



ISSN NO. 2320-5407

Journal homepage: <http://www.journalijar.com>

INTERNATIONAL JOURNAL
OF ADVANCED RESEARCH

RESEARCH ARTICLE

Recovery of Uranium from Sulfate Leach Liquor using n-Hexane extractant sourced from Sun Flower Agriculture Waste

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Manuscript Info

Manuscript History:

Received: 11 September 2015

Final Accepted: 22 October 2015

Published Online: November 2015

Key words:

Uranium, Solvent extraction, Sun Flower, *Helianthus annuus* extractant, Abu-Zeneima ore material

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Abstract

The possibility of using the sunflower *Helianthus annuus* extractant (HAE) as a solvent extractant for uranium from sulfate leach liquor has been studied. Several experiments were conducted to determine the relevant factors affecting both the extraction and stripping of uranium from a synthetic standard solution. At the optimum conditions, it was found that the maximum saturation capacity of the HAE attains about 33 mg/1g of the extractant for uranium. Kinetic characteristics of the loading process have been found to satisfactorily fitting to the pseudo-first-order equation. The obtained optimum conditions have also been applied to investigate the potentiality of the working HAE for extraction of uranium from an actual sulfate leach liquor of Abu-Zeneima ore material (South Eastern Sainai, Egypt).

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INTRODUCTION

Generally agricultural wastes can be a valuable resource for economical improvement but if these wastes not treated, kept or disposed of properly, there are probable to cause pollution to the environment or even harm to human health. For these reasons is also an urgent need to set up centers of excellence in waste management. In this regard, sunflower plant waste conceded as one of the huge waste produced around the world. The domesticated sunflower (*Helianthus annuus*), is the most familiar species. Perennial sunflower species are not as popular for gardens due to their tendency to spread rapidly and become invasive. (Subashini and Rakshitha ; 2012) evaluated the methanolic extract seeds of *Helianthus annuus* L. for the phytochemical present in the plant and results shown that, the carbohydrates, flavanoids, tannins, alkaloids, sapanins, phytosterols, steroids and fixed oils were present in the extract.(Macias et al ; 2008)

In nature, uranium can be found in the Earth's crust at an average concentration of about 2.5 mg/kg but anthropogenic activities, such as utilization of depleted uranium in munitions and nuclear accidents, introduce uranium to the environment on a larger scale. Uranium resulting from mining, reprocessing and disposal activities related to the nuclear industry is a problematic environmental pollutant. The monitoring of the movement of uranium from soil to plants especially to edible plant parts is very important due to possible contamination of the food chain. Uranium presents an exposure hazard due to its chemical toxicity as well as the radioactivity resulting from its decay and its decay products. In plants, uranium is stored mainly in roots, which was demonstrated on hydroponically cultivated sunflower (Dushenkov et al., 1997). Dushenkov et al., (1997) reported that sunflower plants were found to have a high affinity for uranium extraction and were selected for treatment of contaminated water.

Blanco et al. (2006), tested the linearity assumption of the validation of soil-to-plant transfer factors of uranium and Ra226 using *Helianthus annuus* L. grown in a hydroponic medium in addition, transfer of the studied species in both the aerial parts of plants and in the overall seedlings. The results show that the linearity assumption can be considered valid in the hydroponic growth of sunflowers for the radionuclides studied. The ability of sunflowers to translocate uranium and Ra226 was also investigated. In this sense, the removal percentages obtained for uranium and Ra226 were 24% and 42%, respectively. Practically all the uranium is accumulated in the roots. However, 86% of the Ra226 activity concentration in roots was translocated to the aerial part. **Shahandeh and Hossner (2002)**, investigated uranium accumulation from uranium contaminated soil among sunflower plant species. They found also that, uranium accumulated mainly in the roots of plant species

Generally uranium is influenced by its speciation and low pH conditions (**Lauria et al., 2004**). Uranium is present as a positively charged uranyl ion UO_2^{2+} in low pH samples and is very mobile U accumulation and distribution in plants has been reported by several authors (**Straczek et al., 2010; Véra-Tome et al., 2008, 2009, Ebbs et al., 1998**). Sunflower heavily accumulates U in its roots where it is stored (**Straczek et al., 2010; Véra-Tome et al., 2008**). Conversely, wheat shows low U transfer factors in roots and shoots (**Shahandeh and Hossner, 2002**). This differential response with respect to plant species is explained by their cation exchange capacity (**Dufey et al., 2001; Straczek et al., 2010**).

The present work aims to study using the sun flower hexane extractant from its waste by mixing synthetic solution of uranium as means for its recovery. The obtained optimum conditions were applied upon real sulfate leach liquor of gibbsite ore materials as a case study.

2. Materials and Methods

2.1. Materials

2.1.1. Plant materials.

The aerial part of *Helianthus annuus* (HA) was collected on April (2013) and identified by Botany department, Faculty of Science, ZagazigUniversity, Egypt.

2.1.2. Extraction of HAE

For the extraction, 100kg of the plant was put in stainless steel extractors. N-hexane as a solvent for the extraction process was poured until it covers all the plant. The solvent is kept inside the extractor with the plant for 1/2 h (first wash). The solvent is then sucked from the extractor directly into the primary evaporator where indirect steam is applied to evaporate the solvent. The plant left in the extractor will undergo the same process two times more (second and third wash) for 1h of each wash. After filtration, the mixture is put on final evaporation unit where most of the solvent is evaporated using heat from indirect steam and under vacuum in order to avoid excessive heating which could affect the quality of the final product. The final product coming out from the final evaporation unit and the yield was 0.5kg. It should be stored in temperature of 10°C.

2.1.3. Preparation of standard U (VI) and interferences solutions.

A synthetic uranium solution assaying 200 ppm has been prepared by dissolving the required weight of the uranyl acetate salt in distilled water that slightly acidified with sulfuric acid solution. The solution pH was adjusted at 4 using sulfuric acid solution. On the other hand, for studying the possible metals interference that might be associated with uranium in its solutions, proper weights of some of their compounds have been dissolved in the prepared synthetic uranium.

2.2. Experimental procedures

2.2.1. Uranium extraction procedure from sulfate solution by HAE

Uranium extraction from either the synthetic solution or that of Abu-Zeneima leach liquor solutions by the HAE has been undertaken after its dilution/kerosene to 10 vol % were carried out by shaking the two phases in separating funnels. The aqueous phase was analyzed for its uranium content and that in the organic phase was calculated by the difference. Several series of experiments were carried out to study the effects of the diluent type, HAE concentration, pH, the shaking time, the extraction temp., the interfering metal ions and the O/A phase ratio. On the

other hand, the practical saturation capacity of the HAE for uranium has also been determined by using the multiple contact technique.

2.2.2. Uranium stripping procedure from the loaded HAE:

A number of mineral acids, alkalis and NaCl solutions have been used for studying the uranium stripping efficiency from uranium – loaded upon the HAE. For choosing the eluent, both the shaking time and temperature together with O/A phase ratio have been studied. The resultant strip solution is treated in subsequent circuit to produce a metal concentrate while the stripped solvent is returned for cycle to extraction circuit.

2.3. Analytical procedures

2.3.1. HAE characterization

As mentioned above, HAE was analyzed for its acid content in the quality control laboratory of Hashem Brothers for Essential & Aromatic products using the Gas Chromatography Mass Spectrometry (GC-MS) HP 6890 Series A (Agilent) using A Thermo Scientific (TR-5MS), (5% Phenyl PolysilPhenyleneSiloxane) capillary column (30 m x 0.25 mm i.e. 0.25 μm film thickness). On the other hand, Infra-red analysis has been achieved using Thermo Scientific Nicolet IS10 model.

2.3.2. Control analysis for Uranium

Control analysis of uranium in the different aqueous stream solutions as well as in the product has been undertaken by the oxidimetric titration after its reduction using a standard solution of ammonium metavanadate (Mathew, 2009). On the other hand, various metal ions including; Ni, Cu, V were determined by using atomic absorption spectrometer (Unicam 969, England).. Also, using prism ICP-OES, Teledyne technologies (Inductively Coupled Plasma Optical Emission Spectrometer) for Ce, La, and Y analysis.

2.3.3. Abu-Zeneima gibbsite ore characterization

Abu-Zeneima gibbsite ore representative sample which was subjected to complete chemical analysis of both major and trace elements content. For the former the conventional wet chemical technique was applied (Shapiro and Brannock, 1962) where SiO_2 , Al_2O_3 , TiO_2 and P_2O_5 were determined using their relevant spectrophotometric methods while Na_2O and K_2O were assayed by the flame photometric technique. Total Fe as Fe_2O_3 , MgO and CaO were determined by titration methods against dichromate and EDTA solutions respectively. The loss on ignition (L.O.I) was gravimetrically determined at 1000°C for CO_2 . The estimated error for these major constituents is not more than $\pm 1\%$. The trace elements were also analyzed at the laboratories of the Nuclear Materials Authority by the X-ray fluorescence technique (XRF) using Philips Unique II unit fitted with an automatic sample changer PW 1510 (30 position), connected to a computer system using X-40 program for spectrometry. The detection limit of the measured elements by XRF technique was estimated to be 5 ppm

3. Results and Discussion

3.1. Characteristics of *Helianthus annuus* extractant (HAE).

3.1.1. Infra-Red spectrum of HAE:

From the achieved FTIR spectral analysis of the un-reacted HAE plotted in Fig. (1) before complexation with uranium species it is clearly evident that, a number of characteristics peaks have been obtained. Thus, the carboxylic acid O-H groups are shown at 2926 cm^{-1} while the carbonyl groups ($-\text{C}=\text{O}$) are shown at 1702 cm^{-1} , at 3400 cm^{-1} corresponds to alcohol O-H and aromatic C=C at 1549 cm^{-1} .

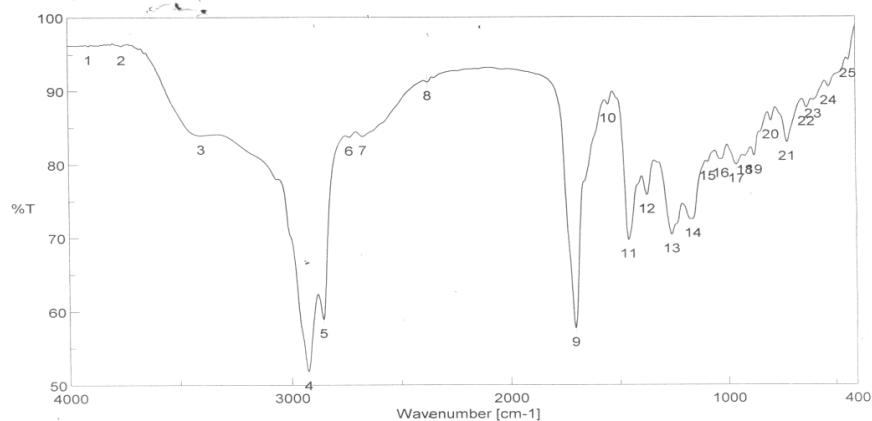


Fig.(1) : IR characteristic spectrum of the HAE

3.1.2. Chromatographic analysisHAE:

The separated organic compounds analyzed on Gas Chromatography Mass Spectrometry (GC-MSD) indicated that, retention time for all compounds were determined while, identification of the components was based on comparison of their mass spectra with those of internal (computer) library W9N11.L (Minimum Quality: 50) and NIST11.L (Minimum Quality: 50) libraries and some reference compounds. As shown in **Fig.(2)** the major components are 40% Linolenic acid, 5% Palmitic acid ethyl ester, 6% Linoleic acid, 5% 4-Qinolinol-2,7,8-trimethyl, and 5% Bisabololoxide A.

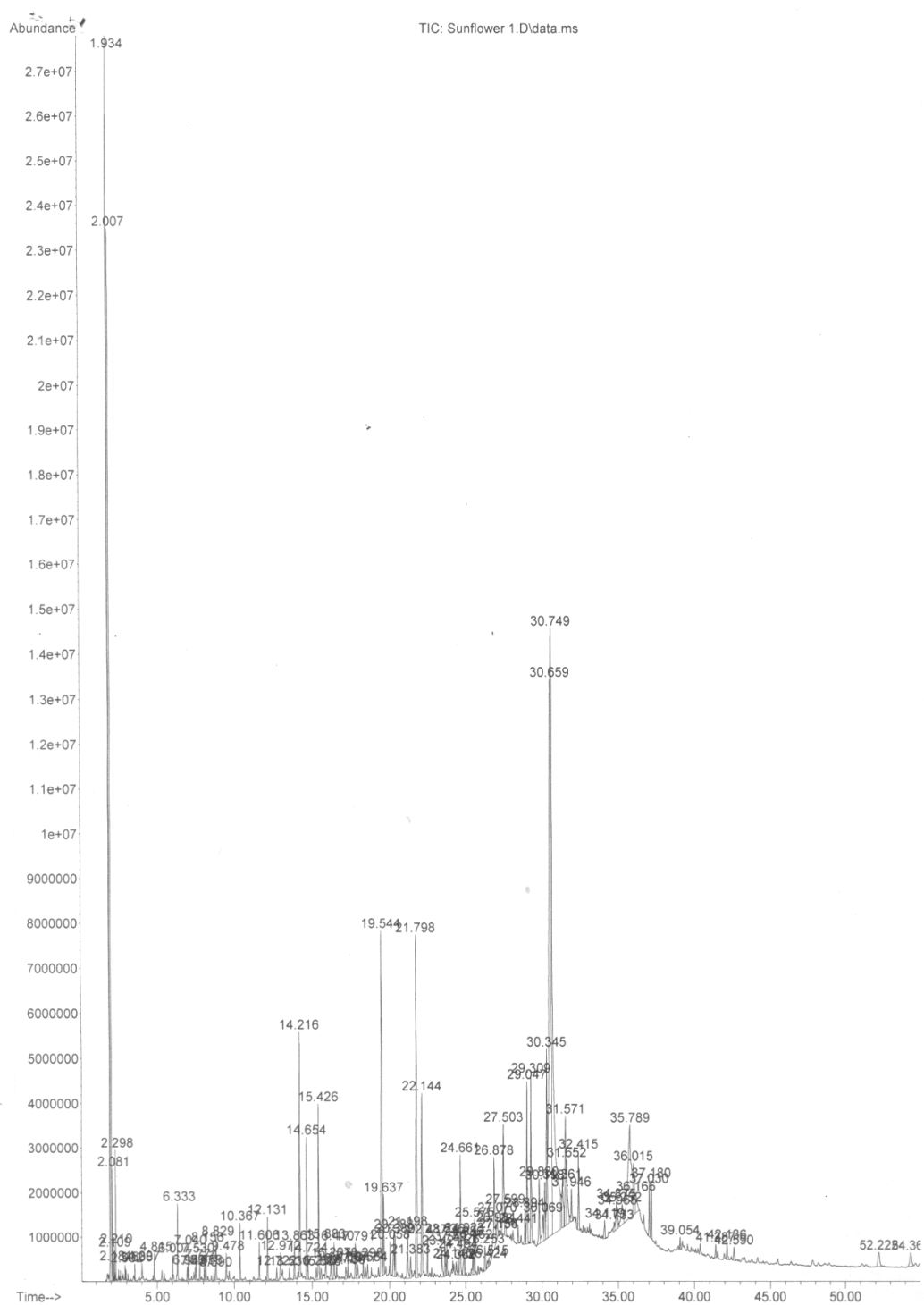


Fig.(2) : Gas chromatography-mass Spectrometry (GC-MS) of the HAE

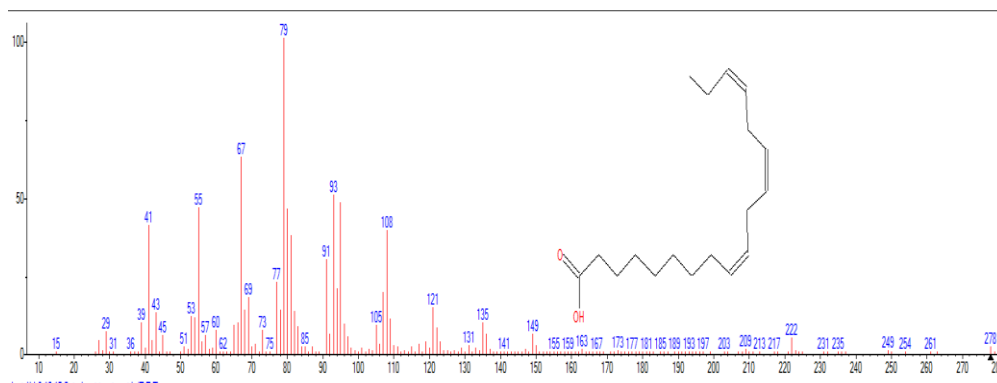


Fig. (3): Chemical structure of Linolenic acid.

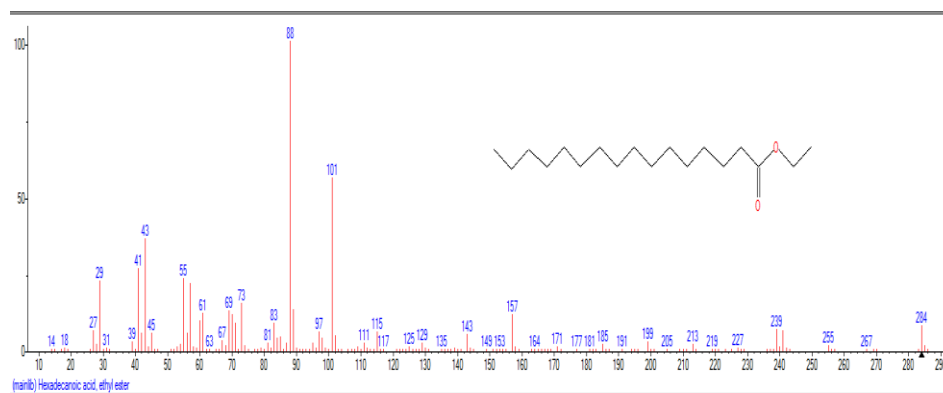


Fig. (4): Chemical structure of Palmitic acid ethyl ester.

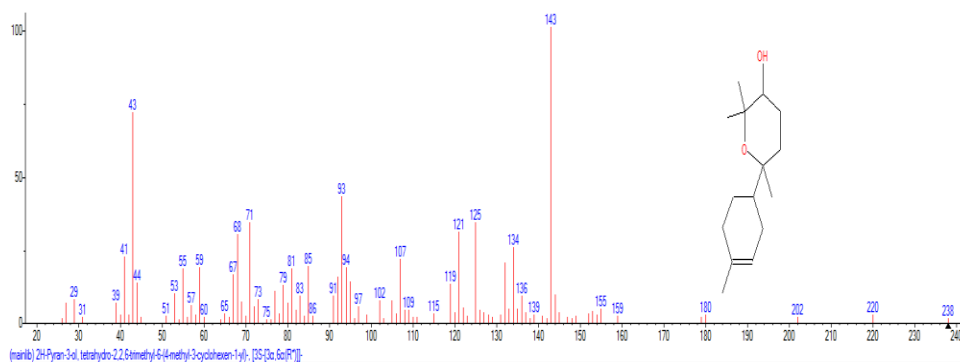


Fig. (5): Chemical structure of Bisabolol oxide A.

3.2. Optimization of uranium extraction.

3.2.1. Effect of diluent type

To study the effect of the diluent type on uranium extraction from the prepared synthetic solution assaying 200 ppm of uranium three different organic diluents have been used namely; benzene, kerosene and toluene. The extraction process was performed under fixed conditions of a pH 4, a shaking time of 10 min. in an A/O ratio of 1:1 at room temperature and using 10 vol. % HAE. The obtained results indicate that kerosene is the best diluent in which 99% for uranium extraction has been achieved while the toluene and benzene diluents only 50% and 40% for uranium extraction were achieved respectively. Thus kerosene was chosen as the best diluent in all extraction experiment.

3.2.2. Effect of pH:

The effect of pH upon uranium extraction was investigated. For this purpose, a series of experiments were performed at different pH values of synthetic solution ranging from 1 to 5 at fixed condition of O/A 1:1, using 10% vol. HAE for 10 min. as contact time. From the resulted in **Fig. (6)**, it is clear that, the maximum uranium extraction efficiency 99% was achieved at pH 4. Rising the solution pH over 4, leads to decreasing uranium extraction efficiency.

3.2.3. Effect of solvent concentration:

The effect of the HAE concentration on uranium extraction efficiency by contacting equal volumes of the synthetic solution and solvents with concentration ranging from 2 to 20% in kerosene at fixed condition of pH 4 and contact time 10 min. at room temperature. From the obtained data in **Fig.(7)**, the results indicated that, uranium extraction efficiency increased from 50 to 90% as increasing the concentration of the HAE increased from 2 to 8. By extending the concentration of the HAE to 10% the uranium extraction attained to 99%.

3.2.4. Effect of the O/A phase ration

The effect of the O/A ratio upon uranium extraction percent was studied by doubling and tripling the aqueous phase with respect to the organic phase. In both experiments, the conditions for uranium extraction were fixed at a pH of 4, a shaking time of 10 min. using a 10 vol % of the HAE in kerosene. The obtained result revealed an extraction efficiency of uranium attaining 98% and 97% respectively at the O/A ratios of 2/1 and 3/1 in a manner to indicate that 1ml of the HAE can adsorb about 3.92 and 5.82 mg U respectively.

3.2.5. Effect of contact time:

To study the effect of contact time upon uranium extraction efficiency by the HAE a set of experiments have been performed at different contact times 1,2,3,5 and 10min. at fixed conditions of O/A 1/1, pH 4 and using 10vol of the HAE. The obtained results illustrated at **Fig.(8)** have indicated that uranium extraction is rapidly achieved where at 5 min., up to 95% have been obtained and 99% at 10 min. thus the latter considered as the optimum shaking time.

3.2.6. Effect of temperature

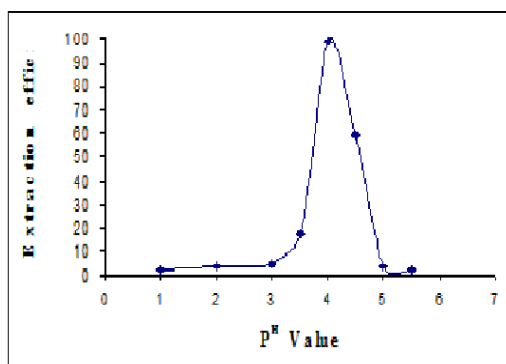
Using the previously optimum conditions of pH 4, O/A ratio of 1/1, a shaking time of 10 min. and 10 vol. % HAE for the studied system and diluted in kerosene, a series of experiments was made to study the effect of temperature in the range from 25 to 70 °C. As shown in **Fig.(9)**, it was found that by progressively increasing the temperature an adverse effect upon the uranium extraction efficiency from 98 down to 40% has been obtained. This is most probably due to the decomposition of the components of the organic solvent under high temp.

3.2.7. Effect of interfering metal ions upon uranium extraction.

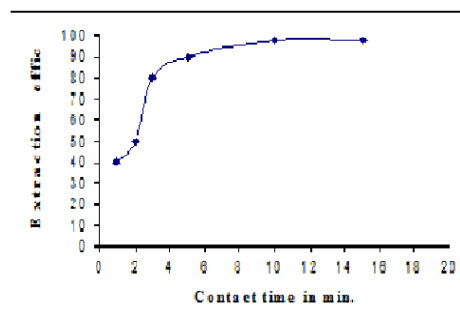
In order to investigate the possible and extent the interference of some metals ions- that might be associated with uranium in their ores, solution of Cu, Ni, Fe, Zr, V, Ba, and La, Ce, and Y as REEs have been prepared (1000 ppm) concentration for each. To study the effect of latter, 10 ml of the mentioned 9 metal solutions together with 10 ml of a uranium solution assaying also 1000 ppm have been mixed in a manner that each of which would assay 100 ppm. The concerned experiments was then performed under different pH values varying from 1 to 4 at the previously determined optimum conditions. All the obtained results are summarized in **Table (1)** for the studied metal values at the different pH values.

Table (1): Effect of pH upon the extraction percent of uranium with some interfering metal ions

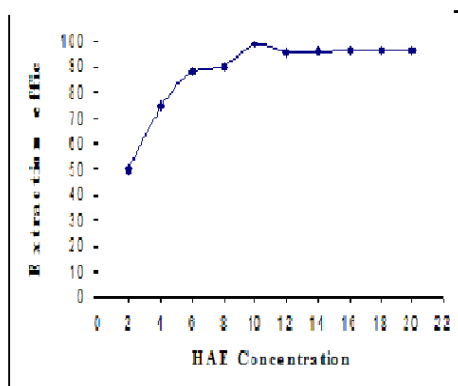
pH	Extraction %									
	U	Y	Ce	La	V	Fe	Zr	Ba	Ni	Cu
1	2.5	2	5	3	17	12	15	14	18	44
2	4	1	2	2	15	9	12	9	14	32
3	5	3	6	2	10	7	8	7	8	21
3.5	18	3	3	3	8	4	5	4	6	11
4	96	2	1	3	1	20	1	2	3	3
4.5	60	1	1	2	1	2	1	2	3	3



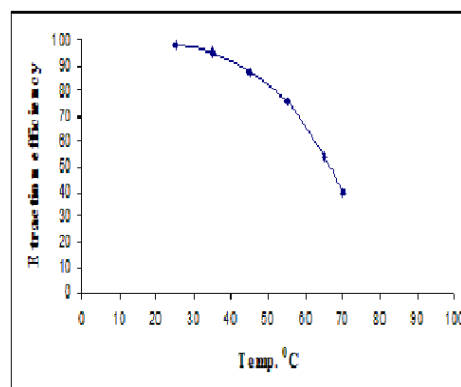
Fig(6): Effect of pH upon uranium extraction efficiency % by HAE



Fig(8): Effect of contact time upon uranium extraction efficiency % by HAE.



Fig(7): Effect of HAE Concentration upon uranium extraction efficiency, %



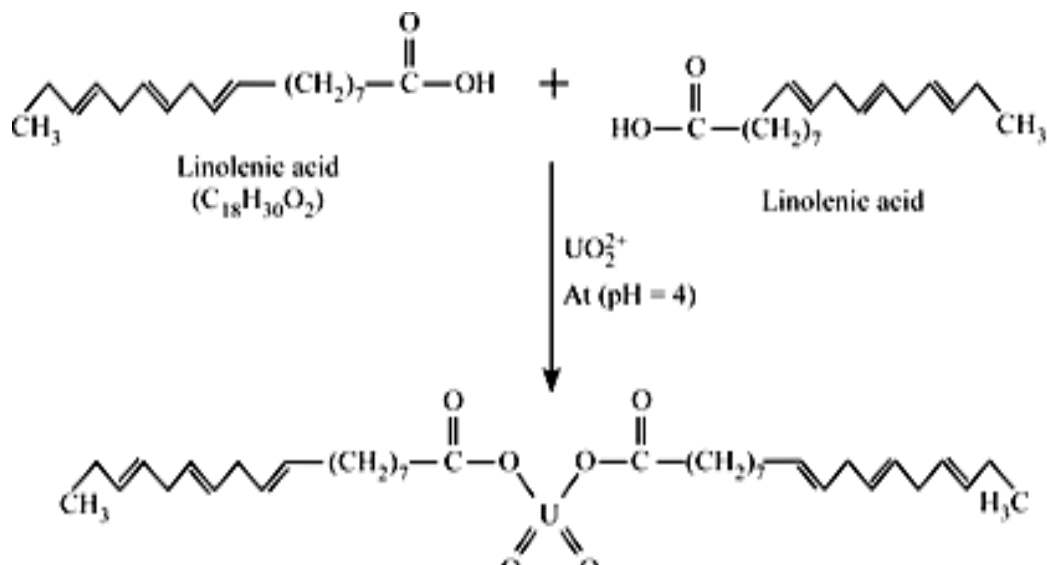
Fig(9): Effect of temperature upon extraction efficiency % by HAE.

From the above studied of uranium extraction factors, it can be concluded that the optimum extraction conditions for about 98% of uranium content from sulfate solution via HAE would be summarized as following :

A/O	:	1:1
Contact time	:	10 min.
HAE concentration	:	10 %
Temperature	:	room temp.
pH:		4

3.3. Uranium saturation capacity and the extraction mechanism.

To determine the saturation capacity of the HAE a known volume of the extractant has repeatedly been contacted with the prepared synthetic solution under the previously determined optimum conditions using 10 vol. % in kerosene HAE. After each contact, uranium was analyzed in the obtained raffinate till almost saturation of the extractant. From the results shown in **Table(2)**, it is clearly evident that the saturation capacity of the HAE attains about 33 mg/1g of the extractant for uranium,. The obtained data support indeed the possible mechanism of uranium species extraction by the HAE. which is believed to be achieved through the carboxylic acid groups of the free fatty acid content of the extractant via; .



The free acid content of HAE which would be responsible for uranium (metal) extraction has also been determined according to KEM application method by using KOH in presence ph. ph. as indicator **Saad et al, (2007)**. Accordingly, the determined free fatty acid in the HAE was found to attain 0.33. Thus, the Linolenic acid content of the HAE (major component) would attain about 67.32 g/l. As the mechanism of uranium extraction corresponds to a molar ratio of 1/2, and then the calculated uranium capacity of 1 g of the HAE would attain about 39.27 mg.

Table (2): Uranium saturation capacity of the HAE

Contact number	Uranium distribution	
	Assay in raffinate , ppm	Loaded amount mg/1 gHAE
1	Nil	6
2	Nil	6
3	Nil	6
4	Nil	6
5	150	4.5
6	350	2.5
7	450	1.5
8	550	0.5
9	600	Nil
Total		33

As mentioned above, the gas chromatography technique has been used to determine the chemical composition of the HAE in terms of its acid constituents and the obtained results as shown in **Fig. (10)**. it is clearly that linolenic, , palmitic acid ethyl ester and Bisabolol oxide A summation represent about 50% of the HAE as the main constituents, and which have been decreased to only 3.5% after uranium extraction process as shown in **Table (3)** and **Fig.(11)**. These changes are indeed attributed to the process of complexes formation by using solutions of U.

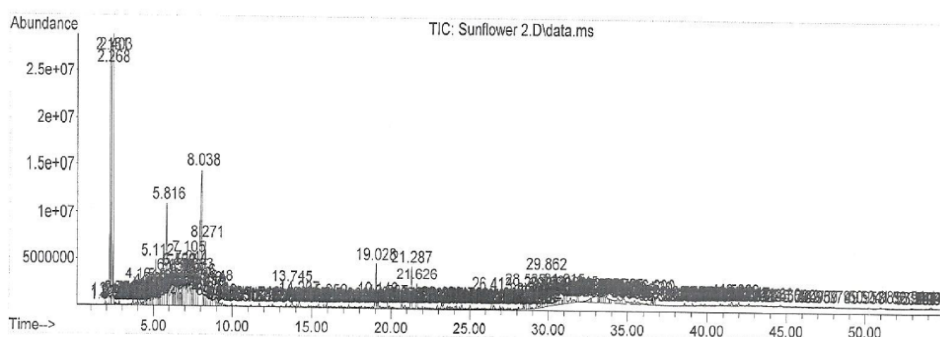
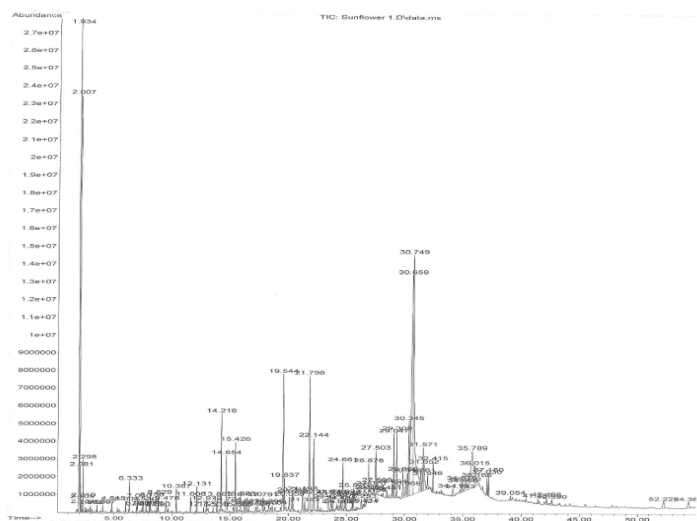


Table (3): Comparative the main chemical composition of the HAE before and after uranium extraction

Type of compound	Before extraction%	After extraction%
Palmitic acid , ethylester	2	0.1
6-Ethyl-5-hydroxy-7-methoxynaphthoquinone	2	0.1
9, 12, 15-Octadecatrienoic acid, methyl ester, (Z, Z, Z).	2.5	0.2
Phytol	3	0.3
Linoleic acid	1.5	0.6
9, 12, 15-Octadecatrienoic acid, ethyl ester, (Z, Z, Z).	3	0.25
Linolenic acid	35	1
5,8,11,14,17-Eicosapentaenoic acid, methyl ester.	1.5	0.05
Bicyclo (5.2.0) nonane, 4-methylene-2,8,8-trimethyl-2-vinyl.	5	0.5

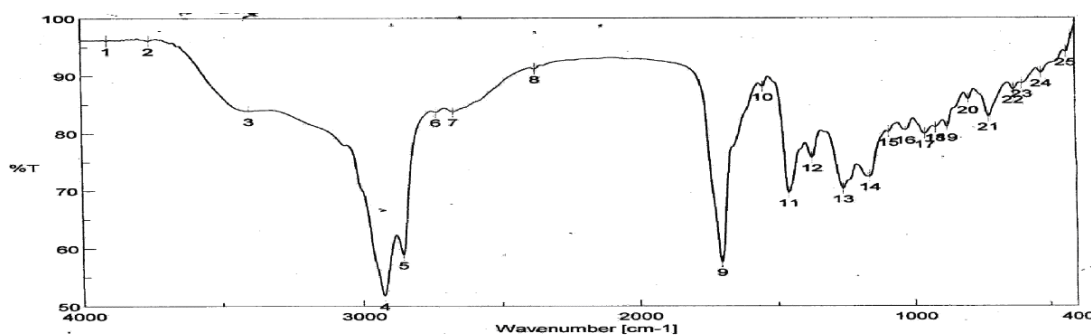


Fig.(12) : IR characteristic spectrum before loading of uranium up on the HAE .

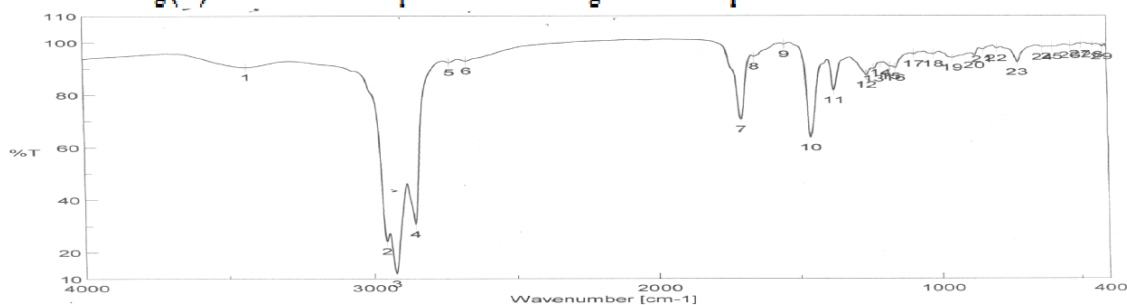


Fig. (13): IR characteristic spectrum after Loading of uranium up on the HAE.

3.4. Physical parameters

3.4.1. Thermodynamic characteristics of uranium extraction:

Variations of uranium extraction data with temperature for uranium extraction from the aqueous phase by used HAE in kerosene was used to calculate the thermodynamic constants including the standard enthalpy (ΔH), and the standard entropy (ΔS) based on Van't Hoff plot using the following formula:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

Where K is the equilibrium constant $R = 8.3145 \text{ J mol}^{-1}\text{K}^{-1}$ and T = absolute temperature in Kelvin. ΔH and ΔS were determined from the slope and intercept of $\ln K_d$ versus $1/T$ graph. **Fig.(14)** Plots $\ln K_d$ versus $1/T$, K^{-1} (in case of HAE) which give a straight line whose slope equals $(-\Delta H / R)$ for the extraction of uranium. The ΔH and ΔS values for uranium, in case of HAE, were -80 kJ/mol and -235.7 J/mol k respectively as calculated from the slope and intercept using the Van't Hoff equation. These values of ΔH and ΔS have then been used to obtain the corresponding free energy ($\Delta G = -9.75 \text{ kJ/mol}$) at 298°K for HAE using the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

The negative value of ΔH indicates that the extraction of uranium in this system is an exothermic process and that the reaction becomes more favorable at room temperature. The negative value of ΔG indicates that the reaction is spontaneous. On the other hand, the observed decrease in the negative values of ΔG with elevated temperature implies that the reaction becomes more favorable at room temperatures.

3.4.2. Kinetic characteristics of uranium extraction by HAE.

In terms of kinetic modeling, the pseudo-first-order and pseudo-second-order equations were used for the mathematical interpretation of the uranium extraction rate from the aqueous phase by HAE. The pseudo-first-order equation is represented as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$

Where q_e and q_t are the amounts of metal ions adsorbed at equilibrium and at time t respectively, and k_1 is the equilibrium rate constant of the pseudo first-order equation (1/min). On the other hand, the pseudo-second-order kinetic model is represented as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

Where k_2 is the equilibrium rate constant of pseudo second-order equation. The slope and intercept of the plot t/q_t versus t were thus used to calculate the pseudo second-order rate constants k_2 and q_e . The pseudo-first -order kinetic model was found to best fit the experimental results of uranium extraction by HAE in kerosene with correlation coefficients very close to unity other than pseudo second-order kinetic model (**Figs. 15 and 16**) and the result agree with that reported by (Mckay et al., 1988).

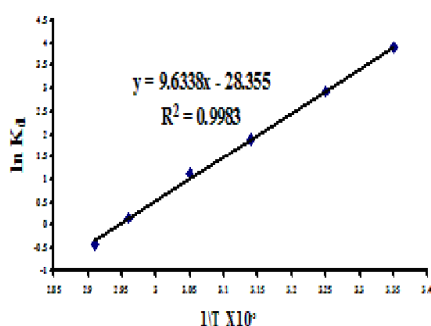


Fig.(14) : Plot of $\ln K_d$ against reciprocal temperature for uranium by HAE.

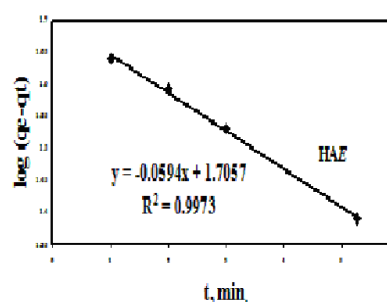


Fig. (15): Plot of $\log(q_e/q_t)$ versus time (t) for kinetic extraction of uranium by used HAE at 25°C.

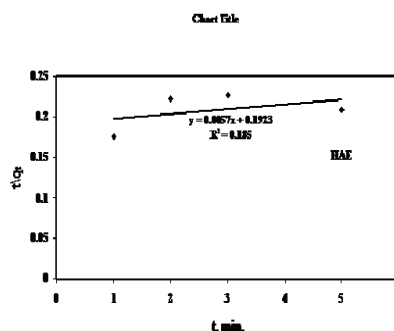


Fig. (16): Plot of t/q_t versus time (t) for kinetic extraction of uranium by used HAE at 25°C.

The parameters of the pseudo-first order kinetic model for uranium from the 200 ppm aqueous solution by used HAE and at 25°C have been calculated and were found as following **Table (4)**.

Table (4): Pseudo First-order constants of uranium extraction from the 200 ppm by used HAE at 25°C.

Result HAE	Pseudo First-order constants
0.146	K_1
52.48	q_e
0.975	R^2

3.5. Optimization of uranium stripping factors loaded upon HAE.

Factors influencing the stripping efficiency include stripping agent type and its concentration, aqueous to organic phase ratio (A/O), stripping time and temperature.

3.5.1. Effect of the stripping agent type:

Different stripping agents were applied to strip uranium from the loaded 10% the HAE/kerosene. These included distilled water and 1 M of mineral acids HCl, H₂SO₄ and HNO₃ as well as NaCl/mineral acids (HCl, H₂SO₄ or HNO₃) mixtures. The stripping experiments were carried out in an A/O ratio of 1/1 for 10 min. contact time at room temp. The obtained results presented in **Table (5)** reveal that NaCl acidified H₂SO₄ at the mentioned molarity is actually the most efficient stripping agent for uranium from the loaded with 95% efficiency.

Table (5): Effect of stripping agent type on uranium stripping efficiency loaded upon HAE

Stripping agent type/ conc.,	U stripping efficiency, %
Water	20
HNO ₃ (1mole)	65
HCl (1mole)	67
H ₂ SO ₄ (1mole)	86
HNO ₃ /NaCl (mole / mole)	75
NaCl /HCl(mole / mole)	90
NaCl/ H ₂ SO ₄ (mole / mole)	95

It is interesting to mention here, that the uranium will stripped with NaCl/H₂SO₄ solution (mole/mole).

3.5.2. Effect of molarity NaCl/H₂SO₄ upon uranium stripping efficiency from the loaded solvent.

The effect of NaCl and H₂SO₄ molarity ratio on uranium stripping from the loaded 10% HAE was studied while keeping the other stripping factors of contact time for 10 min., the settling time for 5 min. in an A/O phase ratio of 1/1. From the obtained results given in **Table(6)**, it is obvious that NaCl/H₂SO₄ ratio equal 1 has resulted 95% uranium stripping efficiency.

Table (6): Effect of NaCl and H₂SO₄ molarity on uranium stripping from the loaded HAE

Molarity of NaCl /H ₂ SO ₄ ratio	U stripping efficiency %
H ₂ SO ₄ / NaCl (mole / mole)	95
H ₂ SO ₄ / NaCl (0.5 mole/1 mole)	85
H ₂ SO ₄ / NaCl (0.25 mole/ 1 mole)	70

3.5.3- Effect of A / O phase ratio:

In a manner to increase the uranium concentration in the stripping aqueous phase the effect of the A/O phase ratio upon the uranium stripping efficiency from the loaded HAE was studied up to the ratio of 3/1 using 1M NaCl /1M H₂SO₄. In these experiments, the other stripping factors were fixed at their studied optimum values. From the obtained results, it was shown that upon increasing the O/A ratio from 1/1 to 2/1, about 98% of uranium stripping was achieved while at the ratio of 3/1 give the same result as the A/O ratio of 2/1 thus the A/O of 3/1 is the optimum phase ratio ..

3.5.4. Effect of contact time:

The effect of a lower contact time upon the uranium stripping efficiency by mixed of 1M NaCl/1M H₂SO₄ from the loaded 10% HAE was studied for 5, 10 15 and 20 min. using the above mentioned optimum molarity of NaCl / H₂SO₄ at an O/A ratio of 3/1 at room temperature and using a settling time of 5 min. The corresponding uranium stripping efficiencies indicate that a contact time of 15 min. as stripping time is the sufficient to achieve about 98% of the total uranium as shown in **Table(7)**.

Table (7): Effect of stripping time upon uranium stripping efficiency for the HAE

Uranium stripping efficiency%	Stripping time
66	5
75	10
98	15
98	20

From the above studied of uranium stripping factors, it can be concluded that the optimum stripping conditions for about 98% of uranium content from the loaded HAE would be summarized as following:

Stripping agent type : 1M NaCl /1M H₂SO₄
 A/O : 1:3
 Contact time : 15 min.
 Temperature : room temp

3.6. A Case study: Abu-Zeneima ore material (South Eastern Sainai, Egypt) as a case study for uranium extraction using HAE.

According to, the optimum leaching conditions of uranium from its mineralization at Abu-Zeneima ore material (South Eastern Sainai, Egypt) include a H₂SO₄ acid concentration 800 g/L, an agitation time of 4h, a S/L ratio of 1/2 at 100°C and using an ore grain size of – 60 mesh. (El Hazek , 2008).

3.6.1. Characterization of Abu-Zeneima gibbsite ore:

As previously mentioned, the working technological sample was provided from Abu Zeneima gibbsite ore lenses found in the shale beds. Results of the complete chemical analysis of the working sample are shown in Table (8).

Table (8): Chemical composition of the working Abu-Zeneima mineralized gibbsite ore material

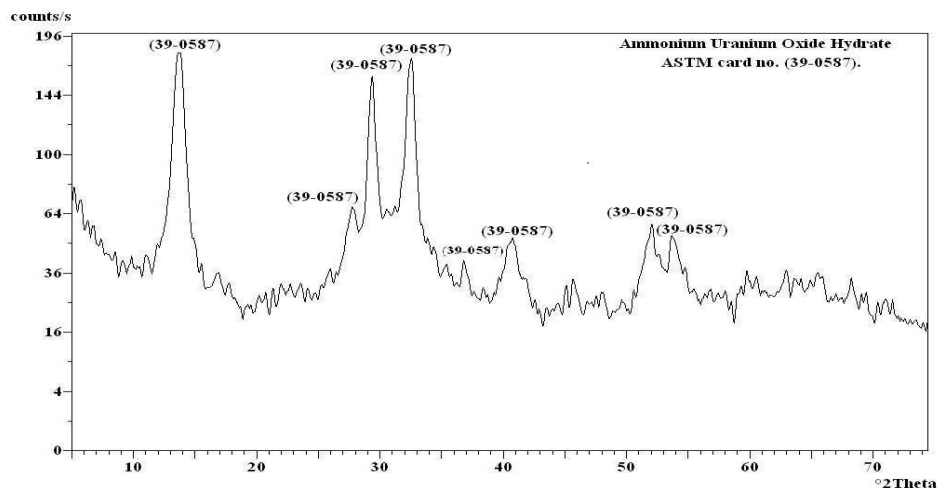
Major oxide	%	Traces	ppm
SiO ₂	21.07	U	560
TiO ₂	0.97	ΣREEs	3000
Al ₂ O ₃	30.43	Zn	3650
Fe ₂ O ₃	8.24	Cr	760
MgO	3.09	V	134
MnO	4.86	Cu	167
Na ₂ O	2.14	Ni	89
P ₂ O ₅	0.33	Mo	19
CaO	7.25	Cd	45
K ₂ O	1.10		
L.O.I.*	20.17		
Total	99.55		

L.O.I.* loss of ignition

From the prepared sulfate leach liquor of Abu-Zeneima mineralization uranium have then been recovered using HAE under the previously studied optimum conditions. Accordingly, a uranium extraction efficiency of 98% has been obtained. Subsequently, the uranium-loaded the HAE was subjected to uranium stripping using 1M NaCl /1M H₂SO₄ under the studied optimum stripping factors. These included an A/O ratio of 3/1 at room temperature for 15 min. contact time.

3.6.2. Uranium Precipitation

The stripping solution containing uranium would then be subjected to pH adjustment by using NH₄OH, which would be added to the solution, with continuous stirring to precipitate uranium at pH 7 as ammonium uranium oxide hydrate [UO₃NH₃H₂O]. After filtration, the produced filtrate would be re-acidified in order to be recycled in a new elution process. **Fig. (17)** Shows XRD analysis of the obtained [UO₃NH₃H₂O] product.

**Fig. (17):** XRD analysis of the obtained [UO₃NH₃H₂O] product.

4. Conclusion

The potentiality of the sunflower as extractant (HAE) for uranium from its sulfate solutions has actually been proven and the studied relevant factors have actually been optimized. These involved a 10 vol. HAE in kerosene, an O/A ratio of 1:1 for a shaking time 10 min. at the pH of 4. Under these conditions, the achieved uranium capacity has attained 33mg/g for uranium. The loaded uranium was afterward completely eluted using NaCl / H₂SO₄ solution. Finally, the working HAE was successfully applied for uranium recovery from an actual sulfate leach liquor mineralization in from the actual sulfate leach liquor of Abu Zeneima ore material (South Eastern Sinaï, Egypt).

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