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Factors Affecting the Refining of Crude Yellow Cake Using Synergistic Organic Mixture of di Ethyl Hexyl Phosphoric Acid (D_2EHPA) and Octanol

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THE PRESENT study deals with the purification of crude yellow cake produced through sulfate leaching of Gattar mineralization, Eastern Desert- Egypt. The Gattar yellow cake is purified through dissolving it in hydrochloric acid which dissolves about 95% of uranium content in the studied cake. Uranium extraction was obtained from the prepared pregnant solution using a synergistic organic solvent mixture of 0.5M di ethyl hexyl phosphoric acid (D_2EHPA) and 0.63M octanol in kerosene diluent. Different factors have been studied such as solvent concentration, stirring time, organic to aqueous phase ratio and temperature. The obtained loaded organic solvent was exposed to different concentrations of sodium carbonate to strip the uranium. After the stripping process, the uranium was precipitated using ammonia solution at pH 6.2. The product precipitate washed and dried then analysed. The analysis of the final precipitate shows upgrading of uranium concentration in the original cake from 46% to 76% while that of Fe has been decreased from 1.6% down to only 0.06% while that of Al and V have been totally removed.

Keywords: Synergistic, D_2 EHPA and octanol, Refining, Yellow cake.

Introduction

Yellow cake is a commercial name for the final uranium concentrate from ore mining and milling process [1]. The processing plants use a variety of processes well known in the art to concentrate the uranium in the ore from conventional mining, or leach-liquor from uranium extraction in leaching processes into a more concentrated product suitable for ultimate purification; The refining of yellow cake generally has employed a dissolution step using hydrochloric acid or nitric acid followed by a solvent extraction step using a suitable organic solvent to extract uranium from the acidic aqueous phase. Recovery of the extracted uranium from the solvent phase is accomplished by stripping and precipitation.

The first commercial process for producing pure uranium in tonnage quantities began at 1942 [2]; in general two common methods have currently been used for uranium refining namely dry and wet refining methods, the first method is dry refining method which is almost devoted for producing the reactor grade UF_6 required for the enrichment processes. The procedure [3] is carried out by roasting the yellow cake in a rotary calciner to remove the volatile components, and then reduced in fluid-bed with dissociated ammonia to UO_2. In a second fluid-bed, the UO_2 is reacted with gaseous HF to produce UF_4 which is fluorinated with CaF_2 and F_2 to UF_6. The product is heated and fed to distillation column to remove the remaining impurities by fractional distillation. The second method is wet refining method which is exclusively applied for producing nuclear grade UO_3 or ammonium uranyl tricarbonate (AUTC). The method is carried out using a number of methods depending upon type of solution which can accomplish the purification of the clarified loading solution [4], the variables include concentration of uranium and the desired final purity of the uranium product. A number of purification combinations may be applicable, for example; Direct precipitation from alkaline and some acid liquor, Ion exchange, elution and precipitation, Solvent extraction, stripping and precipitation and Ion exchange followed by solvent extraction

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These methods concern on applying the solvent extraction technique to purify the crude yellow cake. The recovery of uranium from the ores by using solvent extraction with the use of diethyl hexyl phosphoric acid (D_2EHPA) which called (DAPEX process) and since 1957 secondary or tertiary amines (AMEX process) has been the popular extractions [5]. A common organic phosphate tributyl phosphate (TBP) is widely used for separating uranium (VI) from co-existing elements in nitric acid media but the disadvantage of this method was the co-extraction of both iron and thorium with the uranium in nitric acid media. After achieving the extraction process, scrubbing process was necessary and then stripping process to strip the uranium from the loaded organic solvent by using sodium or ammonium carbonate solution. The final purified yellow cake can be precipitated by using ammonia or hydrogen peroxide solutions.

In United Kingdom [6], a method processing the yellow cake by digestion in nitric acid at 90°C to concentration of 400 g U/L, after filtration, uranium is extracted by 20% (v/v) TBP in kerosene. Scrubbing and stripping steps are performed and the striped uranyl nitrate is evaporated and then denitrated at 300°C to UO_3.

A method for refining the France yellow cake was investigated by Perez[7], uranium concentrate was digested in nitric acid to produce feed solution of 450 g U/L. The solvent used was 40% (v/v) TBP in dodecane, scrubbing was made using pure uranyl nitrate solution while stripping was made using water. The stripped liquor was partially evaporated followed by uranium precipitation as ammonium diuranate (ADU) using ammonium hydroxide.

In Egypt [2], refining trials are still in progress to elaborate a conventional procedure to refine and convert the Egyptian yellow cake to suit the international specification of uranium fuels applied elsewhere. Application of diethyl hexyl phosphoric acid (D_2EHPA) and trioctyl phosphine oxide (TOPO) in uranium refining, was subject to exploratory studies to investigate their suitability for the purpose. Harrington [2] mentioned that, when D_2EHPA in kerosene diluent is used in uranium recovery process, many other elements such as tetravalent ions Ce^{4+}, Ti^{4+}, V^{4+} along with Fe^{3+} and Mo^{4+} are also co-extracted into the system.

The pairing of bicarbonate leaching and peroxide precipitation of U (VI) was applied successfully [8] to purify Abu-Zenima crude yellow cake from most of its contaminants to meet the nuclear grade specification. Uranium is one of few metals that form soluble carbonate complexes and also one of few metals that form very stable, acid-insoluble peroxides. Applying the optimum leaching conditions: 110 g L^{-}1 sodium bicarbonate concentration, S:L ratio of 1:6, 2 h Stirring time and 45 °C leaching temperature on the wet washed YC achieved uranium leaching efficiency by a percent of 91.7%. Almost 98% of uranium in leach liquor was effectively precipitated using 200% excess of hydrogen peroxide at pH 1.8. The proposed method is promising, simple and offers a high purity product of 97.2%. Abu-Zenima crude yellow cake.

Upgrading crude yellow cake was done by 0.05 M Tris 2-ethylhexyl Phosphate / kerosene from 5 M nitrate solution [9]. More than 98 % of uranium extracted after 5 stages of contact, shaking time 5 minutes and volume phase ratio 1/1. Uranium stripping efficiency reached 99 % using distilled H2O, 10 minutes shaking time, (O/A) ratio 4/1 and three stripping stages. The purity of the produced cakes was enhanced by addition of EDTA or CDTA. The produced cake using TEHP followed by EDTA addition to the stripping solution before uranium precipitation step was the most preferable cake with lower gangues.

From all the previous, wet refining methods of yellow cake product are generally used to purify the yellow cake. In the present work, a synergistic mixture of D_2EHPA and octanol in kerosene was used to extract the uranium from the dissolved yellow cake followed by uranium stripping with (20% w/v Na_2CO_3 solution). The aim of the present study is the production of high grade yellow cake by removal and decreasing of the associated undesirable impurities (especially iron) present in the yellow cake which produced from Gattar mineralization , Eastern Desert-Egypt by using a synergistic organic solvent mixture of diethylhexyl phosphoric acid and octanol in kerosene without applying scrubbing stage , the addition of octanol plays an important role to prevent the formation of the third phase which was formed during the uranium stripping step . The suggested refining process includes dissolving of the yellow cake, extraction of uranium then stripping process and eliminates the impurities by filtration process and finally precipitate the purified yellow cake.

Experimental

Material and analytical procedures

Solution and reagents

The studied sample of yellow cake was obtained from Gattar pilot plant by Nuclear Materials Authority, Egypt. Stock solution of uranium (1000 ppm) was supplied from Accu Standard, USA. Chemicals and reagents such as hydrochloric acid, diethyl hexyl phosphoric acid (Merck, 99%), octanol (Panreac, Barcelona, 99.5%), sodium carbonate and others were of A.R. grade and used without further purification. The yellow cake dissolution process was carried out by using 4M HCl [2], while different concentrations of D_2EHPA, octanol and Na_2CO_3 were used in order to reach the extraction and stripping optimum conditions.

Analytical procedures and instruments

Uranium was analyzed in the corresponding aqueous phases using Arsenazo (III) reagent under different conditions (Marczenko, 1976) for this purpose, a Lambada UV/VIS spectrophotometer (Perkin-Elmer, USA) was used. Absorbance of the formed uranium arsenazo (III) complex was measured at 650nm against proper standard solutions. In addition, uranium was also analyzed by an oxidimetric titration method against ammonium metavanadate in the presence of diphenylamine sulfonate indicator prior to titration; proper reduction of uranium was performed using ferrous sulfate [10].

The contained elements in the examined sample were quantitatively detected by the atomic emission spectroscopy inductively coupled plasma (ICP-OES) while the rest elements were determined qualitatively by X-ray fluorescence (JSX-3222 analyzer). The analysis of elements are also confirmed using another analytical instrument, atomic absorption spectrometer (GBC 932-AA).

Procedures

Extraction process

In the present work, uranium extraction process was carried out through laboratory batch technique in mechanically agitated beakers containing 150 ml of aqueous solution of dissolved yellow cake (feed solution) with mixture of D_2EHPA and octanol in kerosene as an organic solvent.

Before choosing the optimum conditions for extraction of uranium from the feed solution, some factors were studied e.g., uranium initial concentration ranged from 153.3 g U/L to 460 g U/L, O/A phase ratio ranged from 0.5 to 4, D_2EHPA/octanol molar ratio ranged from 0.3 to 12.6, effect of temperature of stirring ranged from 25°C to 50°C and time of stirring ranged from 1 min to 15 min. The solutions were agitated at constants stirring rate of 800 rpm and 4M HCl. After stirring, the organic phase was separated from the aqueous phase and the concentrations were measured. The concentration of extracted uranium was determined from the difference between the initial and final concentrations of uranium in aqueous solutions.

Stripping Process

Stripping of the extracted uranium from the organic phase composed of D_2EHPA and octanol in kerosene with initial uranium concentration of 141.1 g U/L was successfully performed using sodium carbonate. Different studied factors e.g., concentrations of sodium carbonate as astripper ranged from (5% to 20%) w/v, effect of stirring time ranged from 1min to 15 min, effect of stirring temperature ranged from 25°C to 50°C, effect of aqueous to organic phase ratio ranged from 1 to 4 at constant stirring rate of 800rpm., the stripping investigations were carried out to choose the best conditions that can successfully strip the uranium from the organic phase.

Precipitation Process

The purified strip solution (pH = 9.98) was subjected to selectively uranium precipitation by adjusting the solution pH at 6.2 with nitric acid and ammonia solution. The formed precipitate was dried at 120 C^0 and then analyzed.

Calculations

The extraction efficiency (E%) and the distribution coefficient D were calculated from the equations:-

$$\mathbf{E\% = 100\ D_u/D_u + (V_{aq}/V_{org})} \qquad (1)$$

The distribution ratio (*D*) was calculated from the equation:-

$$\mathbf{D = (C_{org}/C_{aq}) \times (V_{aq}/V_{org})} \qquad (2)$$

Where, C_{org} is the uranium concentration in the organic phase, C_{aq} is the uranium concentration in the aqueous phase and V_{aq}/V_{org} is the volume ratio between aqueous phase and organic phase.

Experimental tests were carried out using a wet refining process of yellow cake sample.

Results and Discussions

Composition of the impure yellow cake

The examined yellow cake of Gattar pilot plant-eastern desert- Egypt, was formed by leaching the Gattar mineralization with sulfuric acid and then the leach liquor pass through anionic exchange resin then precipitation process was achieved with sodium hydroxide [11], but the produced form of the studied uranium concentrate containing some of undesirable impurities prevents using it in the nuclear applications. In addition the concentration of uranium and undesirable impurities where analyzed by ICP instrument (Inductively Coupled Plasma), and tabulated also in Table 1. Also, the analysis of the impure yellow cake by XRF instrument [(X-ray Fluorescence (JSX-3222 analyzer)] are graphically represented in Fig. 1, to estimate the contributing elements of Egyptian yellow cake. The chart interpretation indicates the presence of the following undesirable impurities, Mn, Al, As, Ba, Cr, Cu, Fe, Na, Zn, Ce, Pr, Sm, Gd, Tm, Yb and Y. The present study aims to decrease these impurities especially iron which present by a large concentration. The chemical composition of the examined sample is listed in Table 1.

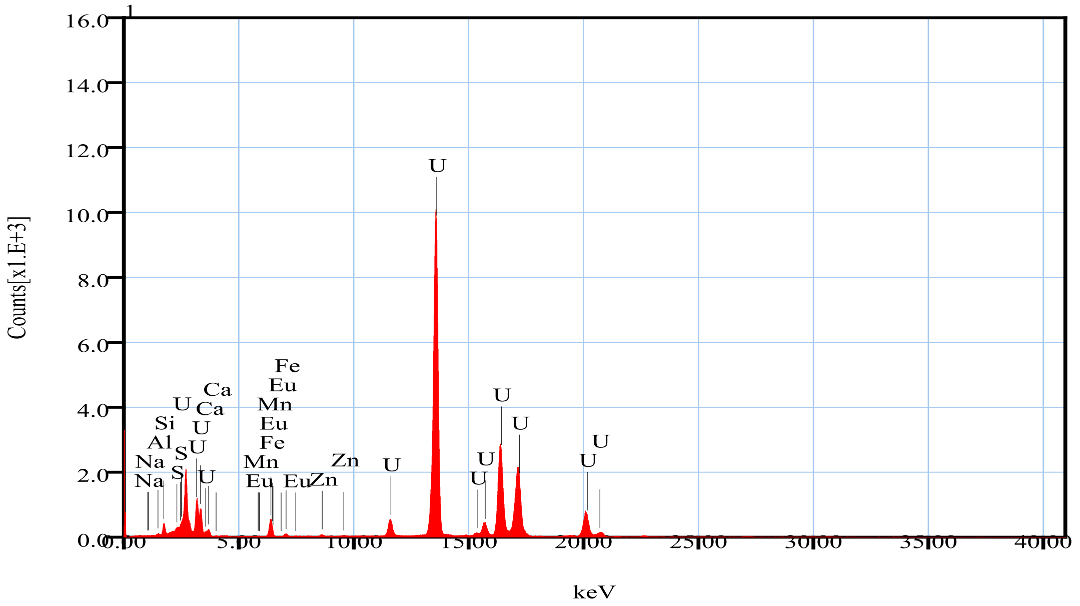


Fig.1. XRF Specification of the uranium concentrate before applying the purification process.

TABLE 1. Chemical analysis of the examined Egyptian yellow cake (Uranium concentrate).

Elements	Concentration %	PPm	Elements	Concentration %	PPm
U	46.00	460000	**Ni**	0.02	200
As	0.04	400	**P**	0.07	700
Cs	0.04	400	**Si**	0.02	200
Ag	0.05	500	**Cd**	0.01	100
Sr	0.03	300	**Ca**	1.98	19800
Zn	0.10	1000	**Ce**	0.03	300
Al	1.40	14000	**Pr**	0.54	5400
V	1.39	13900	**Nd**	0.10	1000
Na	3.9	39000	**Sm**	0.08	800
K	1.00	10000	**Eu**	0.02	200
Mg	0.56	5600	**Gd**	0.04	400
Mn	0.07	700	**Tb**	0.17	1700
Ba	0.02	200	**Ho**	0.11	1100
Co	0.08	800	**Er**	0.02	200
Zr	0.15	1500	**Tm**	0.08	800
Mo	0.40	4000	**Yb**	0.02	200
Fe	1.60	16000	**Sc**	0.01	100
Cu	0.01	100	**Y**	0.07	700
Cr	0.03	300	**Th**	2.50	25000

Uranium extraction process

Uranium extraction process by using D_2EHPA alone gave satisfactory results but when the loaded solvent was represented to undergo uranium stripping process, third phase was formed, so that the addition of a modifier (such as n- octanol) is necessary to prevent the third phase formation during the uranium stripping process. Third phase formation during solvent extraction process is observed at high metal loading of the organic phase [12]. Under certain conditions, the organic phase splits into two layers, the light layer containing most of the diluent, little extractant and metal; and a heavy or third phase containing high concentration of extractant, metal and little diluent. The phenomenon of third phase formation is mainly caused by the limited solubility of the metal-ligand complex in the non-polar organic phase; the occurrence of third phase in the extraction system is undesirable and hence should be avoided. The addition of a modifying reagent to the extractant-diluent mixture may be necessary in order to [13]:

1- Improve the rate of phase disengagement following mixing

2- Increase the solubility of the extracted species in the organic phase, and thus prevent the formation of third phases

3- Decrease the emulsion phase and to increase the extraction efficiency.

The necessity for the use of modifiers and the choice of a particular modifier for the system in question are usually only determined by tests. The most common modifiers in uranium processing have been TBP for the D_2EHPA system and long chain alcohol molecules in the tertiary amine system [14]. The most commonly used alcohol has been isodecanol. However, mere seem to be sufficient indications from plant operations that with continued use and recycling of the solvent mixture the isodecanol is oxidized to isodecanoic acid, and therefore degraded. In this study, n-octanol is used to act as modifier for the D_2EHPA system which represents a new synergistic organic solvent for uranium extraction.

On the other hand, existing literature data on uranyl chloride complexes are conflicting. Some of researches indicated that the uranyl chloride complex has an anionic nature [15], while several other investigations proved the cationic nature of the uranyl chloride complex [15]. In the present study, uranyl complex has been found as cationic species UO_2Cl^+.

Effect of organic to aqueous phase ratio

The extraction of uranium from Gattar yellow cake solution was studied at room temperature after adjusting the pH of the yellow cake solution to be 1.7 [16].The extraction of uranium with synergistic organic solvent (0.5 M D_2EHPA and 0.63 M octanol in kerosene) was investigated by varying the organic to aqueous phase ratio from 0.5 to 4. The extraction was performed during stirring for 15 min. The results are represented graphically in Fig. 2 as a relation between organic to aqueous phase ratio and uranium extraction efficiency percent. From the results, it is clear that, the extraction efficiency percent increases with the increase of organic to aqueous phase ratio were it reaches 89% for org./aq. 1:1, while it reaches to 96 % in the case of org /aq. 4:1.

Effect of D_2EHPA / octanol molar ratio

The extraction of uranium from Gattar yellow cake feed solution containing uranium concentration of 153.3 g U/L under room temperature and organic to aqueous phase ratio 2:1. Different molar concentrations of D_2EHPA and octanol in the range from 0.26 to 12.6 were used with continuous stirring time of 15 min. The results are graphically represented in Fig. 3. The results indicate that the uranium extraction efficiency percent increases with the increase of the D_2EHPA/octanol molar ratio to reach the maximum uranium extraction efficiency 92 % at D_2EHPA/octanol molar ratio of 1.26 (0.5 M D_2EHPA + 0.63 M octanol in kerosene). After this value, the uranium extraction efficiency decreased again to reach its minimum value 33.8 % at molar ratio of 12.6, this is may be attributed to the decrease of D_2EHPA concentration used with the increase of octanol concentration. So that, in this study 1.26 is the preferred D_2EHPA /octanol molar concentration ratio for uranium extraction process.

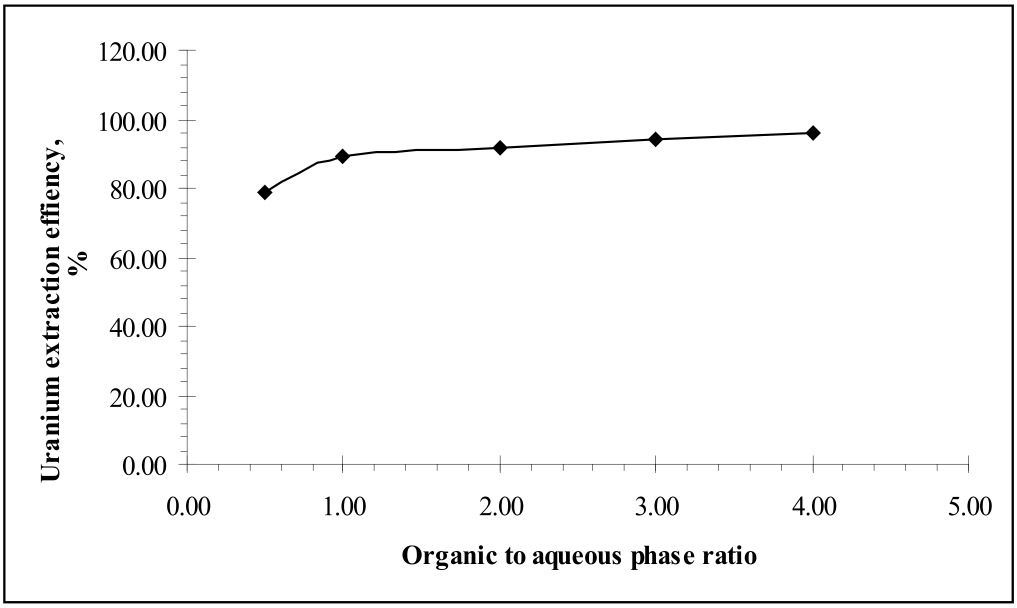


Fig. 2. Organic to aqueous phase ratio as a function of uranium extraction efficiency percent (Stirring time.. 15 min, temperature.. room temperature, 0.5 M D_2EHPA and 0.63 M octanol and uranium concentration.. 153.3 g/l).

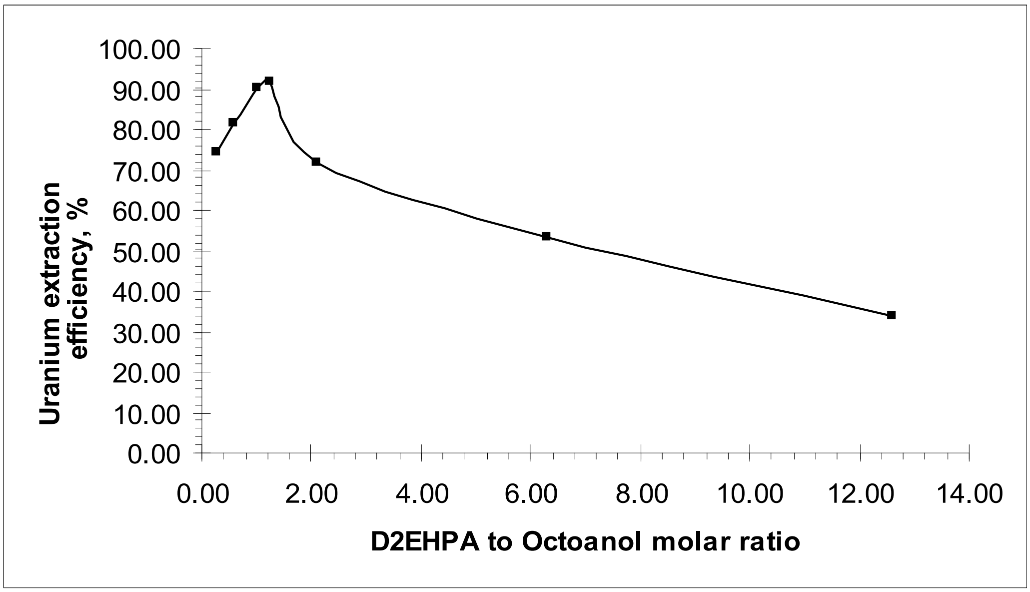


Fig. 3. D_2EHPA to octanol molar ratio as a function of uranium extraction efficiency percent (Stirring time.. 15 min, temperature.. room temperature, organic to aqueous phase ratio..2:1 and uranium concentration.. 153.3 g/l).

Effect of temperature

The extraction of uranium from the crude yellow cake feed solution with uranium concentration 153.3 g U/L at different temperatures was investigated. The extraction experiments were carried out by stirring the aqueous solution with (0.5 M D_2EHPA and 0.63 M octanol) for 15 min. while the org./aq. phase ratio was fixed at 2:1, the temperature of extraction was varied from 25C° to 50C°, the results are shown in Fig. 4, which show that the extraction percent is slightly decreased from 92 to 87 % only with the increase of the temperature from 25C° to 50C°. So that the extraction process was preferable at room temperature. The same results were reprinted by Blake et al. [14], the uranium extraction ability of synergistic combinations decreased with increasing the temperature.

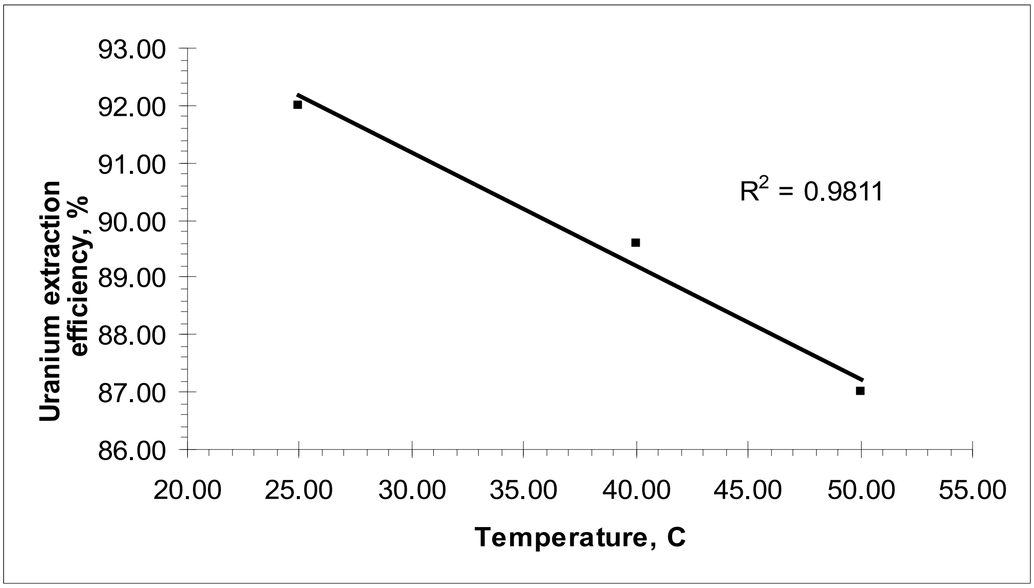


Fig. 4. Extraction temperature as a function of uranium extraction efficiency percent (0.5 M D_2EHPA and 0.63 M octanol, organic to aqueous phase ratio..2:1, uranium concentration.. 153.3 g/l and stirring time.. 15 min).

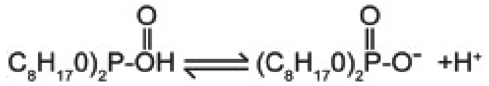
Effect of stirring time

Stirring time is an important factor in determining the efficiency of uranium extraction processes which involve mass transfer between two liquids. The effect of stirring time was investigated between 0.5 min and 15 min, at extraction temperature of $25C^{\circ}$, Organic to aqueous phase ratio 2:1, uranium concentration 153.3 g U/L the results represented in Fig. 5, reveal that (i) within 1 min; the extraction efficiency reached 65 % indicating that the extraction is very rapid. (ii) Stirring time has a positive effect on the extraction efficiency which increased to 92 % within 15 min.

Effect of initial uranium concentration in the feed solution

Figure 6 shows the increasing of uranium extraction efficiency with decreasing the uranium concentration in the initial feed solution. The uranium extraction efficiency reached to its minimum value (25 %) by using a uranium concentration in the feed solution of 460 g/l. while by decreasing the uranium concentration in the feed solution to 153.3 g/l, the uranium extraction efficiency reached to 92 %. So that, 153.3 g/l is the suitable concentration of the uranium in the initial uranium feed solution to give a satisfactory results of the uranium extraction process by applying the optimum conditions (organic to aqueous phase ratio 2:1, stirring time 15 min, D_2EHPA/octanol molar ratio 1.26 and room temperature).

The mechanism of the uranium extraction process was interpreted as follow [15]; D_2EHPA is described as an acidic extractant which can be deprotonated to form an anion



$$C_8H_{17}0)_2\overset{\overset{O}{\|}}{P}\text{-}OH \rightleftharpoons (C_8H_{17}0)_2\overset{\overset{O}{\|}}{P}\text{-}O^- + H^+$$

The hydrophobic anion can chelate a cation from the aqueous phase, the chelate being soluble in the organic phase.

Uranium extraction by dialkylphosphoric acids is represented by the equation [15]:

$$UO_2^{++} + 2(HX)_2 \leftrightarrow UO_2H_2X_4 + 2H^+$$

Where $(HX)_2$ is the dimerized dialkylphosphoric acid. The synergistic enhancement can be explained in terms of adding the neutral reagent to the above complex.

$$UO_2^{++} + (HX)_2 + N \leftrightarrow UO_2\, H_2\, X_4 N + 2H^+$$

Where N is the neutral synergistic additive, Interactions between the dialkylphosphoric acid and the neutral additive [15] also occur:

$$N + (HX)_2 \leftrightarrow N(HX)_2$$

$$N + 1/2(HX)_2 \leftrightarrow N(HX)$$

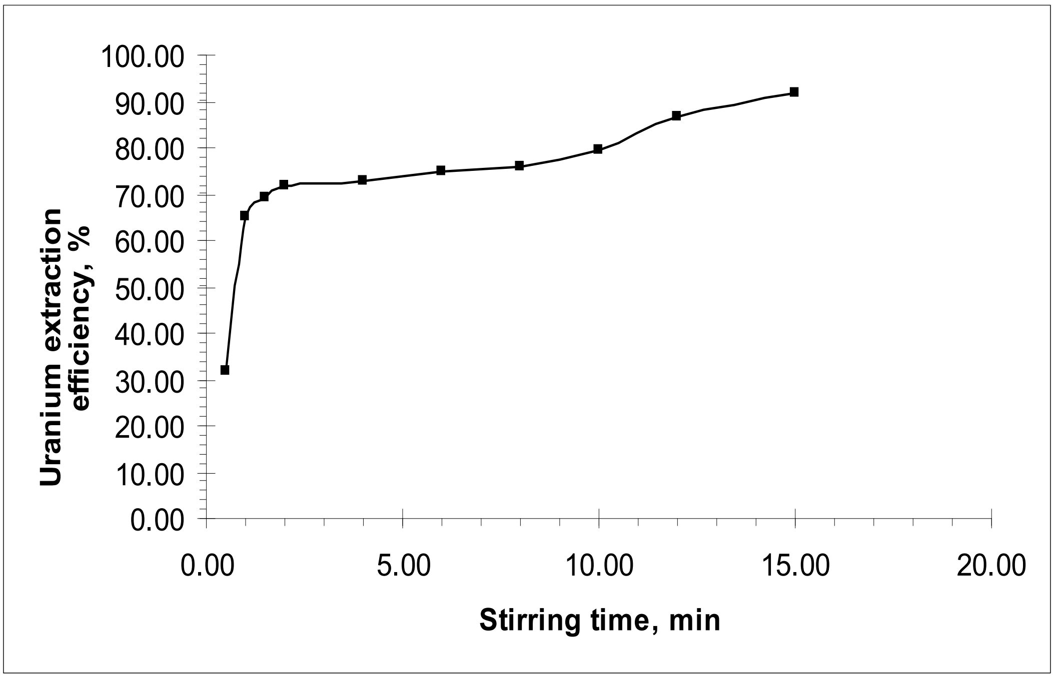


Fig. 5. Stirring time as a function of uranium extraction efficiency Percent (Temperature.. room temperature, 0.5 M D_2EHPA and 0.63 M octanol, organic to aqueous phase ratio..2:1 and uranium concentration.. 153.3 g/l).

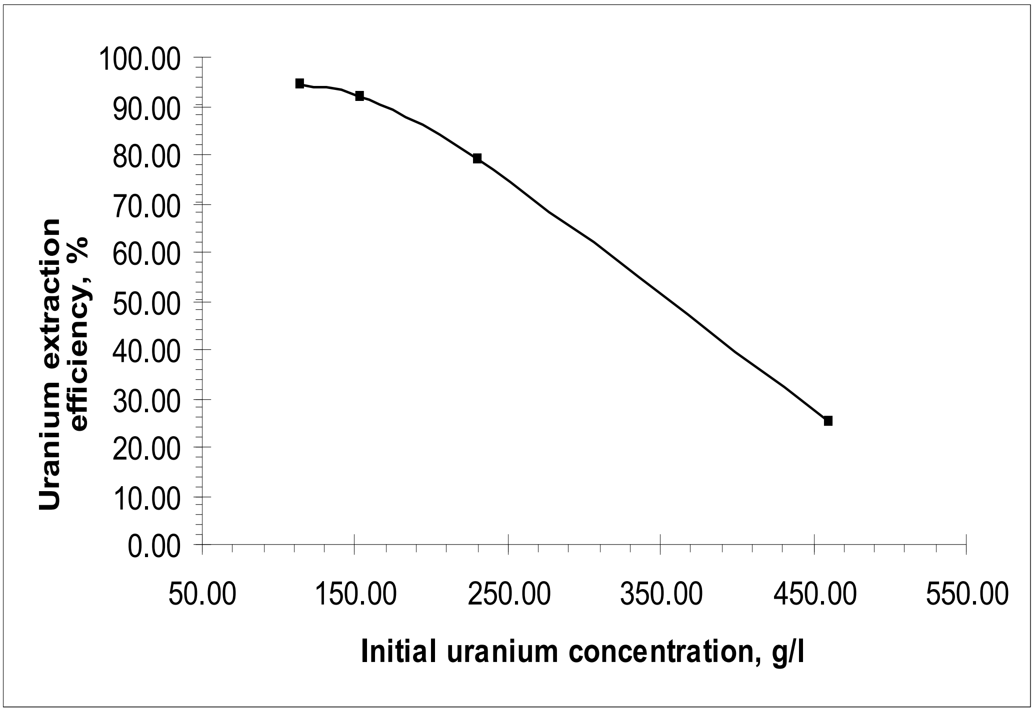


Fig. 6. Initial uranium concentration as a function of uranium extraction efficiency percent (Temperature.. room temperature, 0.5 M D_2EHPA and 0.63 M octanol, organic to aqueous phase ratio..2:1 and stirring time.. 15 min).

Stripping of uranium from loaded organic solvent

Khorfane et al. [17] studied the effect of addition of sodium carbonate, ammonium carbonate or ammonium bicarbonate on the uranium stripping efficiency, the results obtained by them revealed that, sodium carbonate was more preferable than ammonium carbonate and ammonium bicarbonate in the uranium stripping process. In the present study, sodium carbonate is used only for achieving the uranium stripping process from the loaded organic solvent. In this concern, different factors as sodium carbonate concentration, stirring time, aqueous to organic phase ratio and temperature were studied to determine the optimum conditions giving the maximum uranium stripping efficiency.

Effect of sodium carbonate concentration

The stripping process of uranium from the loaded synergistic organic solvent mixture of (0.5 M D_2EHPA + 0.63 M octanol) was investigated at room temperature, with 15 min stirring time and aq/org phase ratio is equal 1:1 by using 20% wt/v sodium carbonate. From Fig. 7, it is noticed that the uranium stripping efficiency percent is increased by increasing the concentration of sodium carbonate to reach 86 % using 20 % (wt/v) solution of sodium carbonate. These obtained data agreed with those obtained by Khorfane et al. [17].

Effect of stirring time

The effect of stirring time on the stripping of uranium was studied in the range of 0.5 min to 15 min at aq/org 1: 1 using 20% wt/v sodium carbonate at room temperature. From Fig. 8, it is noticed that the uranium stripping efficiency percent is increased by increasing the stirring time to reach 86 % at 15min.

Effect of aqueous to organic phase ratio

In order to study the effect of the aqueous/organic phase ratio upon uranium stripping efficiency from the uranium-loaded solvent, a series of stripping experiments were performed using aq/org. ratios ranging from 1/1 to 4/1. In these experiments, 20 % wt/v sodium carbonate solution was used and the time was fixed at 15 min in the room temperature. The obtained data given in Fig. 9, revealed that, the uranium stripping efficiency decreased by increasing the aqueous to organic phase ratio to reach 86 % at aq/org. ratio equal 1:1.

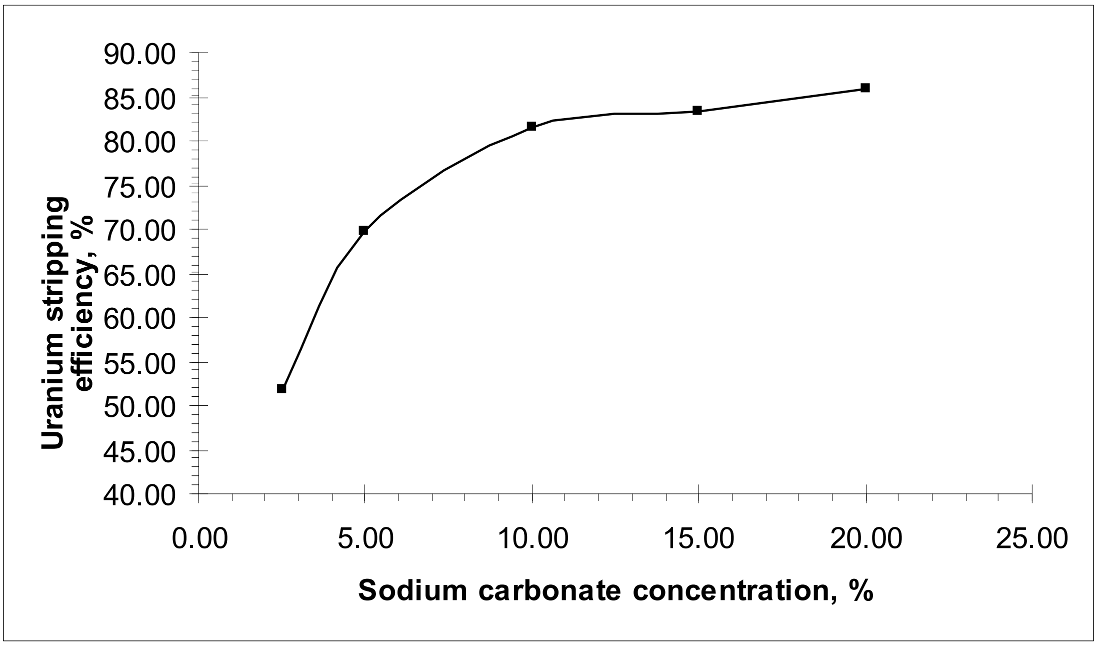


Fig. 7. Sodium carbonate concentration as a function of uranium stripping efficiency percent (aqueous to organic phase ratio..1:1, stirring time.. 15 min and stripping temperature.. room temperature).

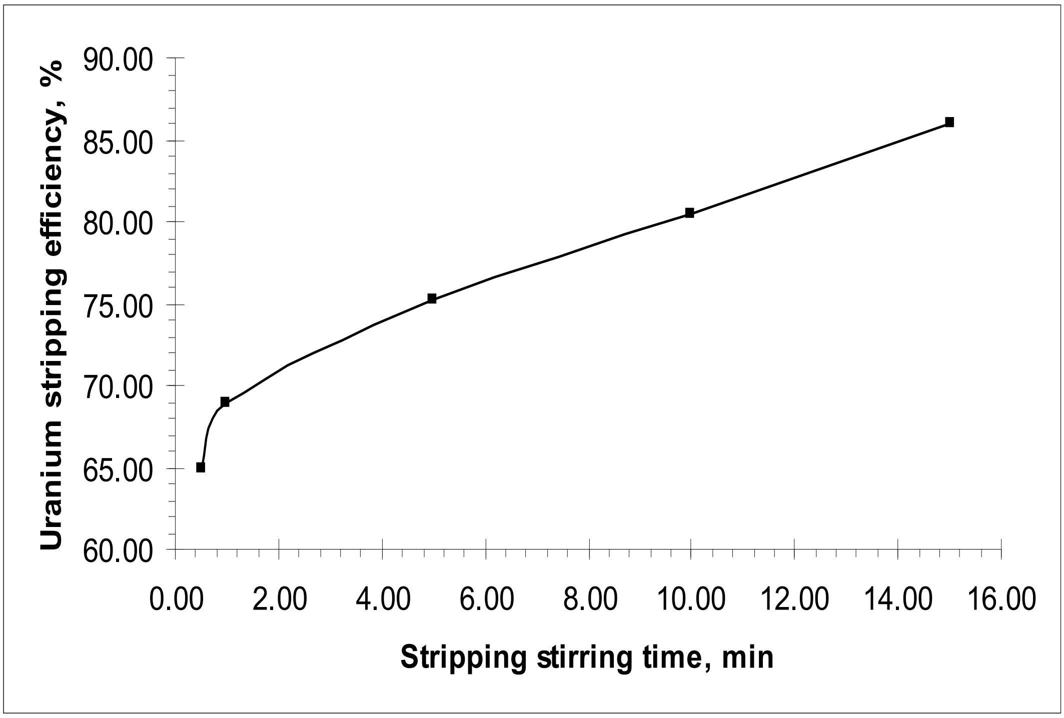


Fig. 8. Stirring time as a function of uranium stripping efficiency percent (aqueous to organic phase ratio..1:1, sodium carbonate concentration.. 20 % wt/v and stripping temperature.. room temperature).

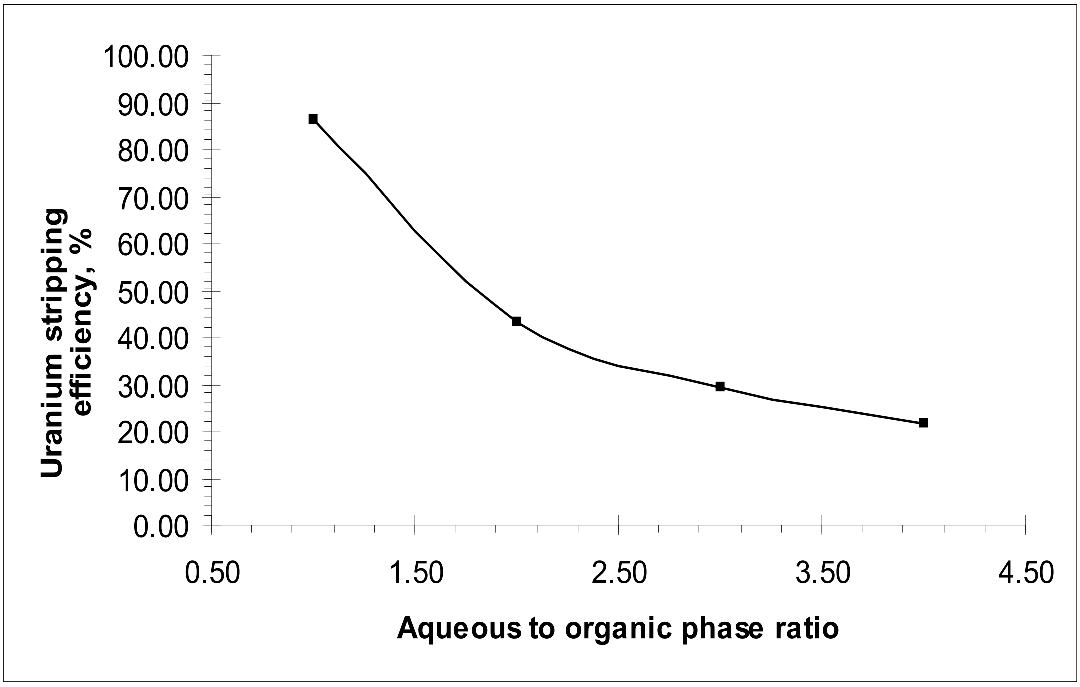


Fig.9. Aqueous to organic phase ratio as a function of uranium stripping efficiency percent (Sodium carbonate concentration.. 20 % wt/v, stirring time.. 15 min and stripping temperature.. room temperature).

Effect of temperature

A series of experiments was carried out at different temperatures (25-50 °C) to study the effect of temperature on the uranium stripping process. The experiments were performed for the feed solution of initial uranium concentration of about 141.1 g/l. The experiments were performed under the following conditions:

a- Sodium carbonate solution : 20 % wt/v
b- Stirring time : 15 min
c- Aqueous/ organic phase ratio : 1:1

The results obtained are given in Fig. 10, which indicates that, the uranium stripping efficiency increased by increasing the temperature to reach its maximum value of 94.7 % under heating at 50 °C. But the preferred stripping temperature was performed at room temperature from the economic point of view. These results agreed with the data obtained by Khorfan et al. [17], they proved that the uranium stripping efficiency increased by increasing the temperature until 55°C and they can not raise the temperature more than this value, the temperature is fixed by the flash point of the kerosene used [17].

Precipitation of the upgraded yellow cake

Uranium was stripped from the loaded organic phase, with 20% (wt/v) sodium carbonate. The strip liquor was filtered to remove the iron and other impurities. The produced filterated impurities were quantitatively detected by (ICP-OES) and qualitatively detected by XRF analyzer. The analysis of the filterated impurities shows that iron is the major element in the separated impurities (about 82%) and this is the aim of this study to remove and decrease iron from Gattar yellow cake. Uranium precipitation was carried out by adjusting the pH value using ammonia solution and nitric acid to decrease the pH from 9.98 to 6.2, In order to bring down the pH of the solution, an addition of nitric acid to the solution was added after the solution had been filtered to remove the iron and other precipitated impurities. In a pH range of 6 - 6.5, the uranium precipitation was completed and reached to (95.1%). Uranium was measured in the raffinate solution after achieving the precipitation process and its concentration was 6 ppm. The precipitate was filtered, washed, dried and then the dried yellow cake was analyzed qualitatively and quantitatively as shown in Fig, 11 and table 2 comparing with the international yellow cake limit [18].

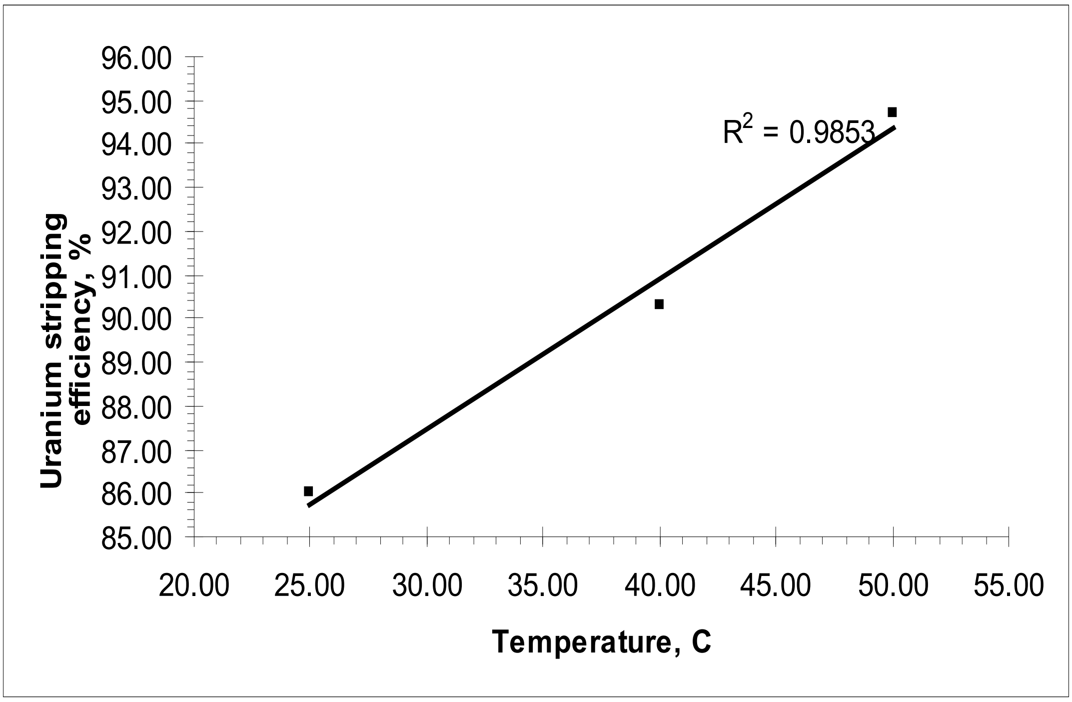


Fig.10. Stripping temperature as a function of uranium stripping efficiency percent (Sodium carbonate concentration.. 20 % wt/v, stirring time.. 15 min and stripping aqueous to organic phase ratio..1:1).

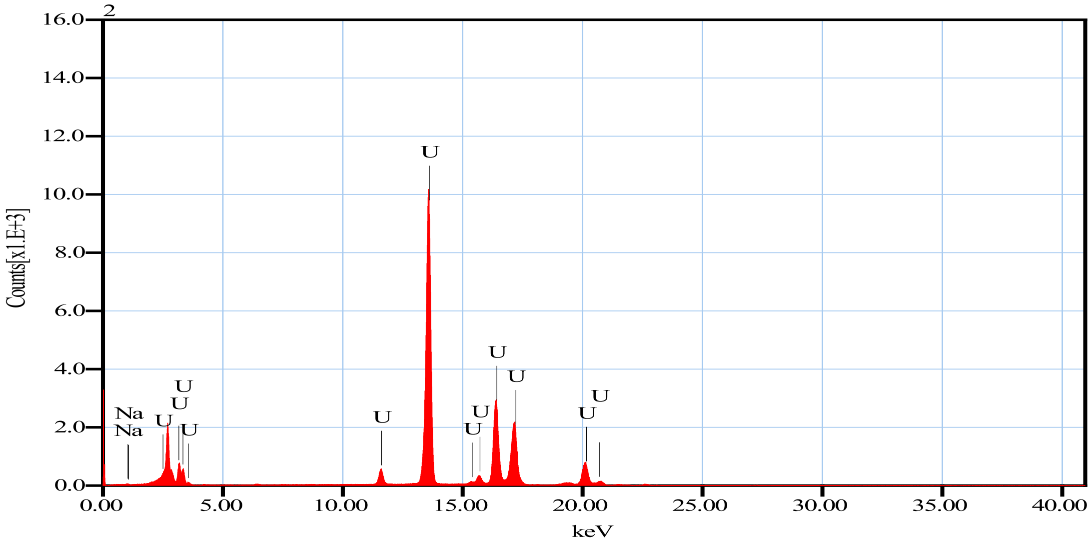


Fig. 11. XRF specification of the uranium concentrate after applying the purification process.

TABLE 2. Chemical analysis of the purified examined yellow cake before and after purification process comparing with the international yellow cake limit [18].

Elements	International Yellow Cake Limit, %[18]	Before purification process, %	After purification process, %
U	65.00	46.00	76.00
As	0.10	0.04	0.003
Cs	-	0.04	0.01
Ag	-	0.05	0.006
Sr	-	0.03	0.0008
Zn	-	0.10	0.0023
Al	-	1.40	-
V	0.30	1.39	-
Na	7.50	3.9	7.8
K	3.00	1.00	0.08
Mg	0.50	0.56	0.0044
Mn	-	0.07	0.0025
Ba	-	0.02	0.0041
Co	-	0.08	0.0033
Zr	0.10	0.15	-
Mo	0.30	0.40	-
Fe	1.00	1.60	0.06
Cu	-	0.01	0.0001
Cr	-	0.03	0.0017
Ni	-	0.02	0.0014
P	-	0.07	0.002
Si	-	0.02	0.005
Cd	-	0.01	-
Ca	1.00	1.98	0.20
Ce	-	0.03	0.01
Pr	-	0.54	0.11
Nd	-	0.10	0.03
Sm	-	0.08	0.01
Eu	-	0.02	0.001
Gd	-	0.04	0.03
Tb	-	0.17	0.02
Ho	-	0.11	0.013
Er	-	0.02	0.001
Tm	-	0.08	0.003
Yb	-	0.02	0.006
Sc	-	0.01	-
Y	-	0.07	0.009
Th	2.50	2.50	0.01

Conclusion

To eliminate the major of the undesirable impurities especially iron from the uranium concentrate (Yellow Cake Of Gattar Pilot Plant). A synergistic organic solvent mixture of 0.5 M D_2 EHPA and 0.63M octanol was used at room temperature and mixed with the aqueous phase of uranium concentrate by org/aq. phase ratio equal 2:1, stirring for 15 min and concentration of uranium feed solution is 153.3 g U/L. By applying these conditions, 92 % of the uranium in the aqueous phase was successfully extracted leaving the most of undesirable impurities in the aqueous phase. After that, direct process of stripping was achieved to strip the uranium from the loaded organic solvent, in this concern, 20 % (wt/v) sodium carbonate solution was used and stirring for 15 minute at aq/org phase ratio 1: 1 under room temperature to strip 86 % of the uranium. An important filtration step was carried out during the applying of the stripping process to eliminate the remained residue of iron and other impurities. The strip solution of uranium was used to precipitate the uranium and filtered.

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References

1. Nasser S. Z., Production of yellow cake from rock phosphate & It's Characterization, *M.Sc. Thesis*, Karary Academy of Technology, Sudan, (2004).
2. Serag H., Refining studies on uranium yellow cake product of El-Atshan uraium ore, *Master Thesis*, Chem-Dept, Faculty of Science, Mansoura University, (1991).
3. Ashbrook A. W., Uranium refining and conversion practice in the western world: An overview, Uranium.82, *12th Annu Hydrometall Meet, Toronto, Ontario,* Canada, 55, (1982).
4. Dean J. A., *Handbook of Analytical Chemistry,* The McGrawHill Inc., Section 8, New York, (1995).
5. IAEA, Uranium Extraction Technology, *Technical report Series No. 359, Vienna,* (1993).
6. Page H., *Proceedings of Technical Committee Meeting on Advances in Uranium Refining and Conversion, Iaea, Vienna,* (1987).
7. Perez P., *Proceedings of An Advisory Group Meeting on Production of Yellow Cake and Uranium Fluoride, Iaea, Vienna,* (1980).
8. El-Ansary A., Abd El-Wahab G., Bayoumi E and Nouh E., Purification of Abu-Zenima wet crude yellow cake using alkaline leaching of U(VI), *Egyptian Journal of Petroleum* (2017).
9. Ali A., Eliwa A and Hagag M., Upgrading of the Crude Yellow Cake to a Highly Purified Form using Tris(2-ethylhexyl) Phosphate in Presence of EDTA or CDTA, *Journal of Modern Materials* (2017).
10. Taha M. H., Chemical studies on the production and purification of phosphoric acid from Abu-Tartur phosphate rocks, Chem-Dept, Faculty of Science, Helwan University (2010).
11. Cheira M. F., Ghazala R. A., and Mahmoud K. F., An upgrading procedure for the uranium concentrate product of Gattar pilot plant via ammonium carbonate, *An Indian Journal of Inorganic Chemistry*, **8**, 61-68 (2013).
12. Gupta K. K., Kulkarni, P. G., Gurba P. B., Janardan P., Changarani R. D. and Dey P. K., Third phase formation in the extraction of U (VI), Th (IV) and Pu (IV) by N, N-Dialkyl aliphatic amides, Emerging Trends in *Separation Science and Technology*, Mumbai, (2006).
13. Uranium Extraction Technology Report, International Atomic Energy Agency, Vienna, (1993)
14. Blake C. A., Horner D. A and Schmitt J. M., Synergistic uranium extractants combination of neutral organophosphorus compounds with dialkylphosphoric acids, *Report, U. S. Atomic Energy Commission,* (1959).
15. Banerjea D and Tripathi, K., Association of uranium VI with anions in aqueous perchloric acid medium, *Journal of Nuclear Chemistry*, **18**, 199-206 (1961).
16. El-Hazek N. K, Mahdy M. A and Kamal H. M., Recovery of uranium and molybdenum from Gebel Gattar Granites, Eastern desert, *Proceedings of 6th Conference of Nuclear Sciences and Applications,*

Cairo, Egypt (1996).

17. Khorfan S, Stas J and Kassem M., Stripping of uranium from D2EHPA/kerosene solvents by different aqueous media, *Journal of Radioanalytical and Nuclear Chemistry*, **238**, 145-148 (1998).

18. Abdel A. A., Preparation of uranium concentrate from crude yellow cake, *Ph.D. Thesis,* Chem-Dept, Faculty of Science, Ain Shams University (2015).

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العوامل المؤثره على تكرير الكعكه الصفراء الخام باستخدام خليط عضوى تأزرى من ثنائى ايثيل هيكسيل حمض الفوسفوريك والاوكتانول

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هذه الدراسه تهدف الى عمل تنقيه للكعكه الصفراء الخام المنتجه من موقع جتار بالصحراء الشرقيه –جمهورية مصر العربيه, حيث تتم اذابة الكعكه الصفراء فى حمض الهيدروكلوريك ثم عمل استخلاص لليورانيوم من المحلول باستخدام خليط من ٠,٦٣ مولار اوكتانول مع ٠,٥ مولار من ثنائى ايثيل هيكسيل حمض الفوسفوريك المخفف بالكيروسين. ولقد اوضحت الدراسه انه يتم استخلاص ٩٢٪ من اليورانيوم وذلك بالتقليب لمدة ١٥ دقيقه عن درجة حرارة الغرفه وبنسبة مذيب عضوى الى محلول الكعكه الصفراء ١:٢ حيث تتم فى هذه الخطوة فصل معظم الشوائب غير المرغوب فيها ثم يتم بعد ذلك اجراء عملية استرجاع لليورانيوم من المذيب العضوى باستخدام ٢٠٪ من محلول كربونات الصوديوم ثم تقليل قيمة الاس الهيروجينى الى ٦,٢ لترسيب ركاز اليورانيوم النقى.