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OPTIMIZATION OF DIFFERENT PHYSICAL PARAMETERS FOR BIOLEACHING OF URANIUM AND RARE EARTH ELEMENTS FROM NUBIA SANDSTONES, WADI NATASH, EASTERN DESERT, EGYPT

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ABSTRACT

Five fungal species were isolated from two Nubia sandstone samples at Wadi Natash, Eastern Desert, Egypt. These species were then tested for their ability in bioleaching of uranium and rare earth elements from the two ore samples (G1&G2) whose assay of U attains 65 and 150ppm respectively while their assay of REEs attains 1590 and 1152 ppm respectively. Among the isolated fungi both *Aspergillus niger* and *Aspergillus flavus* have been the only species that give the highest leaching efficiencies. Thus in case of G2 sample the leaching of U has reached up to 90% of uranium by using *A.niger* while that of REEs has attained 84% by *A.flavus* under the studied optimum conditions. The latter involved shaking at 100rpm for 7days incubation time, 2% pulp density, > 0.2mm grain size and 35°C incubation temperature. Production of organic acids (oxalic and, citric acids) by two fungal species in their culture filtrate represents the key of the realized bioleaching processes.

INTRODUCTION

Worldwide reserves of high-grade ores are diminishing at an alarming rate due to the rapid increase in the demand for metals. However, there exists a large stockpile of low grade ores yet to be demanded. The problem is that the recovery of metals from low grade ores using conventional techniques is very expensive due to high energy and capital inputs required. Another major problem is environmental costs due to the high level of pollution from these technologies.

Microbes are increasingly used beneficially to extract commercially important elements by solubilization (bioleaching) from low grade ores. Bioleaching technology presents a potential solution for the problems which are being faced in many countries, where continuing depletion of high-grade ore deposits has

created a need to develop cost-effective and environmentally acceptable methods for recovery of metals from low-grade resources. The application of biotechnological principles for obtaining uranium and rare earth elements (REEs) offers a number of advantages over conventional hydrometallurgical techniques. The major benefits perceived are low cost, ease of maintenance and safety to the environment (Bhatti et al., 1991 and Torma, 1995). Uranium and REEs are considered as strategic elements where they have a wide range of application in industry especially the military and civilian sectors, metallurgy and nuclear fuel industries (Calsteren and Thomas, 2006 and Joona et al., 2006). Also they are used in medicine and agriculture applications.

The environmental behavior of U and REEs is affected by biotic factors including interactions with microorganisms and their

originated substances, such as citric acid and humic matters. Also, some organic materials as polysaccharides, proteins, nucleic acid and lipids secreted from the organisms represent the extracellular polymeric substances that would bind the metals (Flemming, 1995). Thus, microbial by-products or oxidation of organic matter may contribute directly to dissolution and mobility of REE compounds through increase in abundance of dissolved CO_2 (Taunton et al., 2000).

One of the most effective examples of microorganisms which have the ability to solubilize the low-grade ores is fungi (Heba, 2010). These organisms are able to solubilize heavy metals and metalloids from insoluble compounds such as ores, phosphate compounds sulfides and oxides. Several mechanisms may be involved in bioleaching, as acidolysis; complexolysis and redoxolysis (Schinner et al., 1989 and Bosshard et al., 1996). Acidolysis is the principal mechanism in bioleaching of metals by microbes which would produce organic acids such as citric, oxalic, malic and gluconic acids which can serve as leaching agents for solubilization of metals (Johnson, 2006).

The studied Nubia Sandstones are of most economic value, where they are characterized by the presence of important elements especially U, REEs, Zr, Y, Cr, Ba, Sr and Nb through several mineralization phases. Less attention has been paid to the role of microorganisms for leaching of rare earth elements (REEs) from rock samples. The present work highlights this area where it aims to investigate the ability of certain isolated fungal species to solubilize both uranium and REEs from the Nubia Sandstones of Wadi Natash. The roles of the relevant factors of the bioleaching process and their optimization have adequately been investigated. The metabolic activities of the tested organisms were examined to explain the mechanism of uranium and REEs solubilization by these microorganisms.

MATERIALS AND METHODS

Ore Characterization

Two geologic samples (G1 and G2) were collected from the Cretaceous Nubia Sandstone of Wadi Natash, Eastern Desert, Egypt (Fig. 1). These samples are packed in sterile polyethylene bags. On the other hand, the studied samples were completely analyzed chemically to determine their major oxides, as well as the content of U and REEs besides some trace elements.

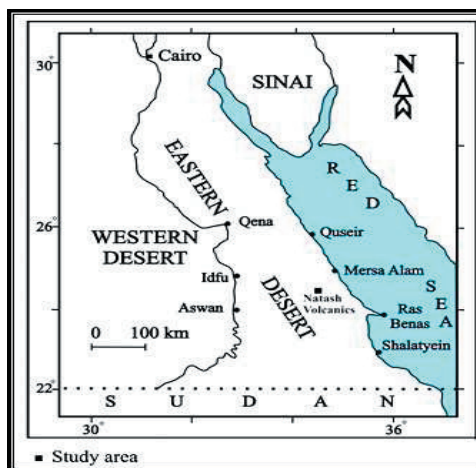


Fig. 1: Location map of the studied area

The major oxides were estimated by wet chemical analyses using spectrophotometer and flame photometer techniques (Shapiro and Brannock, 1962), while the trace elements content was measured with atomic absorption and XRF techniques. Total rare earth elements (REEs) were analyzed using spectrophotometer by ARZ (Marczenko 1986). Uranium in the samples as well as in culture filtrate was measured chemically by titration against NH_4VO_3 , (Davies and Gray, 1964).

Microbial Isolation

The Dox agar medium of composition (g/l): NaNO_3 , 2; $\text{K}_2\text{HPO}_4 \cdot 3 \text{H}_2\text{O}$, 1; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.5; KCl, 0.5; $\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$, trace; sucrose, 30; agar, 15.5g, yeast extract was added to initiate fungal growth. The pH value of the media

was adjusted to be 6.5 before autoclaving at 1.5 atm for 20 minutes. Two techniques were used in fungal isolation from the ore sample. The first one is the direct-plating technique, in which fine ore-powder was spread directly on the surface of Dox agar plates under aseptic conditions. The agar plates were incubated at $30\text{ }^{\circ}\text{C} \pm 2$ until the fungal colonies appear well.

The second technique is the dilution plating in which 1g of the ore powder was taken under aseptic conditions and mixed well with 9 ml of sterile distilled water, 0.1 ml of this mixture was spread under aseptic conditions by sterile glass rod on the surface of agar plate. The plates were then incubated at $30\text{ }^{\circ}\text{C} \pm 2$ until development of the colony. Hyphal tips of each colony were removed and plated on the surface of agar plates. The developed colonies were examined with a microscope to detect contamination. The pure isolated fungi were identified according to Gillman (1957) and Pitt (1979).

Experimental Procedures

Bioleaching procedures

In all bioleaching experiment, one hundred ml of Dox liquid medium was placed in 250 ml Erlenmeyer flasks. The flasks are supplemented with 1gm sample of the working samples. The flasks are then autoclaved at 1.5 atm for 20 min, after cooling the flasks are inoculated with 0.5 ml of spore suspension and finally incubated at $30\text{ }^{\circ}\text{C}$ for 7 days in an orbital shaker at 100 rpm. The liquid media is filtered several times using Whatman No.1 filter paper. Finally the filtrate is centrifuged at 6000 rpm to precipitate any more particles before its analysis for uranium and REEs.

However, before systematic study of the relevant factors affecting the bioleaching efficiency of U and REEs, two experimental sets are performed to determine the effect of the sample portion weight upon the fungal growth as well as to determine the effect of fungal activity on the bioleaching efficiency of studied two metal values. In the former, the mycelia

mats are harvested and washed several times with distilled water, dried at $85\text{ }^{\circ}\text{C}$ for 24 hours and the dry weight was determined.

The relevant factors affecting the bioleaching efficiency of U and REEs have then been systematically studied using *A. niger* and *A. flavus*. The studied factors involve the effect of the ore wt vs. fungal strain liquid volume, the gran size, incubation temperature and incubation time.

Recovery procedures

To study the procedures of recovering REEs and U from the working Nubian sandstone samples, proper leach liquor has been prepared using 2Kg ore and applied the determined optimum conditions. However, the two leached metal values have first been precipitated as their hydroxides followed by their dissolution in one molar sulfuric acid in a manner to increase their concentration for U recovery, Amberlite IRA-400 anion exchange resin has been used while from the obtained U-free effluent, the REEs have been recovered by precipitations as their oxalates

RESULT AND DISCUSSION

Characteristics of the Working Ore Samples

From the geological and mineralogical view point, the studied Nubia sandstone samples are mainly composed of quartz arenite, greywacke and calcareous sandstone. According to Ibrahim et al., (2011), they are characterized by the presences of uranium minerals; metaheinrichite $[\text{Ba}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}]$, uranophane $\text{Ca}(\text{UO}_2)_2(\text{SiO}_3)_2(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ and autunite $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{H}_2\text{O}$ and accessories such as zircon (ZrSiO_4), xenotime (YPO_4) and fluorite (CaF_2), which carry heavy rare earth elements (HREEs), whereas allanite $[(\text{Ca}, \text{Ce}, \text{La}, \text{Y})_2(\text{Al}, \text{Fe})_3(\text{SiO}_4)_3(\text{OH})]$ and monazite $(\text{Ce}, \text{La}, \text{Th}, \text{Nd}, \text{Y}) \text{PO}_4$ are the source of light rare earth elements (LREEs).

Chemical Analysis of Ore Samples

The complete chemical analysis of the two ore samples shows more enrichment in SiO_2 ,

Fe₂O₃, Zr, Y, Cr, Ba, Sr and REEs, in addition to moderate concentration of U (Table 1). The high elemental concentrations may be due to the mineral phase's constituents. Also most of these elements have affinity to be adsorbed on the clay fraction, humic matter and/or oxy-hydroxides especially Fe-Mn oxides.

Table 1: Chemical analysis of major oxides (wt%) and trace elements (ppm)

| Sp. No. | G1 | G2 | Sp. No. | G1 | G2 |
|--------------------------------|-------|-------|-------------|------|------|
| Oxides(wt%) | | | Element ppm | | |
| SiO ₂ | 77.07 | 80.87 | Cr | 185 | 187 |
| Al ₂ O ₃ | 5.24 | 5.60 | Ni | 14 | 13 |
| TiO ₂ | 1.02 | 0.94 | Cu | 11 | 12 |
| Fe ₂ O ₃ | 10.2 | 8.6 | Zn | 51 | 51 |
| CaO | 0.56 | 0.84 | Zr | 4170 | 3719 |
| MgO | 0.4 | 0.4 | Rb | 19 | 15 |
| Na ₂ O | 1.15 | 0.28 | Y | 1869 | 1670 |
| K ₂ O | 0.57 | 0.38 | Ba | 504 | 726 |
| P ₂ O ₅ | 0.16 | 0.24 | Pb | 55 | 41 |
| 1100C | 0.15 | 0.36 | Sr | 195 | 174 |
| 5500C | 1.43 | 0.78 | Ga | 20 | 34 |
| 10000C | 1.01 | 0.53 | V | 25 | 28 |
| Total | 99.96 | 99.82 | Nb | 800 | 715 |
| REEs (ppm) | 1590 | 1152 | Uranium(U) | 65 | 150 |

Determination of the Working Conditions

Ore sample /fungal Dox liquid (w/v)

Five fungal species were isolated from the tested ores. They are identified as *Aspergillus niger*, *Aspergillus spinulosum*, *Aspergillus flavus*, *Penicillium oxalicum* and *Penicillium lividum*. All of the tested fungi could grow in the presence of different ore concentrations up to 8 % (Table 2). The growth of isolated fungi was highly decreased with increasing ore concentrations in the growth media. More than 50% inhibition occurred at 6% of the ore concentrations G1 and G2. At this concentration *P.oxalicum* shows a slightly decreasing in growth. The percentage of growth inhibition of the ore samples G1 and G2 reaches to 36% and 26%, respectively. This may be attributed to the ability of this organism to tolerate and grow under stress of uranium and REEs.

Table 2: Effect of different ore concentrations on the growth of isolated fungi., Data are expressed as mycelia dry weight (mg/100ml culture medium)

| Organisms | Sp.No. | Ore concentrations | | | | | |
|---------------------|--------|--------------------|-----|-----|-----|-----|-----|
| | | 0% | 1% | 2% | 4% | 6% | 8% |
| <i>A. niger</i> | G1 | 783 | 768 | 664 | 558 | 353 | 247 |
| | G2 | 751 | 735 | 652 | 479 | 256 | |
| <i>A.flavus</i> | G1 | 799 | 754 | 565 | 542 | 345 | 283 |
| | G2 | 787 | 637 | 576 | 411 | 228 | |
| <i>P.lividum</i> | G1 | 863 | 672 | 555 | 437 | 254 | 144 |
| | G2 | 749 | 653 | 459 | 227 | 109 | |
| <i>P.spinulosum</i> | G1 | 787 | 755 | 561 | 531 | 262 | 158 |
| | G2 | 692 | 615 | 526 | 353 | 213 | |
| <i>P.oxalicum</i> | G1 | 766 | 664 | 587 | 553 | 500 | |
| | G2 | 867 | 725 | 705 | 665 | 637 | 564 |

Efficiency of fungal strains upon U and REEs bioleaching

The leaching processes of uranium and REEs using isolated fungi show highest efficiency by *A.niger* and *A.flavus* (Table 3). *A.niger* solubilizes 66% and 61% of uranium from the samples G1 and G2, respectively whereas that of REEs is 34% and 51% respectively. *A.flavus* reveals maximum bioleaching values 60% and 28% of uranium and REEs from ore G1 and 58% and 36% from ore G2, respectively. The best leaching of uranium and REEs occurs only when the final pH of the media was shifted toward acidity.

Table 3: Bioleaching efficiency of uranium and REEs using fungal isolates

| Fungus sp. | Sp.No. | U leaching efficiency (%) | REEs leaching efficiency (%) | Final pH |
|---------------------|--------|---------------------------|------------------------------|----------|
| <i>A. niger</i> | G1 | 66 | 34 | 3.24 |
| | G2 | 61 | 31 | 4.13 |
| <i>A.flavus</i> | G1 | 60 | 28 | 3.42 |
| | G2 | 58 | 36 | 3.82 |
| <i>P.lividum</i> | G1 | 40 | 20 | 3.97 |
| | G2 | 38 | 23 | 4.06 |
| <i>P.spinulosum</i> | G1 | 26 | 18 | 4.77 |
| | G2 | 24 | 25 | 5.36 |
| <i>P.oxalicum</i> | G1 | 33 | 9 | 4.44 |
| | G2 | 29 | 11 | 4.83 |

The recognition of organic acids produced by the tested fungal strains during leaching of ores was carried out by using HPLC. Data presented on Fig. (2) indicate that the extracted filtrate had two peaks the first for citric acid while the second for oxalic acid. The charts proved that the acids varied in their quantities according to the fungal strain. The concentration of citric and oxalic acid in the fermented liquor by *A. niger* are 23.35 and 4.90 mg/ml, whereas being 10.186 and 4.44 mg/ml, respectively with *A. flavus*. From the previous observation it can be found that the citric and oxalic acids content produced by *A. niger* was higher than that produced by *A. flavus* often incubation period 7 days. This explains the higher bioleaching efficiency of *A.niger* than by *A.flavus* for uranium and REEs.

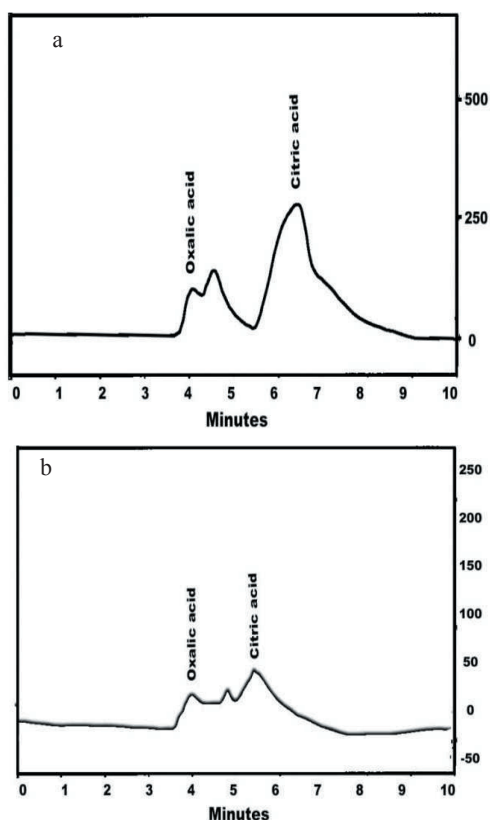


Fig. 2: Determination of organic acids produced by (A) *A. niger*. (B) *A. flavus*

Optimization of *A. niger* and *A. flavus* on Bioleaching Solubilization

Effect of ore sample /fungal Dox liquid (w/v)

Solubilization of uranium and REEs by *A. niger* and *A. flavus* from the studied samples was found to be decreased by increasing ore concentration in the growth media up to 2%, where their highest leaching efficiency was recorded at concentration 2% of G1 and G2 (Table 4). This agree with that recorded by Liu et al. (2008), where they obtain a high leaching capacity of some metals at 2% (w/v) solids concentration by indigenous sulfur-oxidizing bacteria. The highest dissolution of these metals was detected at acidic pH conditions.

A. niger shows higher leaching efficiency of uranium and REEs than that recorded by *A. flavus* (Table 4). This may be attributed to sufficient organic acids produced by this species which enhanced the solubilization of these elements.

Table 4: Effect of different ore concentrations of (G1, G2) on solubilization of uranium and REEs using *A. niger* and *A. flavus*

| Organisms | Element | Ore sample | Ore concentration (%) | | | | |
|------------------|----------|------------|-----------------------|------|------|------|------|
| | | | 1 | 2 | 3 | 5 | 6 |
| <i>A. niger</i> | U (%) | G1 | 61 | 63 | 46 | 15 | 12.8 |
| | | G2 | 53 | 55 | 24 | 13 | 6 |
| | REEs (%) | G1 | 35 | 37 | 17 | 13 | 10.7 |
| | | G2 | 52 | 53 | 27 | 16 | 11.6 |
| | pH | G1 | 2.9 | 2.7 | 3.5 | 4.4 | 5.2 |
| | | G2 | 3 | 3.03 | 3.9 | 4.35 | 4.8 |
| <i>A. flavus</i> | U (%) | G1 | 56 | 57 | 40 | 25 | 10 |
| | | G2 | 44 | 48 | 26 | 18 | 15 |
| | REEs (%) | G1 | 26.6 | 47 | 15.7 | 8.4 | 4.12 |
| | | G2 | 30 | 56 | 17 | 11 | 6 |
| | pH | G1 | 2.7 | 3.9 | 4.6 | 4.9 | 5.7 |
| | | G2 | 3.3 | 3.5 | 4.4 | 5.2 | 5.5 |

Effect of different grain sizes on uranium and REEs solubilization

The illustration of the relationship between grain size of the studied samples and leaching capacity of elements shows maximum solubilization of U and REEs at 0.2 mm grain size of the ore (Table 5). Then the solubilization of these metals was decreased with increasing the grain size of the ores. The final pH was shifted toward alkalinity. This result is agreed with Amin (2007), who obtained highest leaching efficiency of uranium by *Aspergillus* and *Penicillium* species at grain size fraction 0.2 mm. of the ore.

Table 5: Effect of different grain sizes on uranium and REEs solubilization by *A. niger* and *A. flavus*

| Organisms | Elements | Ore sample | Grain size(mm) | | | |
|------------------|----------|------------|----------------|------|------|-----|
| | | | 0.2 | 0.4 | 0.8 | 1.7 |
| <i>A. niger</i> | U (%) | G1 | 67 | 57 | 40 | 25 |
| | | G2 | 44 | 34 | 27 | 19 |
| | REEs (%) | G1 | 21 | 18 | 15.7 | 8.4 |
| | | G2 | 30 | 22 | 17 | 11 |
| | pH | G1 | 2.7 | 3.9 | 4.6 | 4.9 |
| | | G2 | 3.3 | 3.5 | 4.4 | 5.2 |
| <i>A. flavus</i> | U (%) | G1 | 54 | 47 | 40 | 35 |
| | | G2 | 38 | 36 | 26 | 17 |
| | REEs (%) | G1 | 28 | 26.7 | 12 | 9.4 |
| | | G2 | 33 | 30 | 18 | 12 |
| | pH | G1 | 2.6 | 3.9 | 5.7 | 6.7 |
| | | G2 | 3.6 | 3.7 | 4.8 | 6.6 |

Effect of different incubation periods on uranium and REEs solubilization

The obtained results in Table (6) indicate that the dissolution of U and REEs from the ore samples was highly affected by incubation time using *A. niger* and *A. flavus*. The maximum leaching efficiencies of uranium and REEs by *A. niger* are 65% and 47% from the ore G1 and 51% and 55.4 % from the ore G2 respectively at 7 days of incubation. After this time the leaching efficiency decreases. *A. flavus* has maximum solubilization at 9 days of incubation where it leached about 68% and 44% of uranium and REEs from G1 and 57% and 44% of uranium and REEs from G2 respectively, after this time the dissolution of these metals decreases (Table 6).

Table 6: Effect of different incubation period on solubilization of uranium and REEs using *A. niger* and *A. flavus*

| Organisms | Element | Ore sample | Incubation periods (days) | | | | |
|------------------|----------|------------|---------------------------|------|------|------|------|
| | | | 3 | 5 | 7 | 9 | 10 |
| <i>A. niger</i> | U (%) | G1 | 42 | 57 | 65 | 61 | 30 |
| | | G2 | 32 | 43 | 57 | 46 | 16 |
| | REEs (%) | G1 | 22 | 39 | 44 | 18.2 | 15 |
| | | G2 | 32 | 45.5 | 50.4 | 26.3 | 18 |
| | pH | G1 | 3.7 | 3.6 | 3.2 | 3.7 | 5.5 |
| | | G2 | 3.1 | 3.4 | 2.5 | 4.7 | 5.3 |
| <i>A. flavus</i> | U (%) | G1 | 39 | 50.5 | 61.5 | 63 | 37 |
| | | G2 | 23 | 41.6 | 48.3 | 51 | 25 |
| | REEs (%) | G1 | 17 | 22.4 | 45 | 47 | 31 |
| | | G2 | 20.5 | 23 | 33 | 54.2 | 19.5 |
| | pH | G1 | 5.03 | 4.9 | 3.6 | 2.4 | 6.8 |
| | | G2 | 5.1 | 4.3 | 3.2 | 2.8 | 4.1 |

This may be attributed to the effect of some metal ions brought out to the medium. This agree with the suggestion of Pathak et al. (2009), where they solubilized many metals such as Cu, Ni, Zn and Cr from the sludge after 16 days of bioleaching by indigenous iron oxidizing microorganisms

Effect of different incubation temperatures on uranium and REEs solubilization

The data shown in Table (7) emphasize that the maximum leaching efficiencies of U and REEs from the studied ore samples (72% and 56% respectively) was recorded at 35 °C. The solubilization of these metals was decreased with increasing the incubation temperatures. This attributed to the effect of temperature on the activity of the tested fungi. Anjum *et al.*,

(2010) reported that the maximum solubilization of copper (68.5%), zinc (49.0%) and cobalt (60.4%) using media containing mango peel, rice bran and glucose as substrates was achieved at 28 °C.

Table 7: Effect of different incubation temperatures on solubilization of uranium and REEs using *A. niger* and *A. flavus*

| Organisms | element | Ore sample | Incubation temperature (°C) | | | | |
|------------------|----------|------------|-----------------------------|-----|-----|-----|-----|
| | | | 20 | 20 | 20 | 20 | 20 |
| <i>A. niger</i> | U (%) | G1 | 33 | 33 | 33 | 33 | 33 |
| | | G2 | 24 | 24 | 24 | 24 | 24 |
| | REEs (%) | G1 | 19 | 19 | 19 | 19 | 19 |
| | | G2 | 23 | 23 | 23 | 23 | 23 |
| | pH | G1 | 4.6 | 4.6 | 4.6 | 4.6 | 4.6 |
| | | G2 | 5.2 | 5.2 | 5.2 | 5.2 | 5.2 |
| <i>A. flavus</i> | U (%) | G1 | 31 | 31 | 31 | 31 | 31 |
| | | G2 | 18 | 18 | 18 | 18 | 18 |
| | REEs (%) | G1 | 9 | 9 | 9 | 9 | 9 |
| | | G2 | 13 | 13 | 13 | 13 | 13 |
| | pH | G1 | 4.6 | 4.6 | 4.6 | 4.6 | 4.6 |
| | | G2 | 4.2 | 4.2 | 4.2 | 4.2 | 4.2 |

Effect of optimum conditions on uranium and REEs solubilization

All optimum conditions of solubilization (2% ore concentrations, 7days of incubation, 35°C incubation temperature, and 0.2 grain size) are applied on 2 Kg of the sample G2. At these conditions *A. niger* could solubilize approximately 90% and 77% of the uranium and REEs respectively, whereas leaching efficiency of these elements with *A. flavus* reaches 65% and 84% respectively (Table 8). From these results, *A. niger* was considered the best in solubilization of uranium, while *A. flavus* was successfully applied for leaching of REEs.

Table 8: Effect of different optimum conditions on uranium and REEs solubilization from ore sample (G2) using *A. niger* and *A. flavus*

| Fungal sp. | Leaching efficiency (%) | |
|------------------|-------------------------|------|
| | Uranium | REEs |
| <i>A. niger</i> | 90 | 77 |
| <i>A. flavus</i> | 65 | 84 |

Recovery of U and REEs

As previously mentioned a bioleach liquor of 4L have been prepared by *A. niger* using 2kg of G2 ore sample and application of the studied optimum bioleach conditions. According to the studied leaching efficiencies of 90% for U and 77% for the REEs, the leach liquor is found to assay 68.5ppm U and 443.5ppm REEs. However, due to the low concentration of the latter, it was found more convenient to precipitate both metal values in 1mH₂SO₄ acid and their redissolution

Recovery of U

As mentioned above, both uranium and REEs have been precipitated from the obtained 4000ml bioleach liquor after arising its pH to 7.5 using 10% NaOH. The obtained precipitate re-dissolved in 400ml of 1 molar sulfuric acid and the obtained solution was made up to 800 ppm (337.5mg/L of U and 2218mg/L of REEs) being subjected to proper concentration and purification using anion exchange resin which is quite selective for uranium recovery from the obtained sulfate leach liquor. In the latter solution, the competing anions include mainly SO₄²⁻ and HSO₄⁻ and therefore uranium would be better adsorbed at pH value exceeding 1.8 while below this value, HSO₄⁻ would be strongly adsorbed, (Merritt, 1971; Preuss and Kurrin, 1965).

In this work, 2.5ml of wet settled resin (wsr) (Amberlite I.R.A 400 anion exchanger) was packed in a suitable Pyrex glass column (0.5 cm diameter) over a glass wool plug. The prepared uranium and RE- sulfate solution was firstly treated with 5% of NaOH to adjust its pH to 1.8 followed by its passing through the prepared resin column using a contact time of 3 min. (0.33ml/min.). The loaded uranium was then eluted from the resin using 1N NaCl acidified with 0.1M sulfuric acid. An eluate volume of 200 ml was collected at the end of elution process and was found to assay 1269ppm resulting to elution efficiency 94 %. From the obtained eluate, uranium was precipitated by NH₄OH as ammonium diuranate (NH₄U₂O₇·7H₂O) at pH 5.5. The product

(0.3g) was subjected to analysis using ESEM-EDX (Fig.3A).and was found to attain a(U) purity of 88.6%

Recovery of REEs

The uranium-effluent solution containing the bioleached REEs content was then directed to their direct precipitation using 30% oxalic acid at pH 1. The obtained RE- oxalate precipitate was then calcined at 800°C before being analyzed by ESEM-EDEX analysis (Fig.3B).and was found to attain a REEs purity of 78.5% (La,Ce,Pr,Nd,Sm,Gd.).All the data obtained during the present work have been formulated in the form of a working flowsheet (Fig. 4)

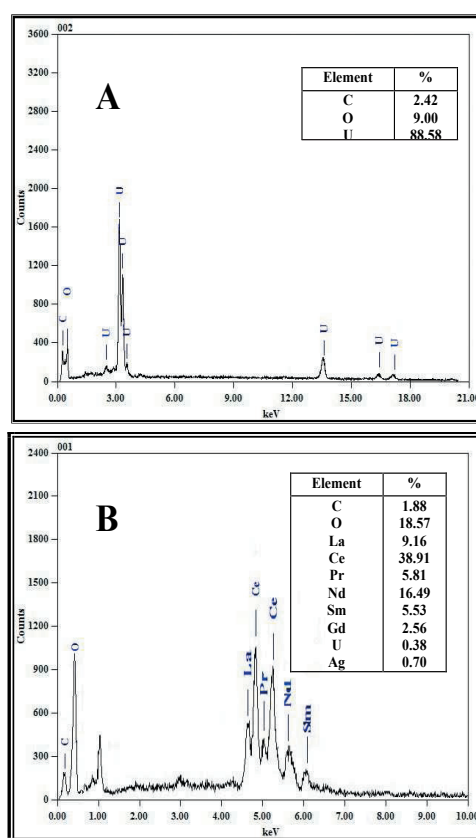


Fig. 3: EDAX chart for the analysis of uranium product (A) and REEs product (B)

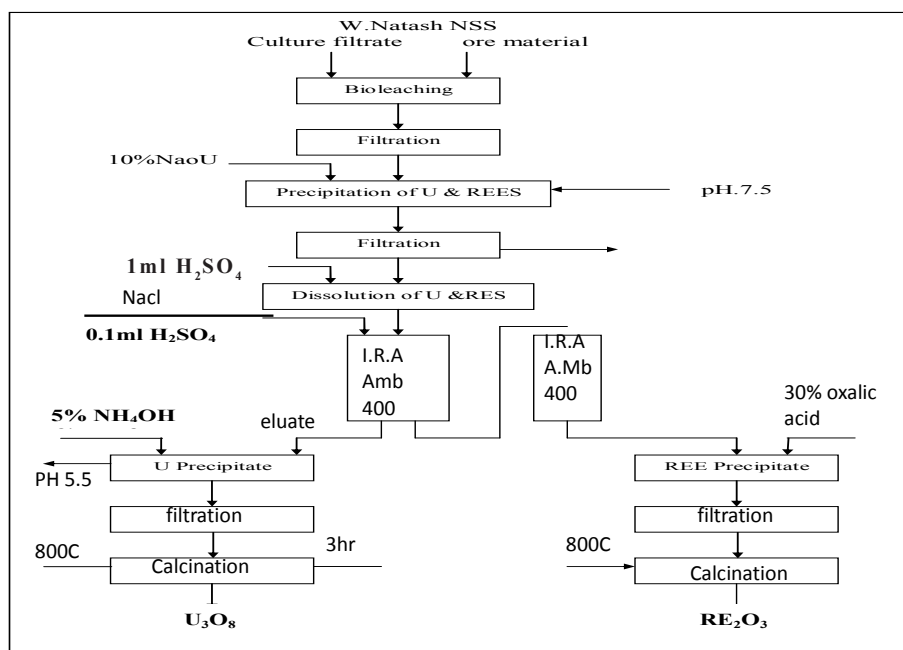


Fig. 4: A worked flow-sheet for the processing of the studied sample

DISCUSSION AND CONCLUSION

The present investigation has shown that the highest bioleaching of uranium and REEs values using *A.niger* and *A.flavus* from the Nubia Sandstone (90% and 84% respectively) for particle size 0.2mm, 2% w/v pulp density, 7 days of incubation periods and 35C incubation temperature. Further, citric acid was the major lixiviant among the metabolites produced by the tested fungi.

The recorded oxidizing *Aspergillus niger* and *Aspergillus flavus* are known for their ability to form a broad spectrum of organic acids such as citric acid, oxalic acid, acetic acid, desferrioxamine siderophore and non-acidic biomolecules mainly phosphatase enzyme. In the studied sample, uranophane, autunite, Xenotime, allanite, monazite and zircon minerals were considered as a source for REEs and U ions. Under the acidic conditions and the microbial activity, these minerals would dissolve releasing these chemical ions in the solution.

REFERENCES

- Amin, A.M.,2007. Fungal activity for solubilization and accumulation of uranium from various grade ores and subsequent chemical recovery. Ph.D. Thesis, Fac. Sci., Menoufia Univ., Egypt.
- Anjum, F.; Bhatti, H.N.; Asgher, M., and Shahid, M.,2010. Leaching of metals from black shale using organic acids produced by *Aspergillus niger*. J. Appl. Clay Sci., 3–4, 356–361.
- Bhatti, T. M.; Malik K. A; Khalid A. M., and Malik. K.A.,1989. Microbiol leaching of low grade sandstone uranium ores: Column leaching studies. Biotechnology for energy Proc. Inter. Symp. Biotechn. Energy faisalabad, Pakistan, 329-340.
- Bosshard, P.P.; Bachofen, R., and Brandl, H.,1996. Metal leaching of fly ash from municipal waste incineration by *Aspergillus niger*. Environ. Sci. Technol., 30, 3066–3070.

- Calsteren, P.V., and Thomas, T., 2006. Uranium-series dating applications in natural environmental science. *Earth Sci. Rev.*, 75, 155-175.
- Davies, W., and Gray, W., 1964. A rapid and specific titrimetric method for the precise determination of uranium using iron (II) sulphate as reductant. *Talanta*, 11, 1203-1211.
- Flemming, H.C., 1995. Sorption sites in biofilms. *Water Sci. Technol.* 32, 27-33.
- Hass, J.H.; Dichristina, T.J., and Wade, R. Jr., 2001. Thermodynamics of U(VI) sorption onto *Shewanella putrefaciens*. *Chem. Geol.*, 180, 33-54.
- Gilman, J. C., 1957. A manual soil fungi. The Iowa State Univ. Press, Ames, Iowa, USA.
- Heba, M. A.M., 2010. Solubilization of Some Valuable Elements from Phosphate Ores Using Certain Microorganisms and Potentiality of Their Extraction by Some Plant Wastes. MS. theses. Botany Dept., Fac. Sci., Ain Shams Univ.
- Ibrahim, M. E.; Mehanna, M.A.; Zohair, A.B.; Abu Zeid, E. K., and El-Tohamy, A. M., 2011. Geology and Mineralogy of Cretaceous Volcanic Rocks, East Wadi Natash, South Eastern Desert, Egypt. *J. Nat. Sci.* (In press).
- Johnson, D.B., 2006. Hydrometallurgy, 83, 153-166.
- Joona, J. K.; Mikko, J. S.; Hanna J. HH., and Simo K. T.T., 2006. *Optics Express*. 14, 11539-11544.
- Liu, Y.G.; Zhou, M.; Zeng, G.M.; Li, X.; Xu, W.H., and Ting, F., 2007. Effect of solids concentration on removal of heavy metals from mine tailings via bioleaching. *J. Hazardous Materials*, 141, 202-208.
- Marczenko, Z., 1986. Spectrophotometric determination of elements. John Wiley and Sons, Inc., New York, 99, 578.
- Merritt, R.C., 1971. Extractive metallurgy of uranium. Colorado school of Mines Research Inst., Golden Colorado.
- Pathak, A.; Dastidar, M.G., and Sreekrishnan, T.R., 2009. Bioleaching of heavy metals from sewage sludge by indigenous iron-oxidizing microorganisms using ammonium ferrous sulfate and ferrous sulfate as energy sources; A comparative study. *J. Hazardous Materials*, 171, 273-278.
- Pitt, J., 1979. The genus *Penicillium* and Teleromorphic state. *Eupenicillium* and *Talaromyces*. Acad. press, London, New York, Toronto, Sydney.
- Preuss, A., and Kurrin, R., 1965. A general survey of types and characteristics of ion exchange resin used in uranium recovery.
- Schinner, F., and Burgstaller, W., 1989. Extraction of zinc from industrial waste by *Penicillium* sp. *Appl. Environ. Microbiol.*, 55, 1153-1156.
- Shapiro, L., and Bronnack, W.W., 1962. Rapid Analysis of Silicate, Carbonate and phosphate rocks, U.S.G.S., 1144-A, 56 p.
- Taunton, A.E.; Welch, S.A., and Banfield, J.F., 2000. Microbial controls on phosphate and lanthanide distribution during granite weathering and soil formation. *Chem. Geol.*, 169, 371-382.
- Torma, A.E., 1995. The role of *Thiobacillus ferrooxidans* in hydrometallurgical process. *Adv. Biochem. Eng.*, 6, 1-37.

العوامل الفيزيائية المختلفة والمناسبة لإذابة اليورانيوم والعناصر الأرضية النادرة من الحجر الرملي – وادي نتش – الصحراء الشرقية – مصر

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تم عزل خمس سلالات من الفطريات من عينيتين من الحجر الرملي النوبي – وادي نتش – الصحراء الشرقية – مصر. ثم اختبار قدرة الكائنات المعزولة على إذابة اليورانيوم، العناصر الأرض النادرة من العينات موضع الدراسة. كانت أفضلها من عملية الإذابة هو فطر اسبرجيليس نيجر، اسبرجيليس فلافس.

و بتطبيق أفضل الظروف على الفطريات موضع الدراسة (٢٪ تركيز الخام، ٠.٢ حجم الحبيبات، ٣٥٠م، ٧ أيام تحضين) اثبتت الفطريات كفاءة عالية في الإذابة من العينة G٢ للفطر اسبرجيليس نيجر ٩٠٪، ٧٧٪ للعناصر اليورانيوم و عناصر الأرضية النادرة على التوالي. اما فطر اسبرجيليس فلافس حقق في نفس العينة ٦٥٪، ٨٤٪ لعناصر اليورانيوم والعناصر الأرضية النادرة على التوالي. و اعتمدت نسبة الإذابة على ما يفرز من احماض عضوية للفطرين و هما حمض الستريك و حمض الأوكزاليك و هما يعتبران مفتاح عملية الإذابة.