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ORIGINAL ARTICLE

Extraction of some strategic elements from thorium–uranium concentrate using bioproducts of *Aspergillus ficuum* and *Pseudomonas aeruginosa*

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Rare earth elements;
Aspergillus ficuum;
Pseudomonas aeruginosa;
Bioproducts

Abstract The activity of the bioproducts from *Aspergillus ficuum* and *Pseudomonas aeruginosa* for extraction of thorium (Th^{4+}), uranium (UO_2^{2+}) and rare earth elements (REEs) from thorium–uranium concentrate was studied. *P. aeruginosa* produce element-specific ligand (siderophore) that is able to change pH and enhance chelation of Th^{4+} and UO_2^{2+}. The produced siderophore at pH 5.3 has the ability to bioleach and is complexed with 68.00% of uranium and 65.00% of thorium. Also, *A. ficuum* produced different kinds of organic acids which leached 30.00% of uranium and 29.12% of thorium in addition to 20.00% of lanthanum, 33.00% of cerium and 2.51% of yttrium as rare earth elements at pH 3.0. Oxalic acid was efficient for Th^{4+}, UO_2^{2+} and REEs precipitation. The binocular stereo-microscope (BSM), environmental scanning electron microscope (ESEM) and X-ray diffraction (XRD) analyses confirmed the percentages of extracted metals. Exogenous poly-

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saccharides (EPSs) seem to play an important role in bioleaching and removal of these elements. It was found that EPSs produced by *A. ficuum* adsorbed Th^{4+}, UO_2^{2+} and REEs while that produced by *P. aeruginosa* adsorbed REEs only.

1. Introduction

Thorium, uranium and rare earth elements were considered strategic elements. Thorium is used as an alloying element in magnesium, used in aircraft engines, imparting high strength and creep resistance at elevated temperatures (Raju et al., 2007). Uranium used in major application in the military sector is in high-density penetrators also, in the civilian sector it is to fuel nuclear power plants (Calsteren and Thomas, 2006). Rare earth elements and their compounds have wide range of applications especially in metallurgy, ceramic industry and nuclear fuel control (Joona et al., 2006). Under iron-deficient conditions, special microorganisms synthesize secondary metabolites called ''siderophores'', which strongly scavenge extracellular Fe^{3+}. There are some species of fungi and bacteria able to produce siderophores. The most common siderophores-producing bacteria were *Pseudomona aeruginosa*, *P. fluorescence* and *Pseudomonas stutzeri*. The most common producing fungi were *Aspergillus flavus*, *A. niger* and *Rhizopus sp.* in case of fungi (Kalinowski et al., 2004). Siderophores have different chelation moieties, including hydroxamic acid, catechol and carboxyl group in the same molecule (Winkelmann, 1991). Acidolysis is the principal mechanism in bioleaching of metals by microbes which produced organic acids such as citric, oxalic, malic and gluconic acids during bioleaching (Johnson, 2006). The metabolites contained organic acids which dissolve metals from minerals by displacement of metal ion from the ore or soil matrix by hydrogen ions, or by the formation of metal complexes and chelates (Ren et al., 2009). The exogenous polysaccharides (EPSs) seem to play a vital role in bioleaching for the winning of precious metals. EPSs consist mainly of neutral sugars and lipids. The functions of the extracellular polymeric substances of this leaching bacterium seem: (i) to mediate attachment to metal sulfide surface, (ii) to concentrate iron (III) ions by complexation through uronic acids or other residues at the mineral surface and, thus, allowing for an oxidative attack on the sulfide. Consequently, dissolution of the metal sulfide is enhanced, which may result in an acceleration of 20- to 100-fold over chemical leaching (Kinzler et al., 2003). Thorium, uranium and REEs precipitated as rare earths oxalate using oxalic acids of 10% (Soe et al., 2008). Many techniques were used for characterizing the produced metals as BSE, ESEM, and XRD (Duďa and Rejl, 1986; Vijayaraghavan et al., 2009 and Sar et al., 1999).

2. Materials and methods

2.1. Microorganisms and growth conditions

The fungal strain *A. ficuum* was isolated from (Th–U) concentrate using Modified Czapek's–Dox agar (MCDA). The medium composition is as follows: sucrose 30 g/L; $NaNO_3$ 3 g/L; KH_2PO_4 1 g/L; $MgSO_4{\cdot}7H_2O$ 0.5 g/L; KCl 0.5 g/L; $FeSO_4$ 0.01 g/L; yeast extract 10 and agar-agar 20 g/L (Oujezdsky et al., 1972). While *P. aeruginosa* was obtained from previous work (Holt et al., 1994) was cultured on nutrient agar (NA) which is composed of: beef extract 3 g/L; bacteriological peptone 5 g/L; yeast extract 1 g/L; sodium chloride 5 g/L and agar-agar 20 g/L. *A. ficuum* culture was incubated at 28 °C for 5–7 days on MCDA and *P. aeruginosa* cultures were incubated at 35 °C for 1–3 days on NA.

2.2. Bioleaching and complexation of thorium, uranium with siderophore from (Th–U) concentrate

Production and extraction of siderophore by *P. aeruginosa* were carried out as the method previously described by Hussien (2007). This experiment was carried out to dissolve and precipitate thorium, uranium by making complexes with siderophore. Erlenmeyer conical flask (250 mL) containing 100 mL of extracted siderophore pH (5.3) was mixed with 1.2 g of (Th–U) concentrate. The mixture was shaken at room temperature using rotary shaker at 175 rpm for 24 h (Ren et al., 2009). Then the mixture was filtered using Whatman filter paper No. 1. The residue will be dried in the oven at 65 °C. On the other hand, the filtrate contained thorium, uranium and REEs in supernatant estimated as previously described by Marczenko (1976) and Busev et al. (1981). Also, these elements will be precipitated as previously described by Desouky (1998). The precipitated crystals of thorium oxalate and ammonium diuranate were characterized using BSM, ESEM then calcinated at 550 °C to obtain its oxide which was subjected to XRD analysis for identifying the unknown crystallized mineral.

2.3. Bioleaching of residual (Th–U) concentrate by the extracted organic acids produced by A. ficuum

This experiment aimed to bioleach the residual (Th–U) concentrate which mainly contained REEs and traces of thorium and uranium. Erlenmeyer 250 mL conical flask containing 100 mL of metabolite containing organic acids was produced by *A. ficuum* pH (3.0) mixed with 0.75 g of residue of (Th–U) concentrate. The mixture was shaken at room temperature using rotary shaker at 175 rpm for 24 h. Then the mixture was filtered using Whatman filter paper No. 1. The released REEs, thorium and uranium were estimated as mentioned in the previous experiment.

2.4. Binocular stereo-microscope (BSM)

Binocular stereo-microscope equipped with digital camera (Model Meiji EMZ-TR-Japan) was used to examine the crystals structure and photograph it. The apparatus was presented in (NMA), Cairo, Egypt.

2.5. Environmental scanning electron microscope (ESEM)

Environmental scanning electron microscope equipped with electron dispersive X-ray (EDX) was used to determine the biosorbed REEs on the biomasses. The samples were dried and examined by ESEM (Philips XL30, Holland). The operating conditions were vacuum 30 kV and BSE equals 10.0 BSE (back scattered electron) which is presented in Nuclear Materials Authority (NMA), Cairo, Egypt.

2.6. X-ray diffractometer (XRD)

X-ray diffraction pattern of dry, powder samples of REEs-free control and REEs sorbed *A. ficuum* and *P. aeruginosa* biomasses were recorded using (PHILIPS PW 3710/31 diffractometer with automatic sample changer PW 1775, (21 positions), Scintillation counter, Cu-target tube and Ni filter at 40 kV and 30 A. This instrument is connected to a computer system using X-40 diffraction program and ASTM cards for mineral identification. The apparatus was presented in NMA, Cairo, Egypt.

2.7. Removal of thorium, uranium and rare earth elements by exogenous polysaccharides (EPSs)

Exogenous polysaccharides (EPSs) were extracted from the culture filtrates of *A. ficuum* and *P. aeruginosa* in presence of 1.2 g/100 mL of (Th–U) concentrate as previously mentioned (Yan et al., 2008). The adsorbed REEs and other elements by EPSs of *A. ficuum* and *P. aeruginosa* were examined by ESEM. 0.05 N HCl was used for desorption of REEs adsorbed through EPSs of *A. ficuum* while 0.05 N H_2SO_4 was for desorption of REEs adsorbed by EPSs produced by *P. aeruginosa*. The desorbed REEs were precipitated by 10% oxalic acid.

2.8. Statistical analysis

All obtained experimental results were subjected to statistical analysis using statistical software SPSS (Ver. 10) as described by Steel et al. (1997).

3. Results

3.1. Chemical composition of (Th–U) concentrate

The chemical composition of monazite was illustrated in Table 1. It consists of 20.07% RE_2O_3, 4.45% Fe_2O_3, 19.01% ThO_2 and 2.44% UO_2.

3.2. Bioleaching and complexation of thorium, uranium with siderophore from (Th–U) concentrate

Fig. 1 indicates that the extracted siderophore bioleached and complexed with 68.00% of uranium, 65.00% of thorium highly than 4.3% of lanthanum, 5.4% of cerium and 1.2% of yttrium as rare earth elements.

3.3. Bioleaching of residual (Th–U) concentrate by the extracted organic acids produced by A. ficuum

Fig. 2 illustrates that *A. ficuum* metabolite leached 30.00% of uranium and 29.12% of thorium in addition to 20.00% of lanthanum, 33.00% of cerium and 2.51% of yttrium as rare earth elements. From the pregnant solutions, at pH 0.9 thorium precipitated as thorium oxalate using 10% oxalic acid. While, at pH 5–6 uranium precipitated as ammonium diuranate using 33% ammonium solution. In addition to, at pH 8.0–8.3 REEs precipitated as rare earth oxalate using 10% oxalic acid. Then all products were calcinated at 550 °C for XRD analysis.

Table 1 Chemical analysis of (Th–U) concentrate.

Samples	Elements (%)											
	RE_2O_3	Fe_2O_3	MnO_2	CaO	MgO	ThO_2	U_3O_8	Na_2O	K_2O	SiO_2	Al_2O_3	P_2O_5
(Th–U) concentrate	20.07	4.45	UDL	0.14	0.31	19.01	2.44	0.50	UDL	UDL	UDL	0.96

UDL: under detection limit.

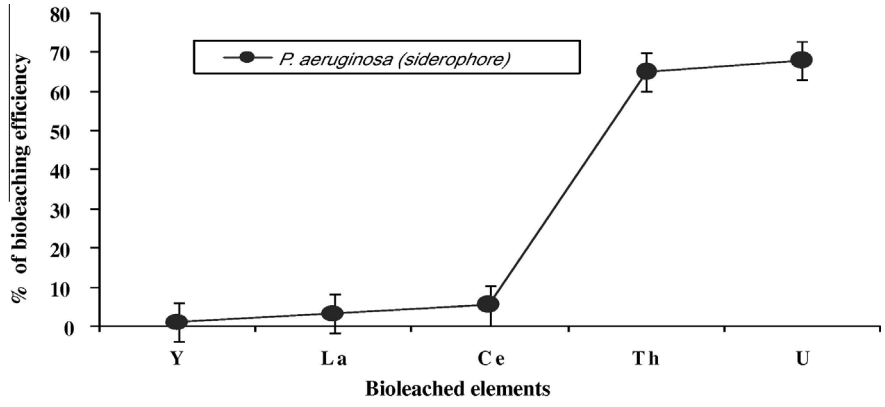

Figure 1 The affinity of siderophore produced by *P. aeruginosa* on bioleaching and complexation of thorium, uranium and some REEs from (Th–U) concentrate liquor.

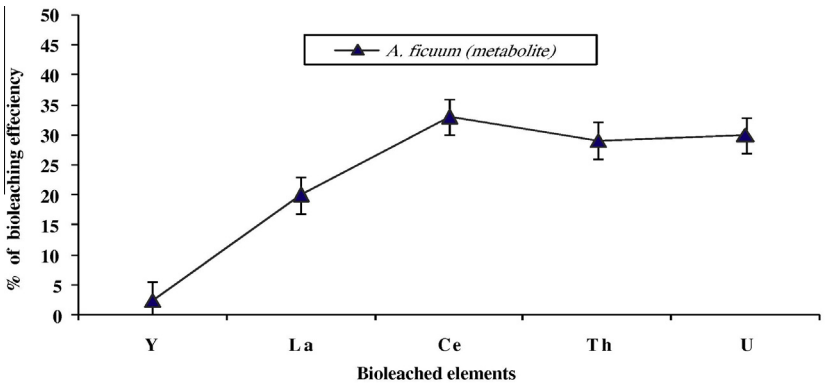

Figure 2 The affinity of organic acids produced by *P. aeruginosa* on bioleaching and complexation of thorium, uranium and some REEs from (Th-U) concentrate liquor.

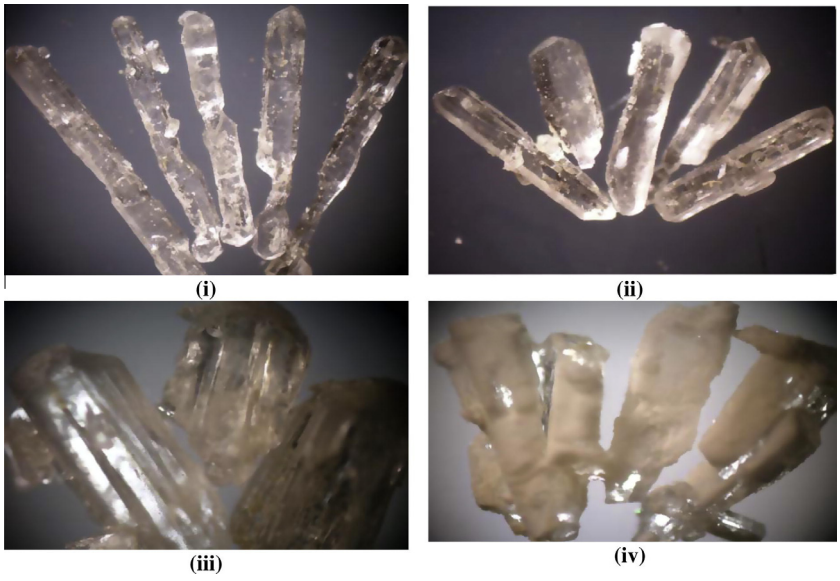

Plate 1 Stereo-photographs for the crystals of thorium oxalate complexed with siderophore extracted from *P. aeruginosa* : (i) long prismatic crystals of thorium oxalate, $X = 20$. (ii) Short prismatic crystals of thorium oxalate, $X = 20$. (iii) Shorter prismatic crystals of thorium oxalate, $X = 20$. (iv) Transparent prismatic crystals of thorium oxalate covered by chalky material, $X = 20$.

3.4. Characterization the crystals of thorium, rare earth oxalate and ammonium diuranate using BSM, ESEM and XRD

3.4.1. Stereo-photographs for crystals of thorium oxalate and ammonium diuranate using (BSM)

Binocular stereo-microscope (BSM) apparatus was used to illustrate the physical properties of the produced crystals of thorium oxalate and ammonium diuranate which were obtained from the previous experiments. It was known that any crystal has three directions, **a** = the width; **b** = the height and **c** = the length of crystal.

It was found that the crystals of thorium oxalate complexed with siderophore were transparent and belong to tetragonal and prismatic system. Plate 1 illustrates stereo-photographs for the crystals of thorium oxalate complexed with siderophore extracted from *P. aeruginosa*. It appeared that there were four shapes of crystals: (i) long prismatic crystals of thorium oxalate where, **c** = four times **a** or **b**; (ii) short prismatic crystals of thorium oxalate where, **c** = two times **a** or **b**; (iii) shorter prismatic crystals of thorium oxalate where, **c** = three times **a** or **b** and (iv) transparent prismatic crystals of thorium oxalate were covered by chalky material.

It was appeared that the crystals of thorium oxalate complexed with organic acids were transparent, monoclinic system where **c** # **a** # **b** and also crystal have a prismatic forms.

Plate 2 illustrates several forms for the crystals of thorium oxalate bioleached by metabolite of *A. ficuum* .These crystals may be: (i) short prismatic crystals of thorium oxalate; (ii) long prismatic crystals of thorium oxalate; (iii): twinned prismatic crystals of thorium oxalate and (iv) aggregate prismatic crystals of thorium oxalate.

Plate 3 illustrates stereo-photographs for the crystals of ammonium diuranate complexed with siderophore extracted from *P. aeruginosa*. It appeared that there were many forms of ammonium diuranate crystals with siderophore where: (i) close up view for uranophane associated with cubic form of

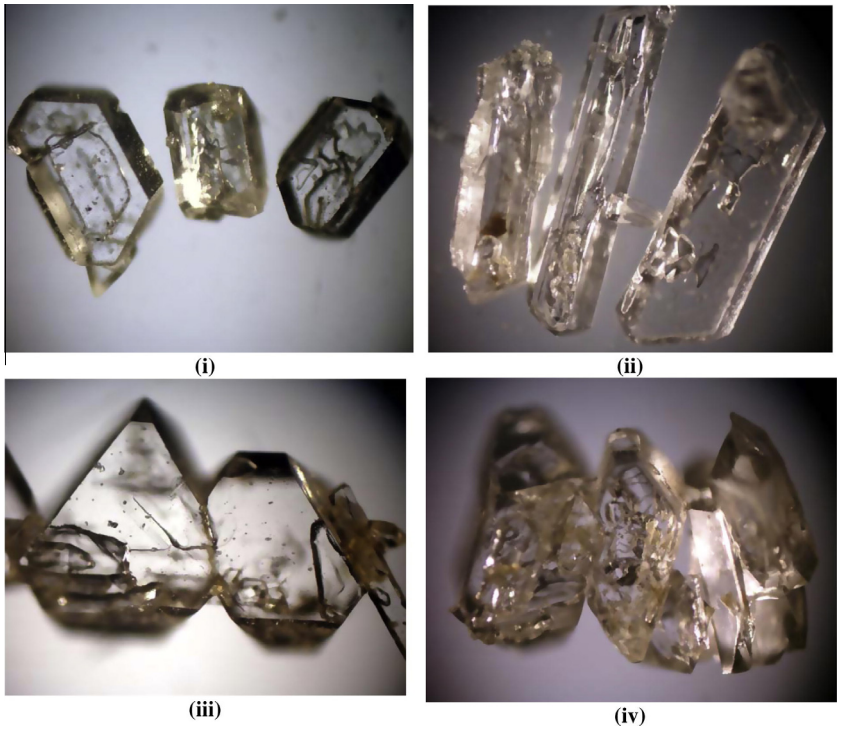

Plate 2 Stereo-photographs for the crystals of thorium oxalate bioleached by metabolite of *A. ficuum*: (i) Short prismatic crystals of thorium oxalate, $X = 20$. (ii) Long prismatic crystals of thorium oxalate, $X = 20$. (iii) Twinned prismatic crystals of thorium oxalate, $X = 20$. (iv) Aggregate prismatic crystals of thorium oxalate, $X = 20$.

siderophore compound, (ii) anhedral crystals of uranophane associated with fine cubic crystals of colorless siderophore compound and (iii) anhedral crystals of uranophane characterized by a lemon yellow color with less crystals of transparent siderophore compound.

Also, some crystals of thorium oxalate and ammonium diuranate were produced through the bioleaching of *A. ficuum* metabolite (including verities of organic acids) and precipitated by oxalic acid (10%) were stereo-photographed using binocular stereo-microscope (BSM).

Also, Plate 3(iv) illustrates stereo-photograph for ammonium diuranate crystals bioleached by *A. ficuum* metabolite may be aggregates of radiated crystals (needles form) of uranophane bioleached by metabolite of *A. ficuum*.

Moreover, it was noticed that, thorium and uranium bioleached and complexed with siderophore were highly pure than that bioleached by *A. ficuum* metabolite. In addition to, Plate 4 which illustrates stereo-photograph for the crystals of rare earths oxalate extracted from (Th–U) concentrate: (i) aggregates of colorless prismatic crystals form of rare earths oxalate, $X = 20$.

3.4.2. Scanning for the calcinated thorium, rare earths oxalate and ammonium diuranate using ESEM

Fig. 3 illustrates SEM micrograph and the corresponding EDX spectrum of thorium oxide. The results indicated that the percentage of ThO_2 was 81.85%. Also, Fig. 4 illustrates SEM micrograph and the corresponding EDX spectrum of calcinated ammonium diuranate where the percentage of U_3O_8 was 64.50%. In addition, Fig. 5 illustrates SEM micrograph and the corresponding EDX spectrum of rare earths oxide extracted from (Th–U) concentrate. The results indicated that REEs were presented in percentages of 20.75% La_2O_3, 34.71% of Ce_2O_3, 6.78% Pr_2O_3, 14.98% Nd_2O_3, 2.42% Sm_2O_3, 2.69% Gd_2O_3, 1.11% Tb_2O_3 and 2.34% Y_2O_3.

3.5. X-ray diffraction analysis of thorium oxide and calcinated ammonium diuranate

The obtained X-ray diffraction spectrum showed distinct peaks indicating the deposition of crystallized Th^{4+}. Diffractogram of the calcinated thorium oxalate displayed maximum number of peaks to Th^{4+} between 2θ of 27.68°, 2θ of 23.04°, 2θ of 47.02°, 2θ of 45.49° and 2θ of 60.35° as illustrated in Fig. 6. Significantly the D values of most of the peaks correspond to thorium oxide. Also, the obtained X-ray diffraction spectrum was shown in Fig. 7 which appears as distinct peaks indicating the deposition of crystallized U^{6+}. Diffractogram of the calcinated ammonium diuranate displayed maximum number of peaks to U^{6+} between 2θ of 8.48°, 2θ of 11.64°, 2θ of 21.04°, 2θ of 31.84° and 2θ of 45.38°. Significantly the D values of most of the peaks correspond to ammonium diuranate. Besides, sulfate displayed maximum number of peaks to ammonium sulfate between 2θ of 16.97°, 2θ of 26.73°, 2θ of 33.45° and also, sodium chloride displayed maximum number of peaks between 2θ of 48.97° and 2θ of 54.49°. In addition, the obtained X-ray diffraction spectrum showed distinct peaks indicating the deposition of crystallized REEs. Diffractogram of the calcinated rare earths oxalate displayed maximum number of peaks to La^{3+} and Ce^{3+} between 2θ of 16.91°, 2θ of 22.70° and 2θ of 45.85°. Also, for La^{3+} between 2θ of 31.33° and 2θ of 57.52° as illustrated in Fig. 8. Significantly

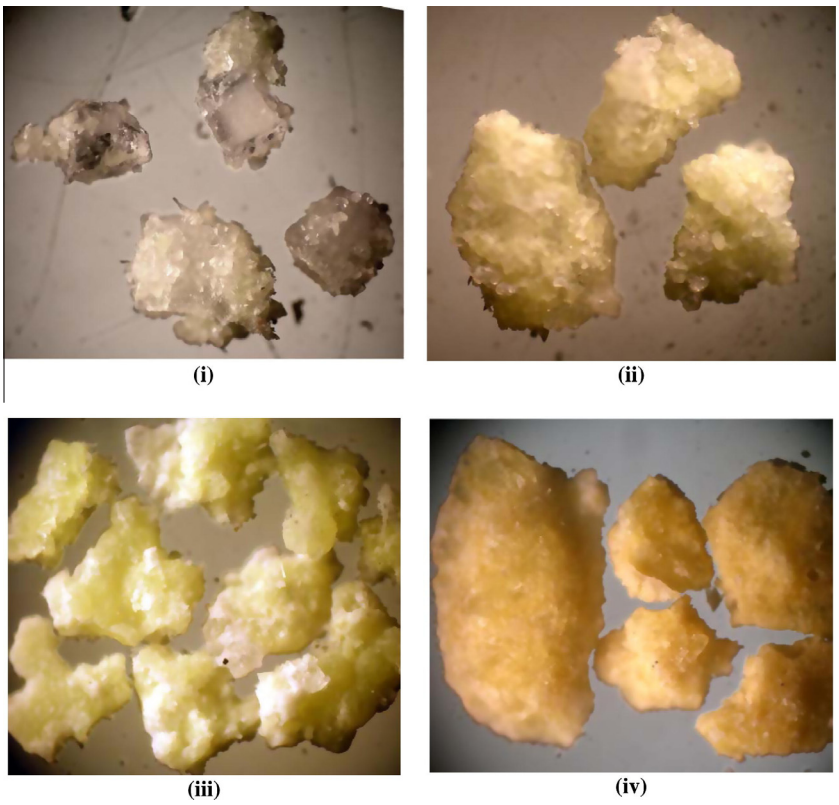

Plate 3 Stereo-photographs for the crystals of ammonium diuranate cake complexed with siderophore extracted from *P. aeruginosa*: (i): Close up view for uranophane and associated with cubic form of siderophore compound, $X = 20$. (ii) Anhedral crystals of uranophane associated with fine cubic crystals of colorless siderophore compound, $X = 20$. (iii) Anhedral crystals of uranophane characterized by a lemon yellow color with less crystals of transparent siderophore compound, $X = 20$. (iv) Aggregates of radiated crystals (needles form) of uranophane bioleached by *A. ficuum* metabolite, $X = 20$.

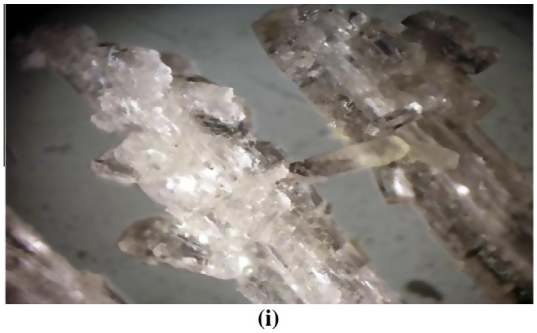

Plate 4 Stereo-photograph for the crystals of rare earths oxalate extracted from (Th–U) concentrate: (i) Aggregates of colorless prismatic crystals form of rare earths oxalate, $X = 20$.

the *D* values of most of the peaks correspond to lanthanum and cerium oxide.

3.6. Removal of thorium, uranium and rare earth elements by exogenous polysaccharides

Fig. 9A illustrates SEM micrograph and the corresponding EDX of spectrum of EPSs produced by *A. ficuum*. It appeared that EPSs adsorbed Na, Mg, Si, P, Th and U with low percentages. While, light REEs were adsorbed on EPSs by higher percentages such as 14.91% of La_2O_3, 27.48% of Ce_2O_3 and 23.59% of Nd_2O_3. The extracted EPSs were desorbed by 0.05 N HCl. Fig. 9B illustrates SEM micrograph and the corresponding EDX spectrum of *A. ficuum* EPSs after the desorption. It appeared that using 0.05 N HCl desorbed REEs with high percent where the remained REEs presented in percentages 0.39%, 1.65% and 0.66% for La_2O_3, Ce_2O_3 and Nd_2O_3, respectively.

On the other hand, Fig. 10A illustrates SEM micrograph and the corresponding EDX spectrum of *P. aeruginosa* EPSs. It appeared that the bacterial EPSs were more selective to adsorb La_2O_3 33.82% than other REEs. The extracted EPS were desorbed by 0.05 N H_2SO_4. Fig. 10B illustrates SEM micrograph and the corresponding EDX spectrum for *P. aeruginosa* EPSs after the desorption. It was appeared that 0.05 N H_2SO_4 desorbed REEs with high percent where the remained REEs presented in percentages 8.50%, 1.42%, 1.89%, 1.56%, 0.99% and 1.23% for La_2O_3, Ce_2O_3, Nd_2O_3 Pr_2O_3, Sm_2O_3 and Dy_2O_3, respectively.

In addition, the desorbed REEs were precipitated as rare earths oxalate using oxalic acid 10% for two eluting solutions as had appeared in Fig. 11.

4. Discussion

Concerning the extraction of Th^{4+}, U^{6+} and REEs using bioproducts, some species of fungi as *Fusarium* sp. and bacteria

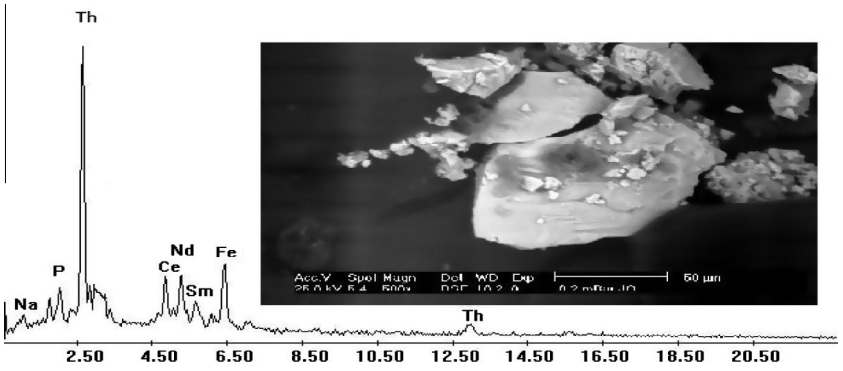

Figure 3 SEM micrograph and the corresponding EDX spectrum of thorium oxide.

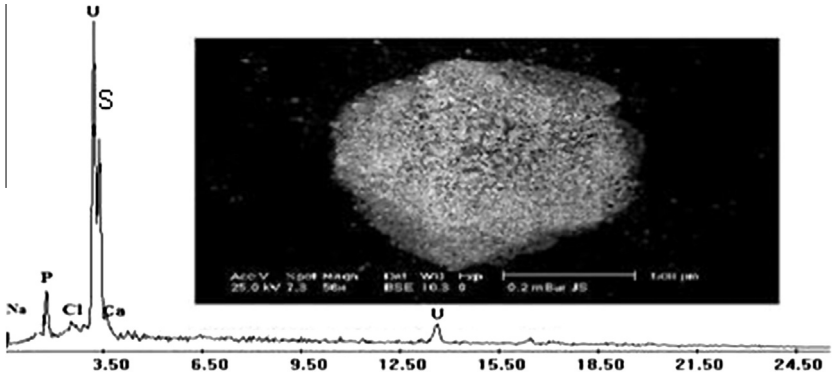

Figure 4 SEM micrograph and the corresponding EDX spectrum of calcinated ammonium diuranate cake.

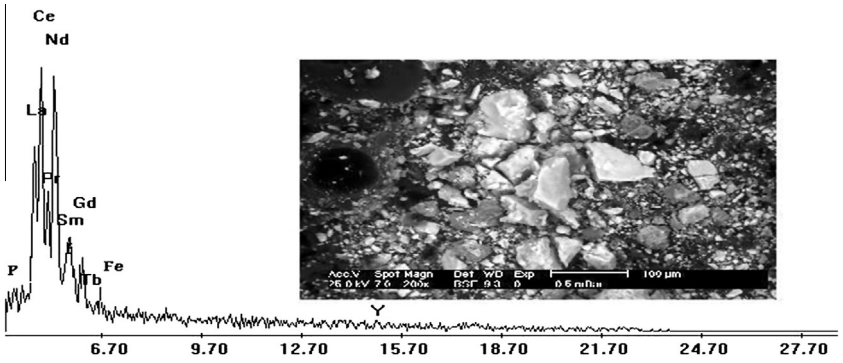

Figure 5 SEM micrograph and the corresponding EDX spectrum of rare earths oxide extracted from (Th–U) concentrate.

P. aeruginosa were able to produce element-specific ligands (siderophores) that are able to change pH and enhance the chelation of some elements as uranium (U^{6+}), thorium (Th^{4+}) as mentioned by Bouby et al. (1998b). The obtained results appeared that the extracted siderophore produced by *P. aeruginosa* bioleached and complexed with 68.00% of uranium, 65.00% of thorium and some REEs as lanthanum 4.3%, cerium 5.4% and yttrium 1.2% from (Th–U) concentrate. Thorium precipitated at pH 0.9 as thorium oxalate crystals using 10% oxalic acid while uranium precipitated at pH 5–6 as ammonium diuranate crystals using 33% ammonium hydroxide. These obtained results were in agreement with that obtained by Kalinowski et al. (2004). They observed the release of U from the batch culture of *P. fluorescence* from shale mine tailing at Ranstad as metal–pyoverdine complexes. Also, hydroxamate siderophores chelate other ions besides Fe(III), such as aluminum (Al(III)), ytterbium (Yb(III)) and dysprosium (Dy(III)), but with low affinity. Bouby et al. (1998a,b) found that 100% of the U^{6+} in their solutions was complexed by pyoverdine A ligand at pH > 4. Pyoverdine is able to effectively chelate Th(IV), U(VI).

The residual of (Th–U) concentrate after bioleaching and complexation of most uranium and thorium with siderophores mixed with 100 mL of *A. ficuum* metabolite leached 30.00% of uranium, 29.12% of thorium and some REEs as lanthanum 20.00%, cerium 33.00% and yttrium (2.51%). At pH 0.9 the

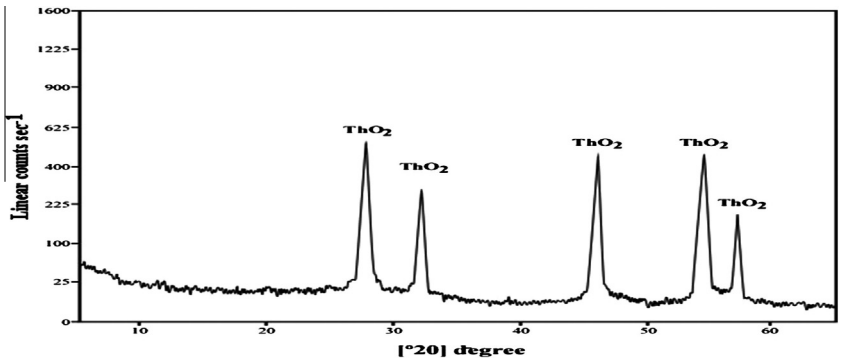

Figure 6 X-ray diffraction spectrum of thorium oxide (ThO_2).

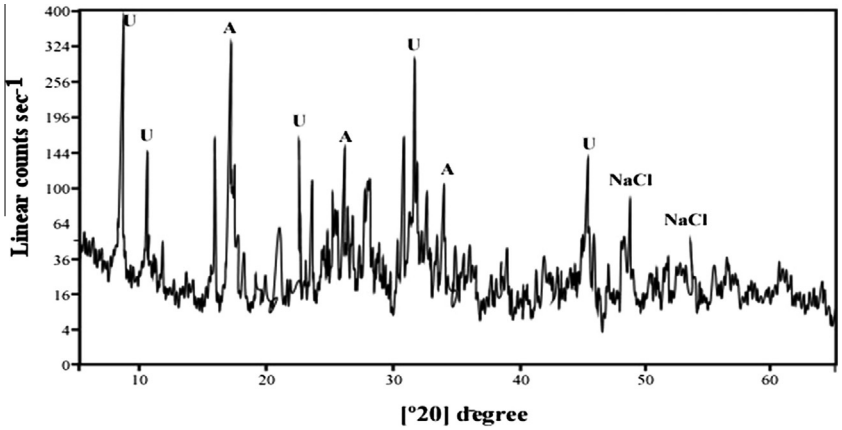

Figure 7 X-ray diffraction spectrum of calcinated uranium diuranate cake. U: ammonium diuranate, A: ammonium sulfate.

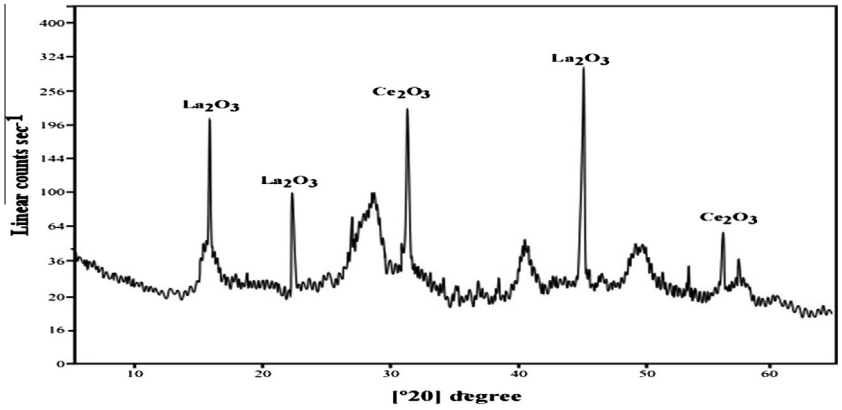

Figure 8 X-ray diffraction spectrum of rare earths oxide (RE_2O_3).

residual thorium precipitated as thorium oxalate using oxalic acid 10%, while at pH 5–6 uranium precipitated as ammonium diuranate using ammonium hydroxide 33%. Also, at pH 8–8.3 through using 20% sodium hydroxide REEs were precipitated as rare earths oxalate by oxalic acid 10%. These obtained results were in agreement with that previously obtained by Goyne et al. (2010). They mentioned that this greater recovery of REEs was due to the formation of REEs citrate complex in the solution under test and thus enhance the solubilization of the metal ions.

The physical properties of the produced thorium oxalate, ammonium diuranate and rare earths oxalate crystals were studied using BSM. It was found that the stereo-photographs of thorium oxalate crystals complexed with siderophore of *P. aeruginosa* were long prismatic, short prismatic, shorter prismatic and transparent prismatic covered by chalky material at $X = 20$. Also, stereo-photographs for thorium oxalate crystals bioleached by metabolite of *A. ficuum* were short prismatic, long prismatic, twinned prismatic and aggregate prismatic at

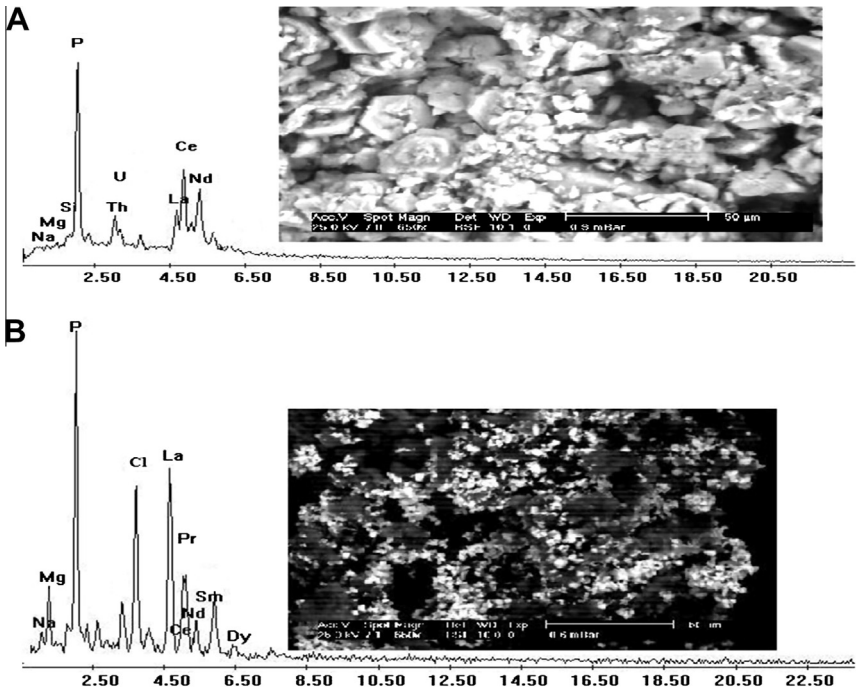

Figure 9 SEM micrograph and the corresponding EDX spectrum of EPSs produced by *A. ficuum* (A) and *P. aeruginosa* (B).

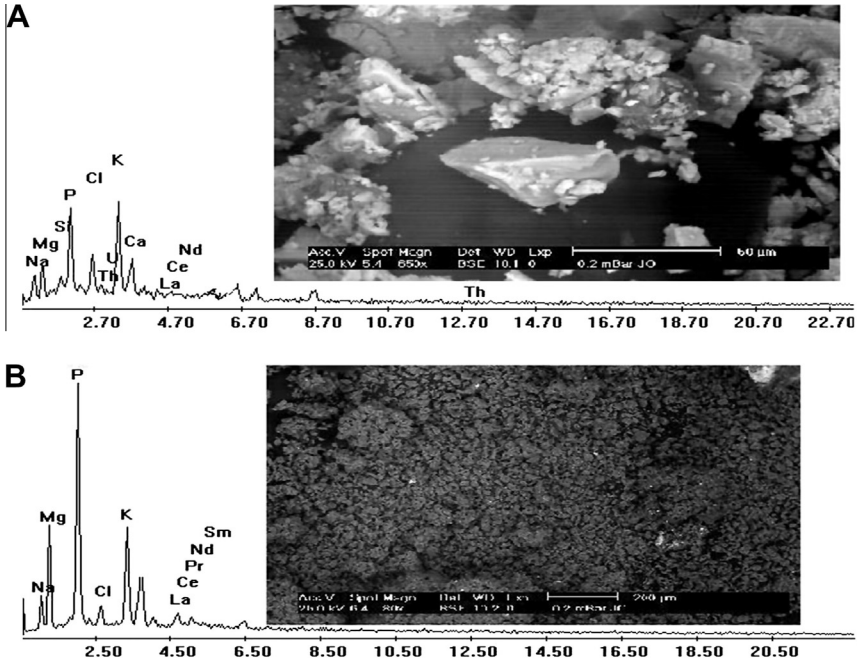

Figure 10 SEM micrograph and the corresponding EDX spectrum of *A. ficuum* (A) and *P. aeruginosa* EPSs (B) after the elution.

$X = 20$. On the other hand, in stereo-photographs for the crystals of ammonium diuranate with siderophore of *P. aeruginosa, it* appeared that, the crystals of uranophane were anhedral characterized by a lemon yellow color with less crystals of transparent siderophore at $X = 20$. While, these crystals which bioleached by *A. ficuum* metabolite appeared as aggregates of radiated crystals (needles form) of uranophane at $X = 20$. In addition to rare earths oxalate crystals were aggregates of colorless prismatic form. These obtained results were similar to that obtained by Duďa and Rejl (1986).

The EDX analysis for crystals of thorium oxalate indicated that the percentage of ThO_2 was 81.85% and U_3O_8 was 64.50%. In addition, the EDX analysis of rare earth oxalate indicated that the percentage of RE_2O_3 was 85.78%. These results were similar to that obtained by Vijayaraghavan et al. (2009).

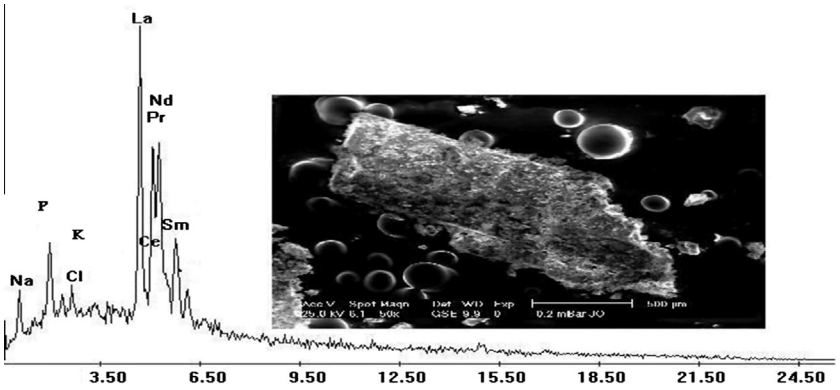

Figure 11 SEM micrograph with the corresponding EDX spectrum for the crystals of rare earth oxalate eluted from exogenous polysaccharides (EPSs).

Moreover, X-ray diffraction analysis illustrated that diffractogram of the calcinated thorium oxalate displayed maximum number of peaks to Th^{4+} between 2θ of 27.6°, 2θ of 23.04°, 2θ of 47.02°, 2θ of 45.49° and 2θ of 60.35°; however, diffractogram of the calcinated ammonium diuranate displayed maximum number of peaks to U^{6+} between 2θ of 8.48°, 2θ of 11.64°, 2θ of 21.04°, 2θ of 31.84° and 2θ of 45.38°. Also, diffractogram of the calcinated rare earths oxalate displayed maximum number of peaks to Ce^{3+} between 2θ of 16.91°, 2θ of 22.70° and 2θ of 45.85°. Also, for La^{3+} between 2θ of 31.33° and 2θ of 57.52°. These results were similar to that obtained by Kazy et al. (2009).

Exogenous polysaccharides (EPSs) produced by several kinds of bacteria and fungi have a direct attention in last years because their importance in metal chelation. The biosorption of metal ions by EPSs is non-metabolic, energy independent and can be caused by interaction between metal cations and negative charge of acidic functional groups of EPSs (Lyer et al., 2004). Exogenous polysaccharides (EPSs) produced by *A. ficuum* and *P. aeruginosa* in presence of monazite during the bioleaching process were extracted and subjected to elemental analysis by (ESEM). The obtained results showed that, the EDX analysis of EPSs produced by *A. ficuum* biosorbed 65.98% of light REEs such as La^{3+}, Ce^{3+} and Nd^{3+} in addition to, some heavy metals as (Th^{4+}) and (U^{6+}). Also, SEM analysis of *P. aeruginosa* EPSs appeared that, it biosorbed 45.72% of light REEs where the higher percentage of it was for La_2O_3 33.82%. Moreover, the results indicated that, the desorption percentages of biosorbed REEs by EPSs of tested fungi and bacteria using 0.05 N HCl and 0.05 N H_2SO_4 were 63.28% and 31.00%. These obtained results were in agreement with (Salehizadeh and Shojaosadati, 2003) who reported that the biosorption of Pb^{2+}, Cu^{2+}, Zn^{2+} has been observed by a novel acidic polysaccharide produced from *Bacillus firmus*. The exogenous polysaccharides are a complex mixture of macromolecular polyelectrolytes including polysaccharides, proteins, nucleic acids, lipids or humic substances (Comte et al., 2006). The functional groups as carboxylic, phosphate and sulfate groups present in EPSs works as a non-specific ion exchange material which may render chelating properties (Lyer et al., 2004).

The desorbed REEs precipitated as oxalate were scanned. In the EDX analysis it appeared that the percentages of REEs were La_2O_3, Ce_2O_3, Pr_2O_3, Nd_2O_3 and Sm_2O_3 were 28.53%, 2.11%, 1.87%, 2.90% and 1.50%, respectively.

5. Conclusions

The present investigation has demonstrated the use of bioproducts in extraction of some strategic elements from (Th–U) concentrate. Siderophore produced by *P. aeruginosa* bioleached and complexed with 68.00% of uranium, 65.00% of thorium highly than REEs While *A. ficuum* metabolite leached 30.00% of uranium, 29.12% of thorium beside 20.00% of lanthanum, 33.00% of cerium and 2.51% of yttrium REEs. The BSM and ESEM analyses were used for characterization the produced crystals where EDX analysis of thorium oxalate crystals indicates that the percentage of ThO_2 was 81.85% and U_3O_8 was 64.50% in ammonium diuranate. In addition the EDX analysis of RE_2O_3 indicated that the percentage of REEs was 85.78%. The X-ray diffraction analysis showed thorium oxide and ammonium diuranate. The EDX analysis of EPSs produced by *A. ficuum* biosorbed light REEs as La^{3+}, Ce^{3+}, Nd^{3+} in addition to, Th^{4+} and U^{6+}. Also, in the analysis of *P. aeruginosa* EPSs appeared the percentage of biosorbed light REEs. These results are considered promising aspects for extraction of Th^{4+}, U^{6+} and REEs using bioproducts of *A. ficuum* and *P. aeruginosa* biomasses as a potential ligands as alternative process which more technical and economic compared to the conventional process.

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