&B shows photographs of date palm seed and grounding date palm seed (DS). The surface morphologies of date seed are shown in Figures 2C&D. The data show that the macro porous of various size and geometry surface of DS are rough surface with irregular morphology. The date seeds samples after Th-adsorption exhibit agglomerated and smooth surface morphology, which could reflect the achieved adsorption processes. The SEM images for DS and Th-loaded DS reveal that Th(IV) ions were trapped on the date seed surface, due to the presence of intermolecular and intramolecular hydrogen bonding and van der Waals forces.

Table 1. The chemical composition of date seed.

Component	Values
Moisture content (%)	9.34
Fat (%)	7.55
Ash (%)	1.17
Protein (%)	5.85
Carbohydrate (%)	75.64
Potassium (mg/kg)	2621.2
Magnesium (mg/kg)	634.3
Calcium (mg/kg)	491.2
Phosphorus (mg/kg)	424.2
Sodium (mg/kg)	92.5
Iron (mg/kg)	38.9

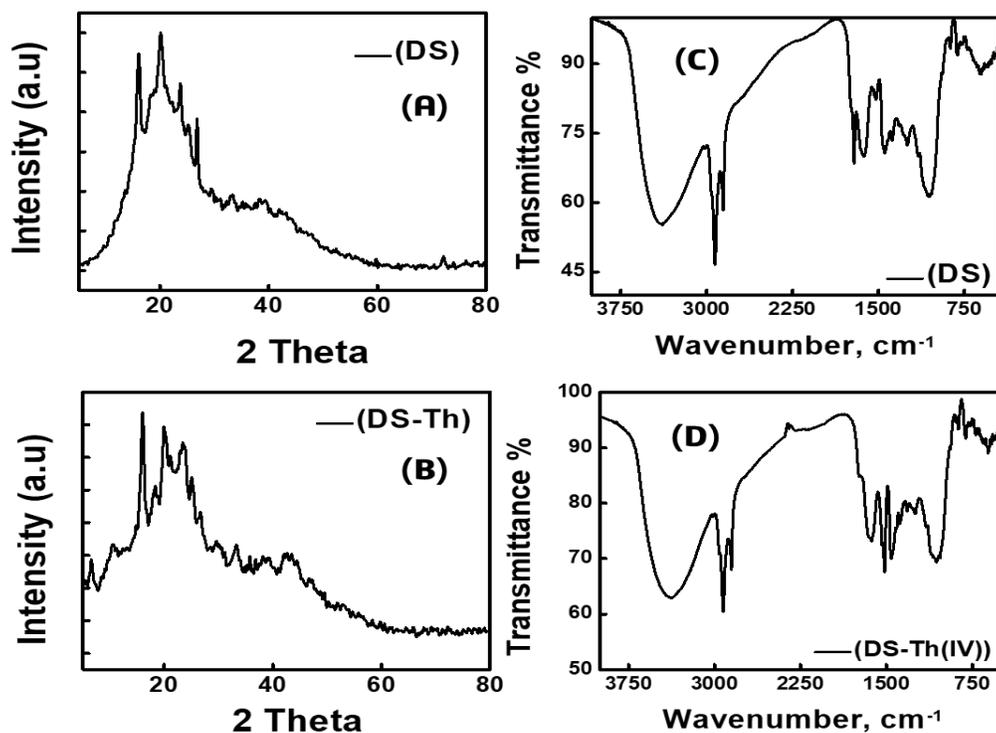


Figure 1. (A&B) X-ray diffraction patterns of DS, and Th-loaded DS; (C&D) FTIR spectra of DS, and Th-loaded DS.

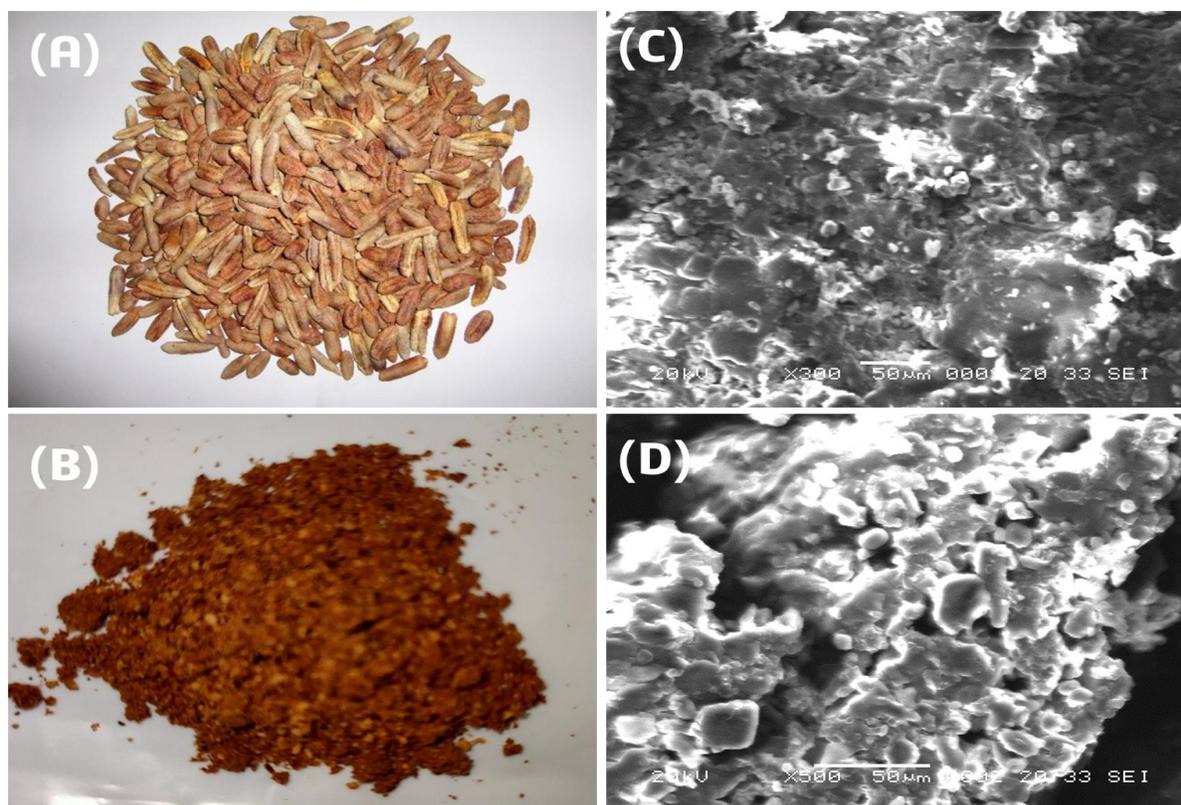


Figure 2. (A&B) Digital image of date seed, and date seed powder; (C&D) SEM micrographs for DS, and Th-loaded DS.

3.2. Thorium adsorption behaviour

3.2.1. Effect of pH

The influence of pH is a vital parameter for gaining a high adsorption capacity during the adsorption process. Thorium ionic species distribution in aqueous media at several pH values were exposed in Figure 3A, which displayed that the hydrolyzation procedures of thorium ions were obviously depended on the pH value. According to Figure 3A, at $\text{pH} < 4$, thorium ionic species distribution in the solution were mainly involved of positively charged species which are Th^{4+} , $[\text{Th}_4(\text{OH})_8]^{8+}$, $[\text{Th}_6(\text{OH})_{15}]^{9+}$, and $\text{Th}(\text{OH})^{3+}$. In addition, soluble thorium ions such as Th^{4+} were the dominant species in strongly acidic solution, while Th^{4+} tended to precipitate out as $\text{Th}(\text{OH})_4$ at higher pH, which were remained compatible with the outcomes of earlier studies (Baybaş and Ulusoy, 2011; Ding et al., 2019; Huang et al., 2018).

To assess the influence of solution pH on the Th(IV) adsorption capacity for DS bio-adsorbent, the pH was examined in pH range from 1 to 7, and the outcomes were manifested in Figure 3B. As a result, that, Th(IV) adsorption was a remarkable dependent on the pH value due to pH influences the thorium ions solubility, and the ionization state of DS surface function groups. The adsorption capacities data displayed that with increasing pH values from 1 to 4, the amount of thorium ions adsorption capacities on the bio-adsorbents surfaces increased sharply due to the competition between H^+ and thorium cations for the capture of the binding sites. In other meanings, at $\text{pH} < 4$, thorium ions adsorption capacities on DS bio-adsorbent were low values because of the competing between the H^+ ions in the medium and thorium ions cationic species.

Also, partial protonation of the surface-bio-adsorbent groups inhibiting the interactions between the bio-adsorbent and thorium ions that could be the chief target for a small quantity of Th(IV) adsorption ability at $\text{pH} < 4$ (Nilchi et al., 2013). At low pH, there will be excess of H^+ ions in the acidic solution which could lead to the protonation of oxygen atoms of the ligand. As the acidity increases, the hydrogen ions compete for the thorium ions during the adsorption process. Therefore, thorium adsorption efficiency is decreased at low pH values.

At pH4, the surface positive charges on the bio-adsorbent decreased and the thorium ions uptake capacities increased due to the increase of the attraction between the sorbate thorium cations species and bio-adsorbent. As seen in Figure 3B, it is obvious that the sorption of Th(IV) increased quickly at pH 1–4, then the maximum adsorption efficiency reaches 94 % at pH 4 for DS bio-adsorbent. The highest adsorption efficiency % of Th (IV) was observed at pH 4 for DS and this pH value was selected as optimum pH for further studies. The pH dependent sorption of Th (IV) on DS suggests that the sorption is attributed to surface complexation. The interaction of Th (IV) with the bio-adsorbent may take place through complex formation with the nitrogen and oxygen atoms of the bio-adsorbent. With further increase in pH, insoluble thorium hydroxide starts precipitating, which also results in lower amount of Th (IV) ions removal at equilibrium (Kırkan and Aycik, 2016). The formation of $\text{Th}(\text{OH})_4$ precipitate results in significant decrease in the adsorption of Th(IV) on DS bio-adsorbent. Therefore, thorium ions adsorption capacity on the DS bio-adsorbent was decreased due to thorium ions was initially precipitated on the bio-adsorbents-surface at $\text{pH} > 4$ according to the species distribution for thorium ions hydrolysis. Consequently, further adsorption studies were conducted at optimum pH4.

3.2.2. Effect of bio- adsorbent dose

The effect of DS bio-adsorbent dose on the adsorption efficiency of Th (IV) ions was investigated under optimum pH conditions by using different doses of DS bio-adsorbent (0.005 to 0.1 g). The illustrated data in Figure 3C refers to the increasing adsorption of Th (IV) species as the bio-adsorbent doses increase until 0.05 g, where the adsorption efficiency for DS is 92.5%. After that, the thorium adsorption efficiencies were increased slightly with growing bio-adsorbent amounts. This increase explains that the adsorption capacity of DS bio-adsorbent depends on the amount of coverage surface active sites. And then, the adsorption efficiencies remain constant was due to the availability of many active sites on the interior/exterior surface of the DS bio-adsorbent. Finally, the suitable amount of the studied individually bio-adsorbent is 0.05 g to obtain the highly thorium adsorption efficiency from its solution.

3.2.3. Effect of contact time

The effect of contact or stirring time on the adsorption/extraction of Th (IV) species (i.e., time required to obtain the most remarkable adsorption) was also investigated because the contact time is significant in the raising of adsorption efficiency as a result of the binding of Th (IV) ions with DS bio-adsorbent. A series of batch contact tests was performed by mixing 0.05 g of the DS bio-adsorbent with 20 mL of Th (IV) solution ($100 \text{ mg}\cdot\text{L}^{-1}$) at pH 4 and room temperature under continuous stirring for 5–180 min. These findings showed that the most remarkable adsorption efficiency of the DS bio-adsorbent at a specific pH can be achieved within 60 min of when mixing began. The adsorption efficiency value shows a relative stability, which provides evidence of the quick interaction between targeted thorium ions and used DS bio-adsorbent due to chemical bonding with the functional groups of the applied bio-adsorbent. The analytical obtained data show the ability of our bio-adsorbent to adsorb more than 92.5 % of Th (IV) ions using DS bio-adsorbent, as shown in Figure 3D. This result proved that the adsorption or

extraction of Th (IV) ions is a rapid and time-dependent process and increasing the contact time lead to enhances the adsorption efficiency. This relatively rapid attainment of equilibrium may be related to the large surface area and adequate active sites of the applied bio-adsorbents besides the relatively low initial thorium concentration of the applied solution. After 60 min, the adsorption efficiencies stay constant, this may be due to the active sites on the interior/exterior surface of the DS bio-adsorbent was completely occupied. Therefore, 60 min as contact time was chosen as optimum stirring time for adsorption of thorium ions upon DS bio-adsorbent.

3.2.4. Effect of adsorption process temperature

Temperature is an important parameter that dominates the physicochemical behaviour of metal ions in the environment (Hassanin et al., 2019). Therefore, the effect of temperature on the adsorption of Th(IV) ions was investigated by performing the adsorption process at different temperature (25 – 60 °C) using DS bio-adsorbent, while the other parameters were kept constant (at optimum pH 4 and stirring time for 60 min, 0.05 g of DS bio-adsorbent, 100 mg.L⁻¹ Th(IV) concentration, 20 mL solution). From the obtained results shown in Figure 3E, the adsorption thorium efficiency and capacity (mg.g⁻¹) decreased with the increase of temperature, this due to the dissolution of the bonds between bio-adsorbent and adsorbate.

The reducing of the adsorption efficiency by stepping up the temperature is due to the higher temperature inactivates the metal ions for enhancing adsorption at the coordinating sites of the bio-adsorbent. Figure 3E illustrated that Th(IV) adsorption capacities (q_e , mg.g⁻¹) reduced with the temperature increasing from 25 to 55 °C. This incident could be due to the adsorption steps environment and the expanding mobility of thorium ions through a lower driving force. Another reason maybe because of the acceleration of several slow desorption steps on the bio-adsorbent surface. Hence, the best adsorption temperature was ambient temperature. The percentage of thorium ions adsorption decreased with increasing temperature indicating that the process is exothermic in nature. Accordingly, the maximum efficiency of thorium adsorption by DS bio-adsorbent is 92.5 % at 25 °C. Therefore, the adsorption processes are clearly favored at room temperature (25 °C).

3.2.5. Effect of thorium initial concentration

Effect of initial thorium concentration is the most important parameters on the sorption system, which can influence the sorption behavior of Th(IV) ions. The initial Th(IV) concentration directly affects the adsorption process and capacity of DS bio-adsorbent. To study the relation of adsorption capacity versus Th(IV) ions concentration in the aqueous phase, it will help us to demonstrate the adsorption behaviour. Therefore, the initial concentration of Th(IV) varied within the range 1–700 mg.L⁻¹, and the other parameters were kept constant (at optimum pH 4 and stirring time for 60 min, 0.05 g of DS bio-adsorbent, 20 mL solution).

From Figure 3F, the data indicated that Th(IV) concentration increased from 1 to 300 mg.L⁻¹, the adsorption capacity increased with the thorium ions concentration. At a 0.05 g dose amount of DS bio-adsorbent that had the limited active sites used when exceeded 300 mg.L⁻¹ Th(IV) were contained in the reaction system, and the adsorption capacities would overload the accessible binding sites at the three bio-adsorbents. Under the present experimental conditions, the maximum adsorption capacity reached was 42.5 mg.g⁻¹ of DS bio-adsorbent. The adsorption capacity is an important factor to evaluate the DS bio-adsorbent. After that, the loaded thorium amounts have remained constant expressing that the working bio-adsorbent have reached to its maximum loading capacity (saturation capacity), due to the mobility of Th(IV) ions in the solutions is the highest and the interactions of these ions with the bio-adsorbent are increased.

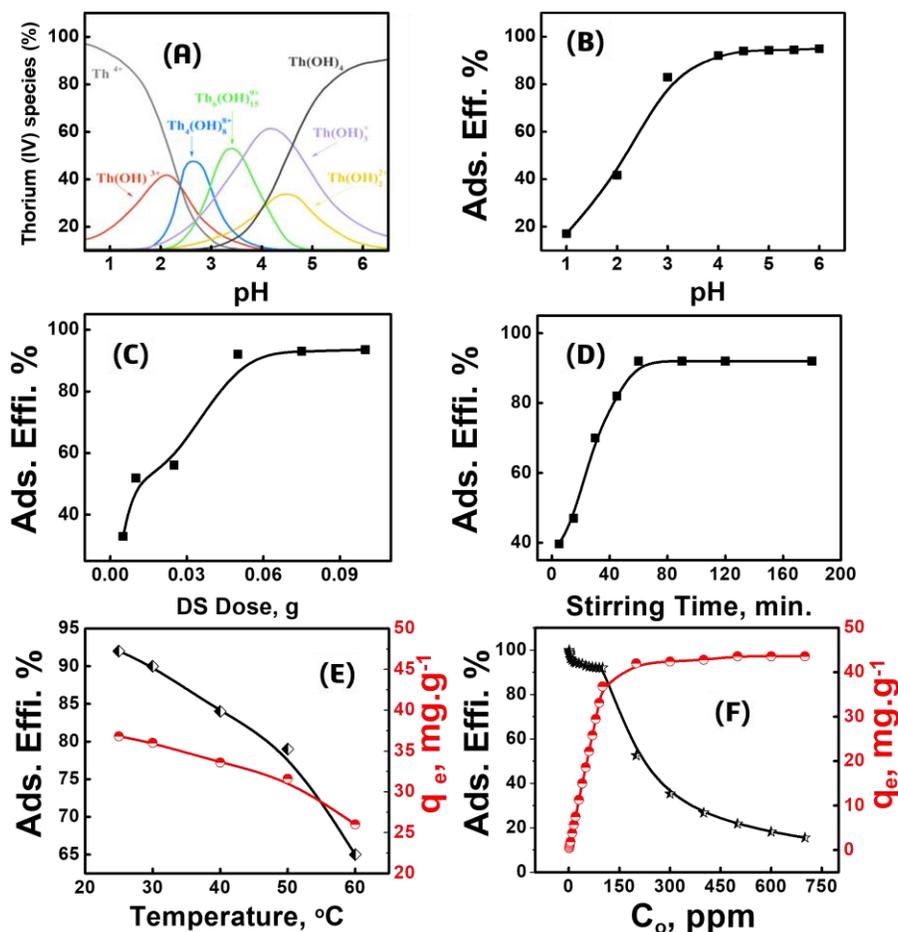


Figure 3. (A) Thorium ions species distribution against pH; (B) Effect of pH on thorium adsorption on DS bio-adsorbent; (C) Effect of DS bio-adsorbent dose on thorium adsorption efficiency; (D) Effect of stirring time on the adsorption efficiency of DS bio-adsorbent toward Th(IV) ions; (E) Effect of temperature on the adsorption efficiency % and adsorption capacity $\text{mg}\cdot\text{g}^{-1}$ of DS bio-adsorbent toward Th(IV) ions; (F) Effect of thorium initial concentration on the adsorption efficiency % and adsorption capacity $\text{mg}\cdot\text{g}^{-1}$ of DS bio-adsorbent.

3.2.6. Effect of interfering ions

The selectivity behavior of DS bio-adsorbent toward Th(IV) ions was investigated in single, binary and mixture batch-contact systems under the optimum pH conditions, at equivalent concentrations. Coexisting ions influence on the adsorption evolutions of target thorium ions through competition for the limited active sites of DS bio-adsorbent. In this section, we carried out a basic study of Th(IV)-selectivity in water at optimal pH condition using our DS bio-adsorbent as a function of adsorption efficiency, as shown in Figures 4. Our study was carried out to evaluate the extraction behaviour of Th(IV) ions in the presence of an equivalent amount of other competitive cations. Target selectivity is a fundamental property in the extraction of a Th(IV) ions from natural sources. Therefore, a series of batch-contact tests was carried out as follows: 0.05 g of DS bio-adsorbent was stirred for 60 min with 20 mL of Th(IV), Cr(III), Cu(II), Ni(II), Zn(II), Zr(IV), Ba(II), Pb(II), Sr(II), V(III), and REEs separately at optimized pH 4, with initial concentration $100 \text{ mg}\cdot\text{L}^{-1}$.

The obtained results in Figure 4A showed that the adsorption efficiencies of other Coexisting ions are negligible compared with the adsorption efficiency of Th(IV) ions using DS bio-

adsorbent. Interfering REEs ions show a weak adsorption response upon interaction with the studied bio-adsorbent due to the rapprochement/similarity of the chemical and physical properties of REEs with those of thorium ions. Consequently, the extraction process and the efficiency of the bio-adsorbent are adversely affected. This challenge can be overcome by using a suitable masking agent. Few drops of 50 mM.L⁻¹ sodium tartrate and citrate, mixture solution used during the thorium ions adsorption processes to avoid the passive impact of the studied coexisting ions.

Furthermore, the same experiments were conducted in binary and mixture systems under the optimum extraction conditions in the presence of one or more coexisting cations with Th(IV) ions at equivalent concentrations, as listed in Figure 4B&C. The obtained findings indicated that the existence of foreign ions exerts no significant effect on the adsorption efficiency of Th(IV) ions. The obtained results in Figure 4 demonstrated that about 85 % of the Th(IV) content can be adsorbed in the absence of other interfering ions using DS bio-adsorbent. This decreasing of adsorption efficiencies may be due to the competitive effect of the interfering ions at the interior/exterior active sites of applied bio-adsorbent. Our findings indicated the possible fast extraction of Th(IV) from its solutions efficiently, selectively, even at low concentrations through extraction/adsorption process. The high extraction/adsorption efficiency may be due to the used bio-adsorbent surface functionalities in terms of (i) porosity nature, (ii) effective surface coverages, (iii) high surface area-to-pore volume ratio, and (iv) the abundance of active sites. Our findings exhibited that the selectivity of DS bio-adsorbent may be due to the higher thermodynamic binding stability of Th(IV) ions with the active groups of modifier molecules than those with other competitive ions under fixed pH conditions.

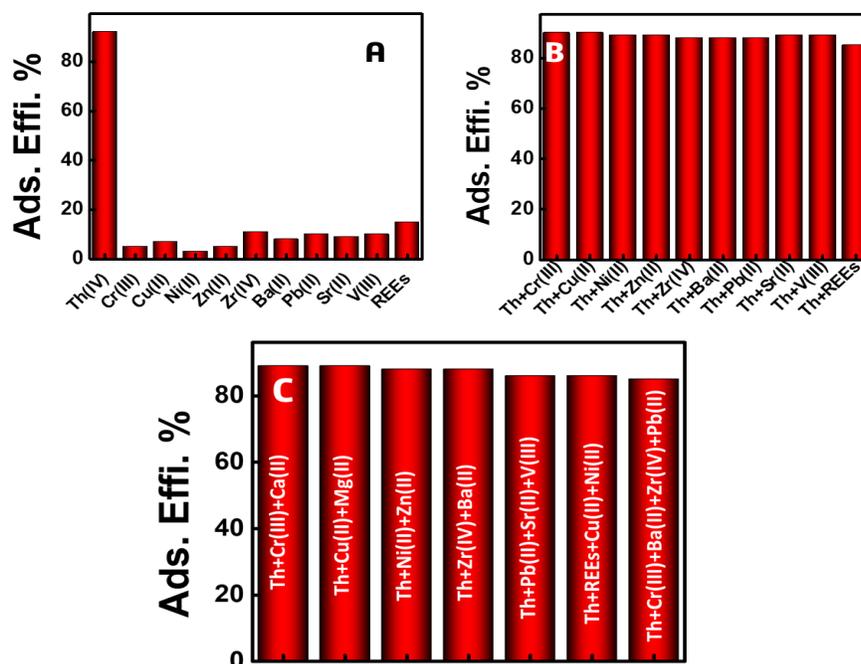


Figure 4. (A) The efficiency of Th(IV) and other coexisting ions adsorption using DS bio-adsorbent in single system; (B) Effect of coexisting ions on the adsorption efficiency of Th(IV) ions using DS bio-adsorbent in binary system; (D) Effect of coexisting ions on the adsorption efficiency of Th(IV) ions using DS bio-adsorbent in mixture system under the optimum adsorption conditions.

3.3. Thorium adsorption isotherm

Langmuir and Freundlich isotherm models were applied to verify the adsorption nature between Th(IV) and DS bio-adsorbent and determine the theoretical maximum adsorption capacity of applied bio-adsorbents (q_m , mg/g). Therefore, a set of batch contact tests was conducted using a wide range of Th(IV) concentrations ranging from 1 to 700 mg.L⁻¹ under the optimum experimental conditions. As shown in Figure 3F, the adsorption capability of applied bio-adsorbent increases until it reaches the saturated point (maximum adsorption capacity, practical 42.5 mg.g⁻¹ of DS bio-adsorbent) at which DS bio-adsorbent cannot assimilate additional amounts of Th(IV) ions. The high adsorption capability of DS bio-adsorbent may be due to the following: (i) high bio-adsorbent surface area, (ii) porosity, (iii) numerous active sites on the interior/exterior surface, (iv) rapid and easy Th(IV) diffusion along the bio-adsorbent pores, and (v) good distribution of modifier chelating agents on the bio-adsorbent's internal/external surface (Cheira, 2015). Langmuir and Freundlich isotherm models were used to estimate the theoretical adsorption capacity of DS bio-adsorbent and determine whether the interaction nature is chemical or physical (Cheira et al., 2017; Gomaa et al., 2017; Zidan et al., 2020):

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \left(\frac{1}{q_m}\right) C_e$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$$

Where, q_m and K_L are the theoretical maximum adsorption capacity of DS (mg/g) and the Langmuir isotherm constant (L/mg), respectively. K_F and n are the constants relative to the adsorption capacity (mg/g) of bio-adsorbent and sorption intensity, respectively. C_e/q_e versus C_e and $\ln q_e$ versus $\ln C_e$ were plotted to calculate the values of these parameters (see Figures 5A&B). R^2 reveals that the Langmuir isotherm model is the most convenient approach to describe the interactive nature of Th(IV)-DS bio-adsorbent binding; the binding between Th(IV) and the functional groups of the DS bio-adsorbent is chemical (monolayer adsorption). The theoretical q_m value (43.82 mg.g⁻¹ for DS bio-adsorbents) is consistent with the experimental q_m value. In addition, the $1/n$ value is less than unity, indicating the chemical nature of adsorption process, as shown in Table 2.

3.4. Thorium adsorption kinetic

Evaluation of the kinetic adsorption mechanism of Th(IV) ions is significant for understanding the adsorption behavior based on the alteration in the contact time. Therefore, a set of batch experiments was carried out at a contact time of 2.5:180 min by stirring 0.05 g of DS bio-adsorbent with 20 mL of 100 mg.L⁻¹ Th(IV) ions at pH 4 and room temperature. Here, the adsorption kinetic models, such as pseudo-first- and pseudo-second-order models, were applied according to the following equations (Cheira et al., 2019; Gomaa et al., 2018).

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_1}{2.303}\right) t$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \left(\frac{1}{q_e}\right) t$$

Where k_1 (min⁻¹) and k_2 (g.mg⁻¹.min⁻¹) are the pseudo-first- and pseudo-second-order rate constants, respectively, and q_t is the adsorbed Th(IV) amount (mg.g⁻¹) at time t (min). The obtained data indicated that the studied adsorption process is considerably quick. Complete

adsorption/extraction can be achieved quickly using DS bio-adsorbent. The massiveness of active sites and easy Th(IV) ion diffusion accelerates the extraction process. Numerical values of unknown parameters can be estimated from the plot of $\log (q_e - q_t)$ and t/q_t versus t , as summarized in Table 2 and Figure 5C&D. These findings showed that according to the R^2 (>0.99) values, the pseudo-second-order model is more suitable than the pseudo-first-order model for the assessment of the extraction process of Th(IV) ions using the presented DS bio-adsorbent.

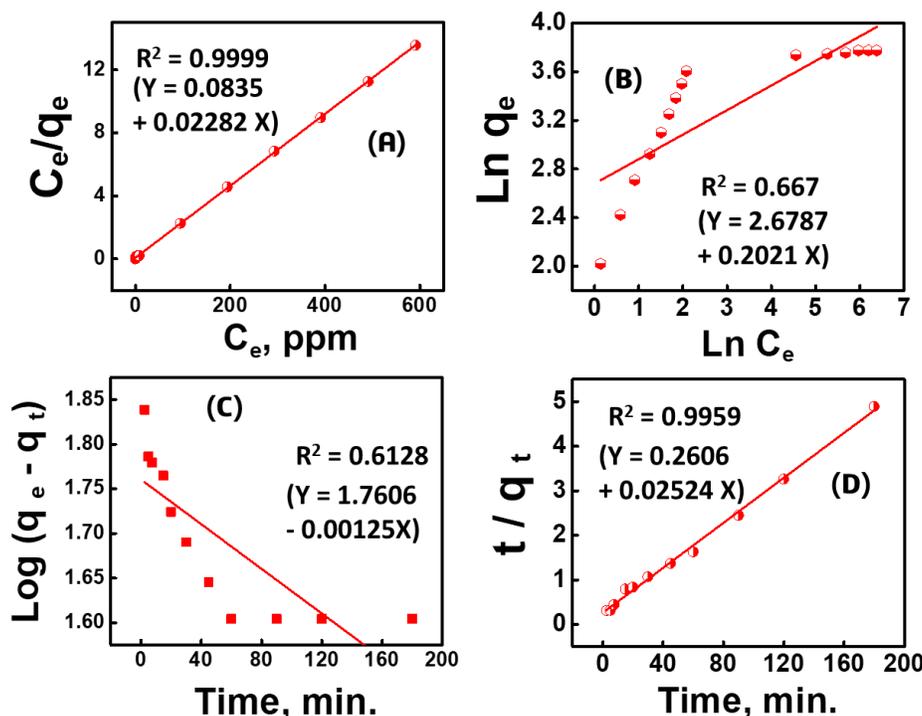


Figure 5. (A) The linear form of the Langmuir isotherm model for DS bio-adsorbent, where initial Th(IV) ion concentration [1–700 mg.L⁻¹] under the optimum experimental conditions; (B) The linear form of the Freundlich isotherm model for DS bio-adsorbent; (C) Linear form of pseudo-first order kinetic models of the Th(IV) ion adsorption using DS bio-adsorbents; (D) Linear form of pseudo-second order kinetic models of the Th(IV) ion adsorption using DS bio-adsorbent, under the optimum experimental conditions.

Table 2. The isotherm and kinetic models of Th(IV) adsorption using DS bio-adsorbent, under the optimum adsorption conditions.

Langmuir isotherm		Freundlich isotherm		Pseudo first-order		Pseudo second-order	
Experimental							
q_m (mg/g)	42.5						
R^2	0.9999	R^2	0.667	R^2	0.613	R^2	0.996
q_m	43.82	K_F , mg/g	14.56	q_e , mg/g	57.63	q_e , mg/g	39.62
K_L , L/mg	0.273	$1/n$	0.2	K_1 , min ⁻¹	0.00287	K_2 , g/mg.min	0.00244

3.5. Thorium elution behaviour

Elution of the interested analytes is performed by an appropriate solvent, without removing retained matrix components. The solvent volume must be adjusted so that quantitative recovery of the analytes is achieved with subsequent low dilution. The adsorbed Th(IV) onto DS bio-adsorbent was eluted with a suitable eluant. The solution was then filtered and the concentration

of Th(IV) was spectrophotometrically determined. The elution process of Th(IV) ions from the DS bio-adsorbent which adsorbed using the standard Th(IV) solution depends largely on a number of factors which have been carefully studied to obtain the optimum elution. These factors include type of eluent, concentration of eluent, contact time, and temperature.

3.5.1. Effect of eluent type

The effect of eluent type upon Th(IV) desorption efficiency was studied using mineral acids such as H₂SO₄, HCl and HNO₃ while the other factors were fixed (0.05g of bio-adsorbent loaded by thorium was stirred with 20 mL of 0.2 M acid for 30 min at room temperature). Under these mentioned conditions, Th(IV) desorption efficiencies using HNO₃ were 43.5 % for the DS bio-adsorbent, as shown in Figure 6A. From the obtained results, all the mineral acids can dissolve thorium ions from the spent DS bio-adsorbent with acceptable efficiencies. According, nitric acid is the best eluent agent for Th(IV) desorption from the used DS bio-adsorbent. The latter has thus been used for studying the other relevant parameters that have been applied in this study; namely the concentration of nitric acid, stirring time and temperature.

3.5.2. Effect of eluent concentration

The effect of eluent concentration (HNO₃) on elution of Th(IV) upon DS bio-adsorbent loaded by thorium ions was studied. For this purpose, elution experiments were carried out using different concentration of HNO₃ ranging from 0.025 to 0.5 mol.L⁻¹ while other factors were kept constant at 0.05 g of impregnated DS bio-adsorbent for 30 min contact time at room temperature. The obtained results in Figure 5B indicated that, the thorium elution efficiency increased with increasing concentration of eluent until reaching maximum value at 0.3 mol.L⁻¹ HNO₃ and the Th(IV) elution efficiency was almost stable after 0.3 mol.L⁻¹ HNO₃.

3.5.3. Effect of contact time

Effect of contact or stirring time on elution of the loaded thorium ions onto the DS bio-adsorbent was carried out by varying contact time from 5 to 60 minutes, while the other parameters were kept constant at 0.5 g of loaded DS bio-adsorbent contact with 20 mL of 0.3 mol.L⁻¹ HNO₃ at room temperature. The results in Figure 6C exhibited that the time required for maximum elution efficiency of Th(IV) ions was achieved within 60 min and then it becomes nearly constant.

3.5.4. Effect of temperature

The most important parameter that would control thorium elution percent is temperature (Cheira et al. 2020). Under the previous optimum conditions, the effect of temperature upon Th(IV) elution from the DS bio-adsorbent loaded by thorium ions was studied from 25 to 55 °C. From the obtained results reported in Figure 6D it can be observed that the Th(IV) elution percent increased with the increase of temperature, this is due to the breakdown of the bonds between bio-adsorbent and adsorbate.

3.6. Recyclability

The applied bio-adsorbent should exhibit efficient extraction and recyclability during several adsorption-elution processes to reduce the overall cost of thorium extraction process. Therefore, the regeneration of bio-adsorbent should be considered before practical applications. This study proved that the DS bio-adsorbent exhibit scientific features like high performance, recyclability, and durability. Stripping experiments were conducted several times by using 0.3 mol.L⁻¹ HNO₃ through a liquid exchange process to release the adsorbed Th(IV) ions and produce thorium-free bio-adsorbent. The treated DS bio-adsorbent was filtered, dried, and then used in successive

adsorption/extraction of target ions. The bio-adsorbent–Th(IV) solid were treated with $0.3 \text{ mol.L}^{-1} \text{ HNO}_3$ to release Th(IV) during batch-contact process as a function of reuse/cycle numbers. Figure 7 shows evidence that the DS bio-adsorbent could be recycled through the de-complexation of the bounded target ions.

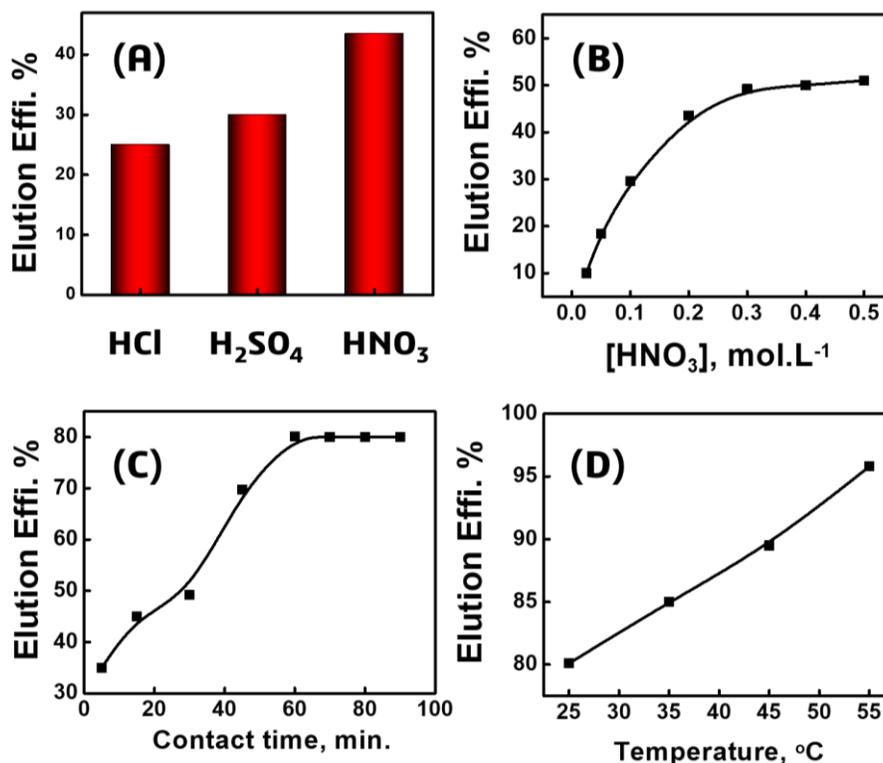


Figure 6. (A) Effect of acid type on the desorption or elution efficiency of Th(IV) ions from the spent DS bio-adsorbent; (B) Effect of HNO₃ concentration on the desorption or elution efficiency of Th(IV) ions from the spent DS bio-adsorbent; (C) Effect of contact or stirring time on the desorption or elution efficiency of Th(IV) ions from the spent DS bio-adsorbent; (D) Effect of temperature on the desorption or elution efficiency of Th(IV) ions from the spent DS bio-adsorbent.

To completely elute the adsorbed ions, a set of batch-contact experiments were performed by mixing 0.05 g of the bio-adsorbents–target solid with 20 mL of the eluent solution. Where, the elution efficiency can be calculated using the $(E_{\text{elution}}\%) = (C_{\text{released}}/C_{\text{adsorbed}}) \times 100$ equation. The high elution efficiency at low pH values could be due to the sufficiently high hydrogen ion concentration, leading to the strong competitive sorption on the DS bio-adsorbent surface. After the regeneration process, the bio-adsorbent was reused for five times (Figure 7). At 5th cycle, the DS bio-adsorbent exhibits high adsorption behavior toward Th(IV) ions (about 81 %), while the elution efficiencies are still high (more than 99%) for the DS bio-adsorbent. The decreasing of adsorption efficiencies may due to the dwindling of bio-adsorbents-surface active sites during the repeated adsorption/elution cycles.

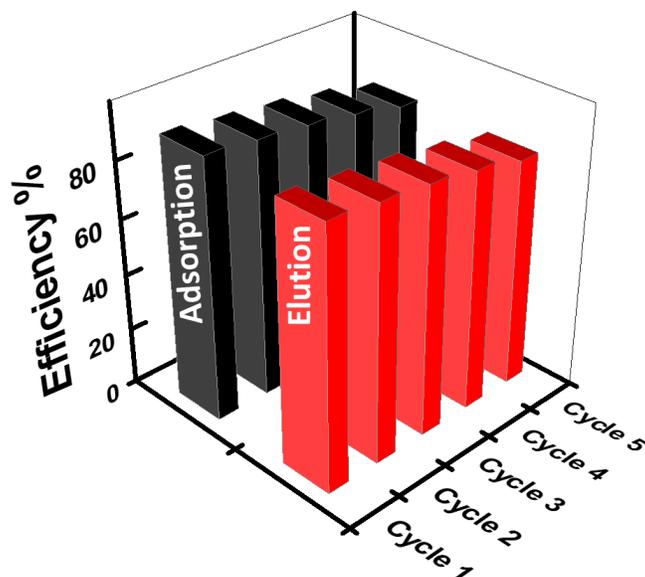


Figure 7. Investigation the recyclability of DS bio-adsorbent by studying the adsorption and elution efficiency of Th(IV) ions during batch-contact process as a function of reuse/cycle numbers.

4. CONCLUSION

Herein, we have presented the design of DS bio-adsorbent for the separation of Th(IV) ions from acidic solutions. The obtained results exhibited acceptable selectivity for Th(IV) in the presence of competitive metals in acidic conditions (pH 4). According to the isotherm studies, adsorption of Th(IV) ions using DS bio-adsorbent has a chemical nature. Langmuir model is more suitable model to fit the equilibrium adsorption data than the Freundlich model. The kinetic adsorption of thorium on these materials has been described by the pseudo-second order rate equation very well and confirms that chemical nature of thorium-adsorption reaction. Finally, the effective reusability of the proposed DS bio-adsorbent was demonstrated through many cycles of adsorption and desorption, suggesting that this material is a promising, sustainable, and green approach for the segregation of Th(IV) ions from secondary resources.

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