



## Synthesis, Characterization and Application of A Novel Extracting Agent 2-(4-methylphenyl)-8,9-Dihydro-8,8-Dimethyl-7H-Pyrazolo[1,5-*a*] Quinazolin-6-one (MPHPQ) for U(VI) Removal from Sulfate Aqueous Solutions



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### Abstract

The recovery of U(VI) from sulfate solutions can be successfully accomplished using reagents of the pyrazoloquinazolinone class. In order to extract U(VI), the substance 2-(4-methylphenyl)-8,9-dihydro-8,8-dimethyl-7H-pyrazolo[1,5-*a*]quinazolin-6-one (MPHPQ) was developed. Utilizing a variety of analytical techniques, including Fourier-transform infrared spectroscopy (FTIR), Nuclear magnetic resonance (NMR), mass spectrometry, and elemental analysis, the extractant (MPHPQ) was identified. A batch technique was used in experiments to identify the variables influencing U(VI) extraction and stripping efficiency. The diluent type, pH, U(VI) initial concentration, starting (MPHPQ) concentration, contacting time, (Organic/Aqueous) O/A phase ratio, and temperature are the regulating parameters for uranium extraction. The extraction efficiency attained 92% with optimal extraction conditions of 0.08 M (MPHPQ) in chloroform at a starting pH of 4, a 1/1 O/A ratio, and 15 minutes contacting time at room temperature. The U(VI) extraction process is spontaneous and exothermic, according to thermodynamic properties. According to the McCabe-Thiele plot, uranium extraction is possible in 3 stages at O/A ratio of 1/2. while the stripping efficiency attained 90% at optimum conditions using 1M HNO<sub>3</sub> at A/O ratio of 1/1 for 15 min. Utilizing the Gaussian 09 program, molecular modeling studies were performed to investigate the ligand's equilibrium geometry (MPHPQ) and [UO<sub>2</sub>(MPHPQ)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] complex. Sulfate leach liquor of impure uranium concentrates from G. Gattar pilot plant. NMA. Egypt was used as a case study.

**Keywords:** Pyrazoloquinazolinone, U (VI), extraction, stripping, Density Functional Theory

### 1. Introduction

We fully recognize the significance of uranium in addressing the world's energy issues and the need for ongoing, vigorous research and development in the field of uranium ore processing [1]. Depending on the type of solution, the amount of uranium present, the concentration and quantity of contaminants, as well as the appropriate uranium product purity in the final stage, uranium was obtained from the starting material using challenging hydrometallurgical procedures that required numerous separation steps. These techniques include solid-liquid extraction, solvent extraction, ion exchange, and direct precipitation [2, 3].

For a very long time, liquid-liquid extraction, sometimes referred to as solvent extraction (SX) was utilized to gather and isolate metal ions from their origins. The SX process is fairly simple to use, requires a less expensive setup, and may result in

zero waste creation when contrasted to other techniques for separation and extraction like ion-exchange, adsorption, or precipitation [4]. Quinazoline is a heterocyclic molecule with nitrogen that is made up of two benzene and pyrimidine rings that have been fused together to form a six-membered simple aromatic ring. According to the position and quantity of the carbonyl group, its oxo-derivative (quinazolinone) is split into three categories: 2(1H) quinazolinones, 4(3H) quinazolinones, and 2,4(1H,3H) quinazolinone. Due to their distinctive skeleton and intriguing uses, quinazoline and quinazolinone derivatives have gained interest in the field of heterocyclic chemistry [5]. Quinazolines and their derivatives, among the most well-known groups of chemicals, exhibit a variety of pharmacological activities and some of them are regarded as common medications [6, 7]. Quinazoline and quinazolinone derivatives have been the focus of numerous studies

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in the extraction of various elements in recent years. Cu (II) ion extraction from aqueous solutions was examined using the pyrazoloquinazolinone derivatives 2-amino-3-(4-(X) phenyl azo)-8,9-dihydro-8,8-dimethyl-7H-pyrazolo [1,5-a] quinazolin-6-one (XPQ), where X = Br, Cl, OCH<sub>3</sub> or CH<sub>3</sub>. The concentrations of the investigated extractants that produced the best results were 0.04% BrPQ, 0.045% ClPQ, 0.05% OCH<sub>3</sub>PQ, and 0.055% CH<sub>3</sub>PQ when used as diluents in carbon tetrachloride. A pH of 2, a ratio of 1 O/A, and 5 minutes of contacting time at ambient temperature were found to have high extraction efficiency. BrPQ was chosen as the ideal reagent structure to extract Cu (II) species [8]. Three synthetic multidentate organic solvents were tested for their ability to extract rare earth elements from Kadabora sulfate leach liquor: 1,2-dihydro-3H-benzimidazolo [1,2-a] quinazolin-4-one (4a), 1,2-dihydro-2, 2dimethyl benzimidazolo [1,2-a] quinazolin -4(3H)-one (4b), and 3- (cyclohexane-1-on-2yl) pyrimido [1,2-a] benzimidazole (4c). Thus, under ideal conditions, 0.2% of the produced extractants (4a, 4b, and 4c) were in contact with equivalent volumes of 0.44M sulphate leach solution for 15 minutes, yielding extraction performances of 96.8%, 88.5%, and 76.3% total REE [9]. Utilizing the extractants 2-amino -3-(4- (X) phenyl azo)-8,9-dihydro-8,8-dimethyl-7H-pyrazolo[1,5-a] quinazolin-6-one (H<sub>2</sub>NXPQ)/benzene (X= Br, Cl or CH<sub>3</sub>) nickel (II) has been removed and separated from sulphate solutions. The best conditions for extracting Ni (II) ions were 2.42×10<sup>-3</sup>M (H<sub>2</sub>NXPQ)/benzene concentration, pH 2.5, and an A/O ratio of 1/1 in 10 min of contact time at room temperature. The maximum loading capabilities demonstrated that after the fourth, loading of the acidic solution, the content of nickel (II) in the organic phase remained constant. As a suitable stripping agent for Ni (II) ions, 0.5 M HCl was subsequently used to remove the loaded solvent (H<sub>2</sub>NXPQ) [10]. Applying 2-Amino-3-(4-bromophenylazo)-8,9-Dihydro-7H-pyrazolo[1,5-a] quinazolin-6-one (PQ) was tested as the extractant in the solvent extraction to separate and purify U(VI) from its uranium concentrate. At pH 1.5, (1/1) O/A, and 5 minutes of contact time at ambient temperature, an organic solution of 0.52% (PQ) in carbon tetrachloride served as the diluent to produce the highest extraction efficiency. Lastly, the sodium diuranate cake has a uranium purity of 74.3% [11].

To assess the solvent extraction of U(VI) from acidic solutions, 2-(4-chlorophenyl)- 8,9-dihydro-7H-pyrazolo [1,5-a] quinazolin-6-one (CPDHPQ) was utilized as an extracting ligand. At pH 2.5 and O/A of 2:1, the highest amount of the extracted uranium ions (90%) was attained [12].

This study is aimed to investigate the maximum extraction and stripping efficiency of uranium (VI) from sulfate leach liquor using a synthetic (MPHPQ)

diluted in chloroform. The extractant (MPHPQ) was identified using various analytical techniques. In addition, the parameters affecting the extraction and stripping efficiency were studied. Finally, the Gaussian 09 program, molecular modelling studies were performed to examine the ligand's equilibrium geometry (MPHPQ) and [UO<sub>2</sub>(MPHPQ)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] complex.

## 2. Experimental Works

### 2.1. Chemicals and Reagents

In this study, numerous chemicals were used. The main ones are piperidine and 1,3 cyclohexanedione, both of them were from Across Organics Co. in Belgium. 5-amino-1H-pyrazole and dimethyl formamide- dimethylacetal acquired from Merck Co., Germany. BDH reagents included ethanol and chloroform. In order to create the uranium standard stock solution (1000 mg/L) from uranyl acetate (obtained from Alfa Aesar), the requisite amounts of solid salt were dissolved in deionized water. Arsenazo III from SIGMA. The remainder of the chemicals were all analytical-grade and utilized exactly as they were given.

### 2.2. Analytical Procedure

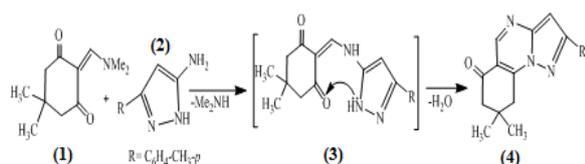
The spectrophotometric studies employing the single beam UV-VIS Metertech SP-8001 spectrophotometer can be used to determine U(VI) utilizing Arsenazo III [13]. Additionally, titrating against the ammonium meta vanadate method (known as Davies and Gray) can be used to quantify uranium [14].

### 2.3. Instrumental Analysis of The Synthesized Ligand

Analytical methods that were appropriate were used to explore and validate the characteristics of the synthesized ligand. Shimadzu FT-IR 8101 PC infrared spectrophotometers with a Pye Unicam SP 3300 were used to capture the infrared spectra on discs of potassium bromide. A Varian Mercury VXR-300 NMR spectrometer was used to obtain the NMR spectra. <sup>13</sup>C spectra were done at 75.46 MHz in deuterated chloroform (CDCl<sub>3</sub>) or dimethyl sulfoxide (DMSO-d<sub>6</sub>), whilst, <sup>1</sup>H spectra were run at 300 MHz. Chemical shifts were concerning to that of the solvent. On a Shimadzu GCMSQP 1000 EX mass spectrometer, mass spectra were obtained at a 70 eV energy level. All melting points were determined without correction using Gallenkamp melting point equipment. Using a 4100 Jasco-Japan infrared spectrophotometer, MPHPQ and U-loaded MPHPQ's FTIR spectra were captured. Elemental analyses took place at the Microanalytical Center of Cairo University. After precipitation with hydrogen peroxide, the U(VI) products underwent a quick, qualitative analysis using an environmental scanning electron microscope (ESEM), Philips XL30 in (Nuclear Materials Authority).

## 2.4. Synthesis of The Extractant (MPHPQ)

2-((dimethylamino) methylene) cyclohexane-1,3-dione 1.672g (10 mmol,) (1) was dealt with 5-amino-1H-pyrazole 0.8309g (10 mmol,) (2), for 30 min in refluxing with ethanol, with the existence of piperidine as a catalytic compound. To obtain the corresponding 2-(4-methylphenyl)-8,9-dihydro-8,8-dimethyl-7H-pyrazolo[1,5-a]quinazolin-6-one (also called 8,8-dimethyl-2-*p*-tolyl-8,9-dihydropyrazolo[1,5-a]quinazolin-6(7H)-one) (4), the solid product was filtered out using a vacuum evaporator, then re-crystallized in dimethyl formamide (DMF) after being washed with ethanol [11], 88% was found to be the yield (Scheme 1). The compound's (MPHPQ) structure was established using its elemental analysis and spectrum data. It is believed that an initial *Michael addition* of the exocyclic amino group in the amino pyrazole leads to the creation of the product (MPHPQ) [11] to the  $\alpha,\beta$ -unsaturated moiety in the enamindione (1), to produce the matching non-isolable acyclic intermediate (3), which is then cyclized and aromatized to produce the finished product (4) (MPHPQ).



Scheme 1

## 2.5. Characterization of The Extractant (MPHPQ)

The extracts analytical specifications showed that it was operative and quickly produced in good yield (88%), having a 247 °C melting temperature (ethanol/dioxane). By using IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and MS to identify and characterize the extract structure (MPHPQ), the synthetic compound's spectral data were displayed in Table (1) and Fig. (1a,b,c).

Product	(MPHPQ)			
Formula	C <sub>19</sub> H <sub>19</sub> N <sub>3</sub> O			
Elemental analysis		C	H	N
	Calcd.	74.73	6.27	13.76%
M. Wt. (305.38)		C	H	N
	Found	74.70	6.28	13.77%
<sup>1</sup> H NMR (DMSO-d <sub>6</sub> )	δ 1.00 (s, 6H, 2CH <sub>3</sub> ), 1.15 (s, 3H, CH <sub>3</sub> ), 2.57 (s, 2H, CH <sub>2</sub> ), 3.41 (s, 2H, CH <sub>2</sub> ), 6.88 (s, 1H, CH), 7.26-8.56 (m, 4H, ArH), 8.79 (s, 1H, CH).			
<sup>13</sup> C NMR (DMSO-d <sub>6</sub> )	δ 21.3, 28.2, 28.2 (3CH <sub>3</sub> ), 34.9 (C), 47.6, 52.6 (2CH <sub>2</sub> ), 92.5 (CH), 119.5 (C), 125.7, 125.7, 129.5, 129.5 (4CH-Ar), 130.0, 131.7 (2C-Ar), 149.4, 155.6 (2C), 156.5 (CH), 172.4 (C), 196.8 (C=O).			
FT-IR (KBr) ν <sub>max</sub> / cm <sup>-1</sup>	1678 (C=O), 1600 (C=N), 1593 (C=N).			
MS (m/z)	305 (M <sup>+</sup> ), 249, 53.			

Table (1): Chemical structure and characterization of synthesized (MPHPQ)

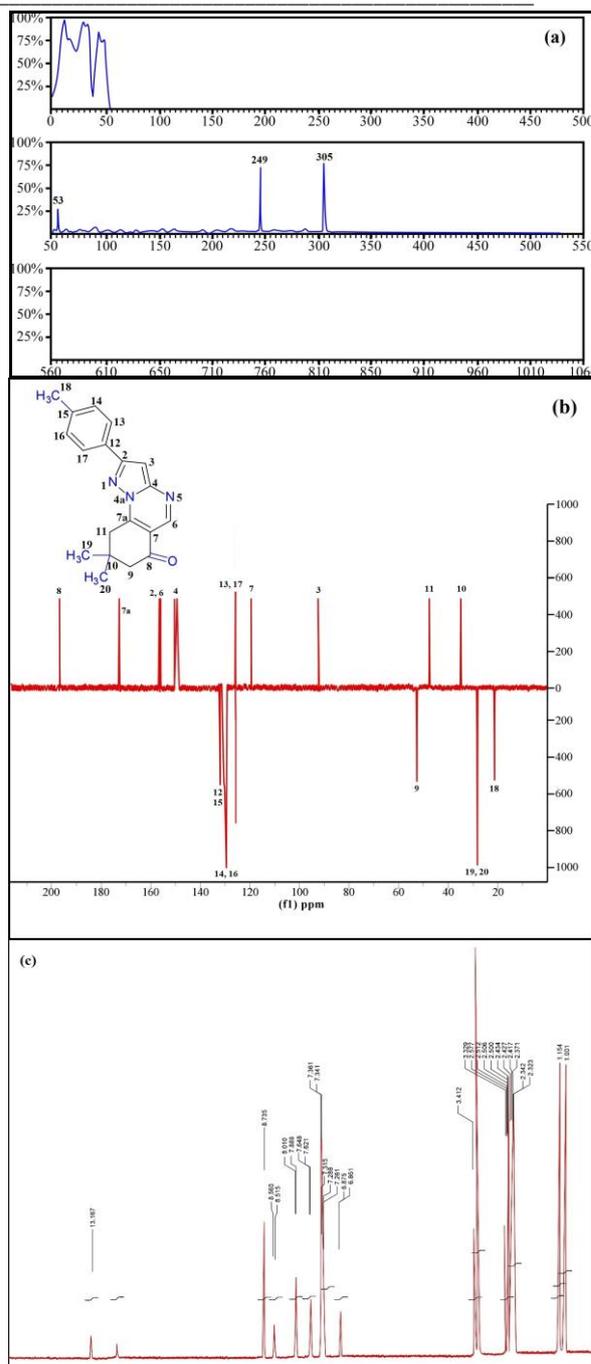


Figure (1): Chemical structure and characterization of synthesized (MPHPQ) a) Mass spectroscopy, (b) <sup>13</sup>C NMR, (c) <sup>1</sup>H NMR

## 2.6. Extraction Experiments

The organic solution 2-(4-methylphenyl)-8,9-dihydro-8,8-dimethyl-7H-pyrazolo[1,5-a]quinazolin-6-one (MPHPQ) that was used as the extracting agent in the batch solvent extraction studies was first dissolved in a chloroform solution before being in contact with the ready-made standard solution of U(VI) ions. Employing a separating funnel, phase separation was performed after equilibration, as well

as using the mass balance differential to calculate the quantity of uranium in the organic phase. The produced extractant was used to evaluate factors impacting the extraction and stripping efficiency of U(VI) ions. It required consideration of the diluents' type, pH of the aqueous solution, U(VI) initial concentration, solvent concentration, contact time, and temperature.

### 3. Results and Discussion

#### 3.1. Extraction Experiments

##### 3.1.1. Effect of Diluents Type

Different kinds of organic diluents have been used in the extraction studies to dissolve the extractant (MPHPQ), among them are benzene, toluene, o-xylene (used as an aromatic diluent), kerosene, chloroform, methylene chloride, and carbon tetra chloride (as aliphatic diluents). The aromatic diluents were excluded since the extractant did not clearly dissolve in them, possibly due to the steric hindrance of their aromatic rings. More so than the aromatic diluents, the extractant visibly dispersed in chloroform, methylene chloride, and carbon tetra chloride. Chloroform was chosen as the diluent in this investigation because it performed greater phase separation, had a shorter equilibrium time, was more readily available, was less poisonous, and was less expensive than methylene chloride and carbon tetra chloride.

##### 3.1.2. Effect of pH

The solution's pH significantly affects the extractant's affinity for uranyl ions. The separation of U(VI) from an aqueous sulfate medium was examined in the pH range from 1 to 5 using 0.08M MPHPQ in chloroform, a 1/1 O/A ratio, and a 50 mg/L uranium concentration at room temperature for 15 min equilibration time. Due to the effect of pH on the settlement of the compounds in the aqueous medium, the extraction of U(VI) reached a maximum of 87.8% at pH 4, as evidenced by the data in Fig. (2a). Where both the metal ion and the extraction are impacted by the pH of the solution [15]. The metal will eventually hydrolyse if the pH is raised above 4, and it will not be extracted. While a pH of less than 4 may cause non-extractable metal species to develop due to complexation with aqueous phase constituents [16]. This happens as a result to the equilibrium between  $\text{SO}_4^{2-}$ ,  $\text{HSO}_4^-$  and  $\text{H}_2\text{SO}_4$ , causes metal complexes to form with these anions as a result. Additionally, at pH values lower than 4, hydrogen ion concentrations will rise and may fiercely compete with  $\text{UO}_2^{2+}$  for extraction sites. Since uranium hydroxides precipitate at pH 5 and above, extraction tests were not tested above that level; pH 4 was therefore preferred for all extraction experiments.

##### 3.1.3. Effect of U(VI) Initial Concentration

The evaluation of the best uranium concentration was investigated due to the dependence of extraction

capacity on it. Different concentrations of uranium (from 50 mg/L to 1000 mg/L) in aqueous solution were using at 0.08M MPHPQ, an O/A ratio of 1/1, at room temperature for 15 min equilibration time. The ability of extractant to load with U(VI) is too large (as presented in Fig.(2b)) which increase with increasing uranium initial concentration which attains to 92% extraction efficiency at 800 mg/L U(VI) concentration due to the availability of free active sites, after 800 mg/L there is no significant increasing may be because of the saturation of extractant and reaching its maximum loading capacity. For that, 800 mg/L U(VI) was chosen as the optimum initial concentration.

##### 3.1.4. Effect of (MPHPQ) Concentration

In order to examine the extraction of 800 mg/L U(VI) ions, the concentration of the synthesized MPHPQ/ $\text{CHCl}_3$  was varied between 0.02 M and 0.1 M with an O/A ratio of 1/1 at 298 K room temperature for 15 min of equilibration period. Because there are more bonding sites available in the extractant for the extraction process, it is evident from the findings obtained and presented in Fig. (2c) that the extraction efficiency of U(VI) ions increases directly with extractant concentration up to 0.08M with extraction efficiency of 92%. There is a decrease in the extraction percentage of U(VI) despite further increases in extractant concentration. This is due to the physiochemical changes in the extractant behaviour. The creation of dimers or trimmers between the extractant molecules by raising their concentration may be the cause of the decrease in extractant affinity for U(VI). This higher Van der Waals attraction between them, combined operating together with the disturbance of the extractant's electronic structure, may also be the cause of the reduced number of extractant binding sites, which limits the effectiveness of extraction [17]. Also, high concentrations of extractant may raise the viscosity of the organic phase and even result in the formation of molecular aggregates that cause a decrease in the mass transfer of U(VI) from aqueous to organic which decrease the extraction efficiency [18]. So, the extraction concentration of 0.08M was chosen as the optimum concentration. The linear relationship between  $\log [\text{MPHPQ}]$  and  $\log D$  depicted in Fig. (1c, inserted), showed a straight line ( $R^2 = 0.9293$ , slope = 2.06) confirms that two moles of MPHPQ are associated with each extracting U(VI) ion in the extracted species.

##### 3.1.5. Effect of Contact Time

A sequence of experiments was conducted to examine the impact of equilibration time from 5 to 25 min. Using 0.08M MPHPQ in  $\text{CHCl}_3$ , an O/A ratio of 1/1 at ambient temperature with 800 mg/L U(VI) ions, and pH 4. According to the findings in Fig. (2d), the extraction efficiency of U(VI) was steadily enhanced from 21% to 92% time increases from 5

min to 15 min, which is related to the large initial concentration gradient between the solution containing U(VI) ions and the active sites of MPHPQ. Further increases have no effect upon extraction efficiency and reach the plateau, due to the decrease in the concentration of both the U(VI) ions and the extractant active groups and reaching saturation, therefore, the appropriate extraction equilibrium was reached in just 15 min. Which is chosen as the proper time for the extraction process. This was a short time for the highest extraction which confirms that MPHPQ was kinetically faster in the extraction of U(VI).

### 3.1.6. Effect of Temperature

The extraction effectiveness of U(VI) ions was investigated at various temperatures ranging from 298 and 323 K. The other conditions were fixed at 0.08M MPHPQ diluted in  $\text{CHCl}_3$ , an O/A ratio of 1/1, pH 4 using 800 mg/L U(VI) concentration and 15 min contact time. The obtained results displayed in Fig. (2e, inserted) indicate that the extraction efficiency of uranium decreases from 92% to 13.92% as temperature increases from 298 K to 323 K, this is due to the decrease in the stability of complex formed between the extractant and U(VI) ions by raising the temperature [17]. Hence, 298 K is chosen as best temperature.

The thermodynamic values derived from the subsequent equations could be used to analyze the influence of temperature on the complex extraction:

$$\text{Log } D = \frac{-\Delta H}{2.303 RT} + C \quad (1)$$

$$\Delta G = -2.303RT \log D \quad (2)$$

$$\Delta G = \Delta H - T\Delta S \quad (3)$$

Where D is the distribution coefficient,  $\Delta H$  the extraction reaction's enthalpy change, R stands for the universal gas constant (8.314 J/mol K) and C is the integration constant, which also involves the extraction reaction's equilibrium constant. Using equations (2) and (3), respectively, these values were utilized to determine the associated free energy ( $\Delta G$ ) and entropy changes ( $\Delta S$ ). From eq. (1), an evaluation is made of the related enthalpy variation ( $\Delta H$ ). Via using eq.(2), the free energy (G) is determined, at standard state 298K. Additionally, by using eq. (3), the entropy variations ( $\Delta S$ ) were provided. From Table (2) and Fig.(1e), the determined values of,  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  were found to be equivalent to -6048.19 kJ/mol, -78.05 kJ/mol. and 20.034 J/mol K; respectively. The exothermic character of the extraction process is indicated by the negative  $\Delta H$  results calculated for the complex forming; the liquid-liquid interface during the extraction process indicates that the extraction process is more random, whereas the positive value of  $\Delta S$  recommends increasing the system

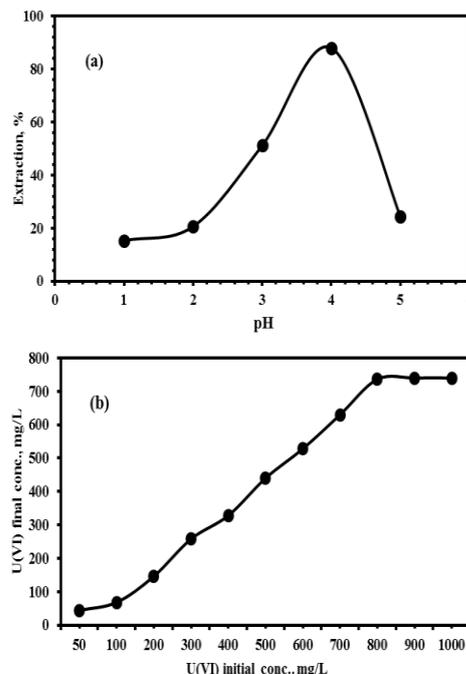
randomization which imply that a small amount of  $\text{H}_2\text{O}$  molecules have been lost from the primary coordination orbital of  $\text{UO}_2^{2+}$  [19]. The spontaneous character of the extraction process and its greater efficiency at low temperatures are indicated by the negative value of  $\Delta G$ , which decreases with increasing temperature.

Table 2: Thermodynamic parameters of U(VI) ions extraction

$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta S$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$\Delta G$ (kJ mol <sup>-1</sup> )				$R^2$
		298K	303K	313K	323K	
-78.05	20.034	-6048.19	-3306.90	-359.58	2102.7 4	0.941 3

### 3.1.7. Effect of Organic / Aqueous Phase Ratio and The Construction of McCabe-Thiele Diagram

The effect of organic to aqueous phase ratio O/A has been investigated in the range from 1/4 up to 2/1 on U(VI) extraction efficiency at 0.08 M MPHPQ concentration diluted in  $\text{CHCl}_3$ , using 800 mg/L U(VI) concentration, pH 4 at 298 K temperature and 15 min. contact time. According to the results shown in Fig. (2f), the variation of O/A from 1/4 to 2/1 lead to increase extraction efficiency of U(VI) from 32.4 % to 100 %. To estimate how many theoretical steps would be required to attain the maximum separation of U(VI); the McCabe-Thiele has been constructed by contacting organic phase to aqueous phase at a different O/A ratio varying from 1/4 to 4/1. Fig.(3) proves that the loaded U(VI) in the organic phase attained to 1.8 g/L and 3 stages required with a 1/2 O/A ratio lead to depletion in aqueous phase at which U(VI) concentration equal 0.0 g/L.



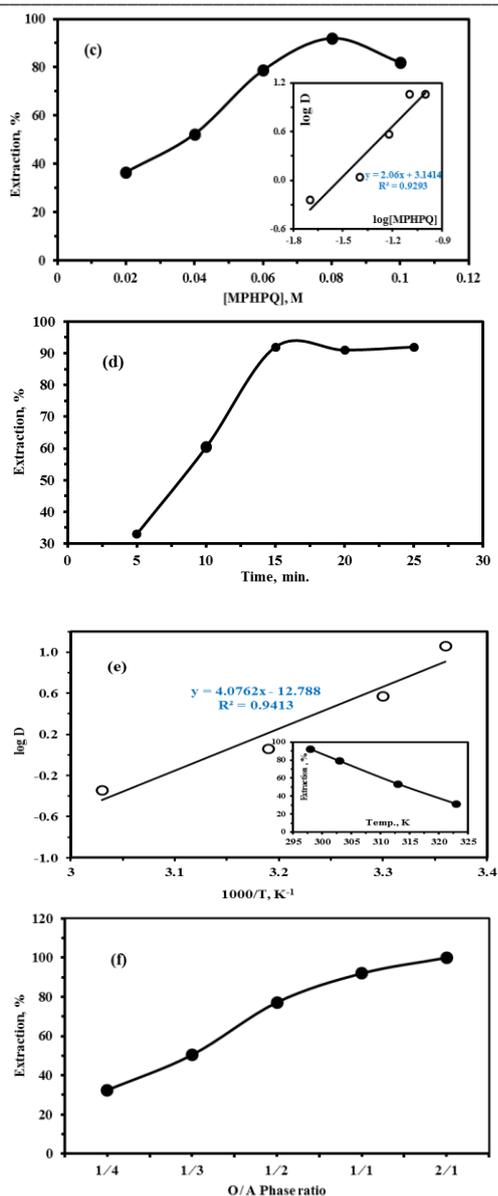


Figure (2): Factors affecting the extraction efficiency of U(VI): (a) pH, (b) U(VI) initial concentration, (c) (MPHPQ) concentration, (d) Contact Time, (e) Temperature and (f) Organic / Aqueous phase ratio.

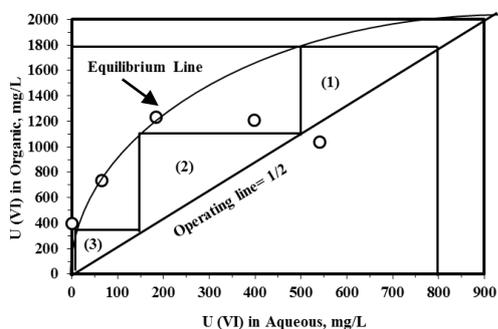


Figure (3): McCabe-Thiele diagram for U(VI) extraction

### 3.2. Stripping Experiments

To improve the economic value of the extraction process, the stripping method was examined. The stripping procedure is the opposite of the extraction procedure; it aids in rejuvenating the used extractant so that it can once more be used to extract uranium ions. It is also feasible to learn more about the mechanism of uranium uptake and the reusability of the extractant by doing stripping experiments. The numerous factors that must be taken into account in order to obtain the best stripping efficiency that is now achievable given the economic climate. The factors under consideration are the effects of various stripping agents (acidic, alkaline, and neutral stripping agents), the concentration of stripping agent, the implications of equilibration time, the impacts of the aqueous/organic phase ratio, and the development of the McCabe-Thiele diagram of the stripping process. In order to confirm the stripping procedure, a stock loaded organic solvent was preparing using the previous optimum extraction conditions of 0.08M MPHPQ diluted in  $CHCl_3$  concentration, O/A ratio of 1/1, pH 4, 15 min contact time and 298 K temperature result in loaded organic phase with 736 mg/L of U(VI).

#### 3.2.1. Determination of Proper Stripping Agent

The removal of U(VI) from the organic phase has been investigated using a variety of stripping agents, including sodium hydroxide (NaOH), potassium hydroxide (KOH), ammonium hydroxide ( $NH_4OH$ ), sodium carbonate ( $Na_2CO_3$ ), hydrochloric acid (HCl), sulphuric acid ( $H_2SO_4$ ), and nitric acid ( $HNO_3$ ), all of which have a concentration of 0.5 M. The findings, which are displayed in Fig. (4a), show that nitric acid had the maximum effectiveness for removing U(VI) ions from the loaded extractant.

#### 3.2.2. Effect of Nitric Acid Concentration

To study this effect upon U(VI) stripping efficiency, various  $HNO_3$  concentrations between 0.5 and 5 M was employed in this regard with 15 min. contact time and A/O ratio of 1/1. It clear from results obtained in Fig (4b) that the stripping efficiency increases from 57.6% to 90% by increasing the concentration of nitric acid from 0.5M to 1M, with further increasing nitric acid concentration, there is no significant changes in stripping efficiency, so 1M was chosen as the best conditions.

#### 3.2.3. Effect of Contact Time

The effect of contact time upon U(VI) stripping efficiency was studied by contacting equal volumes of both aqueous and loaded organic phases at intervals between 5 and 20 minutes the maximal stripping efficiency 90% was attained after 15 minutes of contact time, as shown in Fig.(4c). Thus 15 min. is the best stripping calibration period.

### 3.2.4. Effect of A/O Ratio and Construction of Stripping Isotherm

To investigate the effect of the A/O ratio upon U(VI) stripping efficiency, several experiments were carried out by varying A/O from 1/4 to 4/1 using 1 M HNO<sub>3</sub> for 15 min. contact time. The obtained results shown in Fig.(4d) illustrate that the stripping efficiency increases from 35.5 % to 100 % by varying A/O ratio from 1/4 to 4/1. The number of theoretical stages required for complete U(VI) stripping was obtained through the construction of the McCabe – Thiele diagram by contacting the aqueous solution with the loaded organic phase at different A/O ratios varying from 1/4 to 4/1. The results shown in Fig.(5) reveal that 2 stripping stages with a unity A/O phase ratio will leave about 1.18 g/l in the stripping. The McCabe-Thiele plot results indicate that 2 stripping stages with a unity A/O phase ratio will leave about 1.18 g/l in the stripping solution. The McCabe-Thiele plot results indicate that 2 stripping stages with a unity A/O phase ratio will leave about 1.18 g/l in the stripping solution.

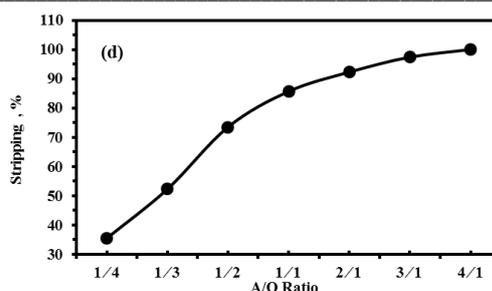
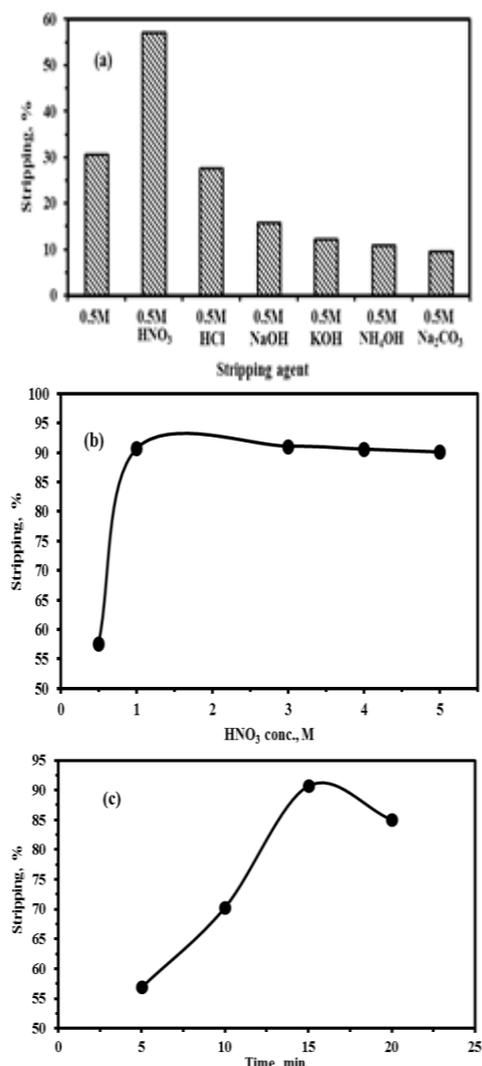


Figure (4): Factors affecting the stripping efficiency of U(VI): (a) Stripping reagent, (b) strip.reagent concentration, (c) Contact Time and (d) Aqueous/Organic phase ratio.

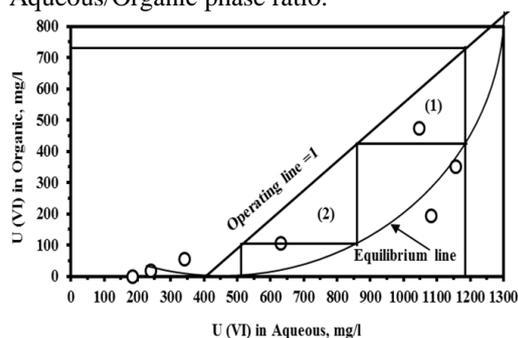


Figure (5): McCabe-Thiele diagram for U(VI) stripping

Table (3) provides a summary of all the information gathered from the extraction and stripping tests.

Table (3): Optimum conditions for U(VI) Extraction and Stripping processes

Process	Parameters				
	Reagent	O/A ratio	Temperature	Contacting time	Efficiency, %
Extraction	0.08M MPHPQ/CHCl <sub>3</sub>	1/1	25°C	15 min.	92%
Stripping	1M HNO <sub>3</sub>	1/1	25°C	15 min	90%

### 3.3. Regeneration and Recycling Capacity of Extractant

The extraction agent was initially loaded with an aqueous phase containing 800 mg/L U(VI) to conduct tests on the recycling capability of 0.08M MPHPQ/CHCl<sub>3</sub> for the extraction of U(VI). Loaded MPHPQ/CHCl<sub>3</sub> with 736 mg/L ions is the result of the first stage of extraction. With an efficiency of 92%, this loaded MPHPQ/CHCl<sub>3</sub> was stripped with 1 M HNO<sub>3</sub>. Then, extraction was carried out using the regenerating organic phase (MPHPQ/CHCl<sub>3</sub>). According to the observations, there was essentially no change in the extractant's extraction and stripping efficiency over the course of the seven extractions and stripping cycles.

### 3.4. FTIR Analysis

The MPHPQ's U(VI) extraction procedure was clarified using FTIR spectroscopy; Fig. (6A,B) depicts the ligand spectra prior to and following uranium extraction. Evidently, after the extraction investigations, the sharp intensity of a number of

characteristic peaks reflecting the major groups of the studied ligand has altered to a moderate intensity, including the C-H(stretch), -CH<sub>3</sub>, -CH<sub>2</sub>-((bend), -C=O, -C=N, and -C=C groups. This indicates that the extractant under study can interact with the U(VI) metal ions in the sulphate solution to form a complex. Three distinct bands are therefore seen at approximately 3396 cm<sup>-1</sup>, 2924 cm<sup>-1</sup>, and 2856 cm<sup>-1</sup>, which are attributed to the anti-symmetric and symmetric stretch vibrational absorption of CH<sub>3</sub>, CH<sub>2</sub>, and CH, respectively [20,21,22]. The bands at 1631 cm<sup>-1</sup> related to C=N and 1459 cm<sup>-1</sup> related to C=C groups, whereas the bands at 1729 cm<sup>-1</sup> and 1727 cm<sup>-1</sup> ascribed to C=O stretching frequencies. The bands at 1376 cm<sup>-1</sup> that correlate to the vibrational frequency of the benzene ring [23]. At 1100 cm<sup>-1</sup>, a distinctive peak of UO<sub>2</sub><sup>2+</sup> has been clearly seen.

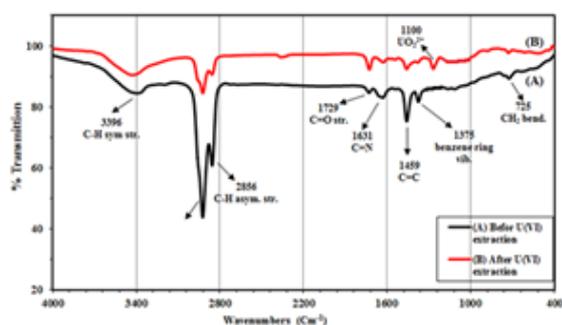


Figure (6): FTIR spectrum of MPHPQ before (A) and after (B) uranium loading

### 3.5. Molecular DFT Calculations

Density Functional Theory (DFT) have been applied to examine the ligand's equilibrium geometry (L) and [UO<sub>2</sub>(L)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] complex at the B3LYP/6-311G+(d,p) for all atoms and B3LYP/SDD level of theory for uranium using Gaussian 09 program.

#### 3.5.1. Molecular DFT Calculation of Ligand

Fig.(7), displays the optimal structure of the ligand as the lowest energy and more stable configuration. The charges obtained from Natural Bond Orbital Analysis (NBO) show that the more negative active sites are in order O1 (-0.579) > N2 (-0.490) > N3 (-0.347) > N1 (-0.227). The UO<sub>2</sub><sup>2+</sup> ions prefer to coordination to two O1 atoms from two ligands and two water molecules to complete the octahedral configuration.

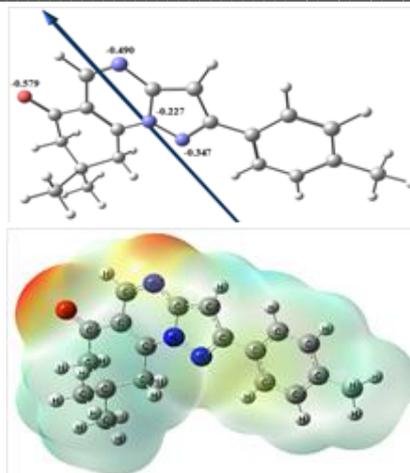
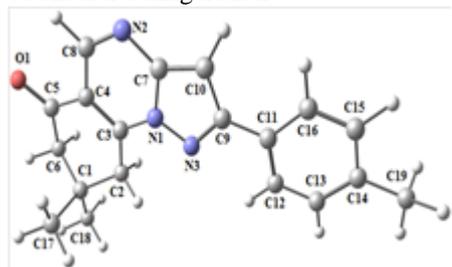


Figure (7): The optimized structure, the vector of the dipole moment, the natural charges on active centres and Molecular electrostatic potential (MEP) surface of L

#### 3.5.2. Molecular DFT Calculation of [UO<sub>2</sub>(L)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] Complex

Fig.(8), shows the optimized octahedral structure of [UO<sub>2</sub>(L)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] complex as the lowest energy configurations. The angles in the octahedral structure are all close to 90°. Moreover, the angles of the three perpendicular axis: O2=U=O3, O1-U-O4 and O5-U-O6 are 180.0°, 180.0° and 179.7°; respectively, showing linearity. This was confirmed by dihedral angles O1-O2-O4-O3, O1-O5-O4-O6 and O2-O5-O3-O6 are close to 0° indicating planar planes, Table (4). The distance between C5-O1 involved in the coordination is elongated upon complex formation from 1.255Å (in free ligand) to 1.310 Å (in the complex). The calculated natural charges from the NBO-analysis on the atoms that are coordinated are U (+1.405), O1 (-0.617), O2 (-0.611), O3 (-0.611), O4 (-0.617), O5 (-0.902) and O6 (-0.902).

Table (4): Important optimized bond lengths (Å) and bond angles (°) of the complex.

Type of bond	Bond length (Å)	Type of bond	Bond length (Å)
U=O2	1.825	U-O4	2.244
U=O3	1.825	U-O5	2.499
U-O1	2.244	U-O6	2.499
Type of Angle	Angle (°)	Type of Angle	Angle (°)
O1-U=O2	89.99	O4-U=O2	90.01
O1-U=O3	90.01	O4-U=O3	89.99
O5-U=O1	90.76	O6-U=O1	89.23
O5-U=O4	89.24	O6-U=O4	90.77
O5-U=O2	89.82	O6-U=O2	89.88
O5-U=O3	90.19	O6-U=O3	90.12
O2=U=O3	180.0	O1-O2-O4-O3	0.004*
O1-U-O4	180.0	O1-O5-O4-O6	0.237*
O5-U-O6	179.7	O2-O5-O3-O6	-0.006*

\*dihedral angle

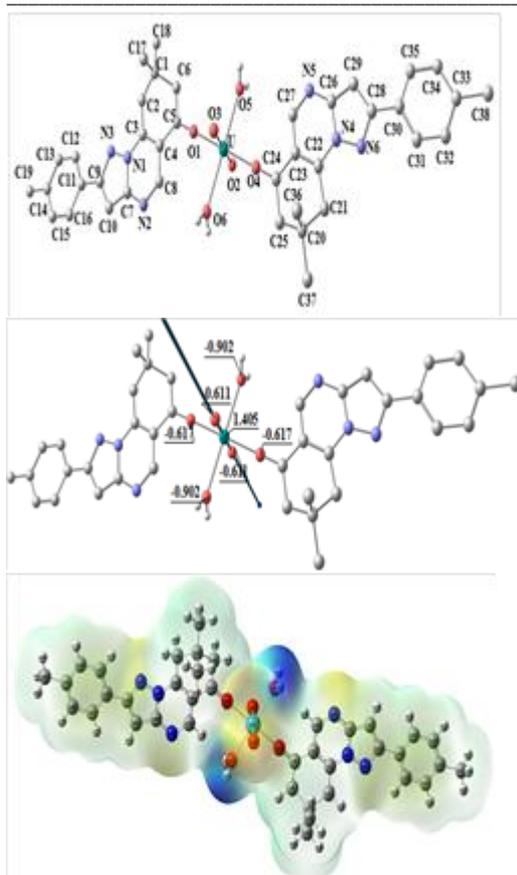


Figure (8): The optimized structure, the charges on active centres, the vector of the dipole moment and Molecular electrostatic potential (MEP) surface of [UO<sub>2</sub>(L)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] complex

The calculated total energy, HOMO (the highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energies, and the dipole moment for the ligand and complexes were listed in Table (5). The complexes have larger negative total energy values than unbound ligands, suggesting that they are more stable. Also, because of ligand chelation of metal ions, the energy gap ( $E_g$ ) =  $E_{LUMO} - E_{HOMO}$  in complexes is less than that of ligand. The charge distribution is concentrated around U atom the complex in Homo and away from the U atom in LUMO, which indicates charge transfer from ligand to metal in complex in the low energy Homo configuration, Fig. (9).

Table (5). Calculated energies of ligand (L) and [UO<sub>2</sub>(L)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] complex

	$E^a$	HOMO <sup>b</sup>	LUMO <sup>c</sup>	$E_g^d$	Dipole moment <sup>e</sup>
L	974.79	-6.268	-2.231	4.037	5.141
[UO <sub>2</sub> (L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	2730.14	-3.179	-2.470	0.709	0.274

<sup>a</sup> $E$ : the total energy (a.u.). <sup>b</sup>HOMO: highest occupied molecular orbital (eV). <sup>c</sup>LUMO: lowest unoccupied molecular orbital (eV). <sup>d</sup> $E_g$ : the energy gap =  $E_{LUMO} - E_{HOMO}$  (eV). <sup>e</sup>dipole moment (Debye).

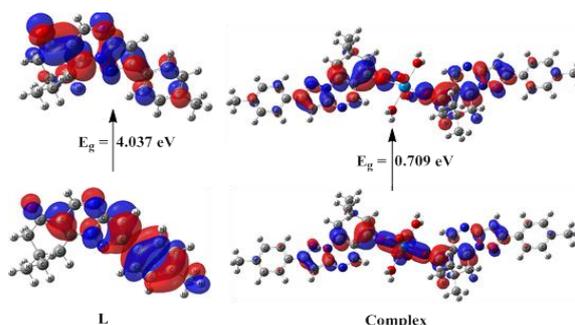
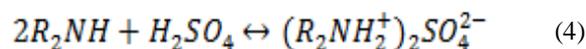


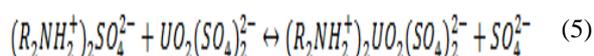
Figure (9): HOMO and LUMO of L and [UO<sub>2</sub>(L)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] complex, red color more negative and blue color more positive.

### 3.6. Reaction Mechanisms

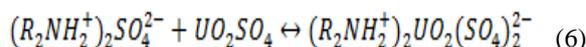
The anion-exchange mechanism of uranium sorption by amine groups has been previously reported [16], the suspected anion-exchange reactions are illustrated as follows (Eqs. 4 & 5): Protonated amine groups (-NH<sub>2</sub> and >NH), formation of ion-pairs:



Overall ion-exchange reaction:



For the sorption of neutral uranium sulfate species, a different mechanism—the so-called molecular-addition mechanism (Eq. 6)—was anticipated to work as follows:



Thus, from Fig. (10), there are different mechanisms contribution modes: where mode (I) forming coordination interaction for cation uranyl species (UO<sub>2</sub><sup>2+</sup>), mode (II) referees to anion exchange mechanism for anion uranyl sulfate species [UO<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>]<sup>2-</sup>, and mode (III) corresponding to molecular addition mechanism for neutral uranyl sulfate species [UO<sub>2</sub>(SO<sub>4</sub>)]<sup>0</sup>.

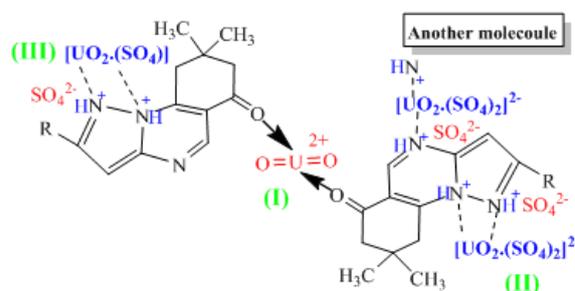


Figure (10): Different reaction mechanisms

### 3.7. Case Study

In the current research, we are examining the prospect of uranium upgrading in the impure crude uranium concentrate of G. Gattar pilot plant (Nuclear Material Authority) Egypt. By dissolving 10g of the crude concentrate in 30g/L of sulfuric acid solution, a suitable 1L sulfate solution for the upgrading technique indicated in the current work has been created. The working crude uranium concentrate was obtained by dissolving a large amount of silica and other insoluble materials, which were then removed insoluble residue and filtered and washed to produce a 1 liter clear solution [24]. Based on the foregoing, it was thought to be quite intriguing to try out a recommended technique for upgrading Gattar impure U-concentrate by properly treating it with organic solvent MPHPQ/CHCl<sub>3</sub>.

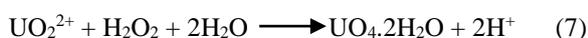
Table (6). Chemical analysis of the studied sample

Element	Wt. %	Element	Wt. %	Element	Wt. %
U	35.8000	Fe	1.2234	Sr	0.0490
Ag	0.0668	K	0.2612	V	1.5270
Al	0.0886	Mg	0.4377	Zn	0.0095
Ca	2.1222	Mn	0.0174	Ce	0.0202
Cd	0.0046	Na	4.2794	Sm	0.6708
Co	0.0086	Ni	0.0266	Tb	0.1888
Cr	0.0094	P	0.0742	Ho	0.1080
Cs	0.0320	Si	0.0120	Tm	0.1024
Cu	0.0164				

Testing was performed on the synthetic MPHPQ/CHCl<sub>3</sub> organic solvent to extract uranium from impure crude uranium concentrate, the solution was first dilute 10 times, then adjusted to pH=4; and filtering off the iron precipitated during pH adjustment. After that, the prepared aqueous phase equilibrated with the organic phase (0.08M MPHPQ) for 15 min contacting time; with O/A ratio 1/1 were all at room temperature. By adding up the loaded uranium and contrasting the extraction efficiency with the case study (~ 87.5%) in conjunction with the synthetic U(VI) sulfate solution's observed extraction efficiency (92%). The rivalry between uranium and various interfering ions or associated elements in the analysed sample may be the cause of the extraction yield of the uranium study solution decreasing from 92% to 87.5%. Uranium-loaded MPHPQ/CHCl<sub>3</sub> working sample successfully stripped using 1M HNO<sub>3</sub>, an A/O ratio of 1/1 at room temperature for 15 min contact time. U(VI) was stripped with an efficiency of 90%.

### 3.8. Precipitation of Uranium(VI)

Using hydrogen peroxide and the following equation (7), uranium was precipitated from the stripping solution:



The precipitate was then dried for 48 hours at 110-120°C, and after SEM (Scanning Electron

Microscope) analysis, it was discovered that the uranium product had a purity of 88.32%, as illustrated in Fig. (11).

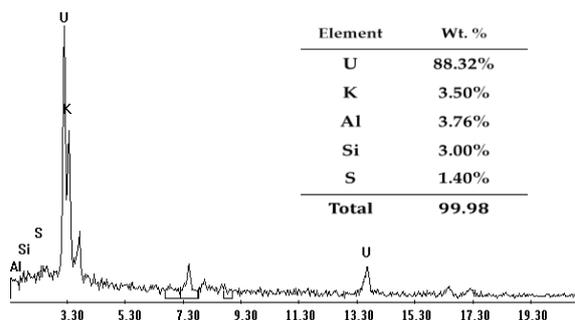


Figure (11): SEM analysis of U(VI) precipitation by H<sub>2</sub>O<sub>2</sub>

### 4. Conclusion

The current work's results showed that the synthetic MPHPQ/CHCl<sub>3</sub> organic solvent could be employed successfully to extract and remove uranium from the investigated crude yellow cake acidic solution. Multiple extraction experiments were carried out during this research to improve the U(VI) extraction under a variety of parameters, including pH, extractant concentration, O/A phase ratio, equilibration time, and temperature. The best conditions for extracting U(VI) metal ions which attained to 92 % were 0.08M MPHPQ/CHCl<sub>3</sub>, (1/1) O/A, 15 min. equilibration time at ambient temperature, and pH 4. Studies on the thermodynamics of the U(VI) extraction reaction using MPHPQ/CHCl<sub>3</sub> revealed that the reaction's ΔH was equal to (-78.05 kJ mol<sup>-1</sup>). The exothermic nature of the extraction is indicated by the negative value of ΔH, with an increase in the system's randomness shown by a positive value for entropy change ΔS (20.034J K<sup>-1</sup> mol<sup>-1</sup>). The extraction process was spontaneous, according to the negative value of ΔG. The stripping efficiency attained 90 % at the best condition of 1M HNO<sub>3</sub>, A/O ratio of 1/1 for 15 min. According to the McCabe-Thiele diagram's structure for extraction and stripping respectively, the former required 3 sages at O/A ratio 1/2 to provide 1.8 g/L loaded U(VI) in organic phase, while the later required 2 stages with a unity A/O phase ratio which leave about 1.18 g/l in the stripping solution. The interaction between uranium metal ions and the extractant would result in the complex formation between U(VI) metal ions and MPHPQ/CHCl<sub>3</sub>, as was validated by FTIR research. Finally, employing H<sub>2</sub>O<sub>2</sub> solution as the precipitating agent, the purity of the U(VI) product from the stripping nitrate solution was 88.32%, as reported. It has been demonstrated that uranium can be collected and extracted from solution using a technology that can be used again. Consequently, it may be used on a big scale.

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