

## Characterization and application of 2-(4-chlorophenyl)- 8,9-dihydro-7H-pyrazolo [1,5-a] quinazolin-6-one in solvent extraction of uranium (VI)

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### ABSTRACT

In the present study, the use of 2-(4-chlorophenyl)- 8,9-dihydro-7H-pyrazolo [1,5-a] quinazolin-6-one (CPDHPQ) as ligand was evaluated in the liquid-liquid (Water carbon tetrachloride) extraction of U(VI). Experiments were carried out to determine the factors affecting uranium extraction; These controlling factors include pH, initial uranium concentration, contact time, organic concentrations and O/A Ratio for maximum extraction for uranium metal ion by ligand, as well as extraction kinetics. The results revealed that the extraction of metal ions is dependent on the pH; maximum extraction was obtained in the pH at 2.5; the ligand CPDHPQ was effective for the extraction of U (VI). © 2014 Trade Science Inc. - INDIA

### KEYWORDS

Uranium;  
Extraction;  
Chlorophenyl dihydro pyrazolo  
quinazolinone.

### INTRODUCTION

The removal of uranium from various matrices, in addition to its continuing relevance to nuclear materials processing<sup>[1]</sup>, remains a separation of importance, not only in industrial applications but also in energy and environmental problems<sup>[2-6]</sup>. Up to now, many separation and pre-concentration techniques for metal ions have been developed, such as the liquid-liquid solvent extraction<sup>[7,8]</sup> and the solid phase extraction (SPE)<sup>[9,10]</sup>.

Liquid-liquid extraction is an efficient analytical method which is extensively utilized in the separation, pre-concentration and selective determination of analytes in solution<sup>[11,12]</sup> where the analyte is distributed between two immiscible phases. In most cases, one of these phases is an aqueous solution or a buffered solution and the second one is an organic solvent<sup>[13,14]</sup>. The simple procedure to transfer an analyte, initially dissolved in an aqueous solution, to an organic phase is by neutralizing its charge. This can be accomplished either by

forming a neutral complex or anionic couple<sup>[15,16]</sup>. In addition, the extractive separation of Ni (II) from aqueous media by 3-phenyl-4-acetyl-5-isoxazolone<sup>[17]</sup> and pyrazolones derivatives<sup>[18]</sup> was also studied. Together with nickel (II), the solvent extraction of uranium (VI) was examined with 3-methyl-4-(p-nitrobenzoyl)-5-oxophenylprazole dissolved in benzene<sup>[18]</sup>. The solvent extraction of uranium (VI) from sulfate solutions was obtained by Alamine 336 in kerosene modified with 5% w/w 1-tridecanol and stripping with a 199 g L<sup>-1</sup> Na<sub>2</sub>CO<sub>3</sub> solution<sup>[19]</sup>. Also, the mixed solvent containing DEHPA (di-2-ethylhexylphosphoric acid) and Alamine 336 was used for uranium recovery from the acidic solution<sup>[20]</sup>. Quinazolines are indeed a big family of heterocyclic compounds, which have shown broad variety of biological activity profiles<sup>[21,22]</sup> e.g. analgesic, narcotic, diuretic, antihypertensive, antimalarial, sedative, hypoglycaemic, antibiotic, antitumoral and many others. Quinazoline and its related skeletons are presented as an important class of heterocycle scaffolds occur-

ring in a large number of bioactive molecules for a variety of biological targets<sup>[23]</sup>. Two different series of N-donor pyrazole ligands were used in liquid-liquid extraction of Cu (II) ions from aqueous solution using methylene chloride as diluents<sup>[24]</sup>. Pyrazole derivatives were currently the subjects of several studies in extraction of copper (II) ions<sup>[25-29]</sup>.

In the present work, the synthesis of 2-(4-chlorophenyl)-8,9-dihydro-7H-pyrazolo [1,5-a]quinazolin-6-one was described. This ligand exhibits high complexing efficiency toward U (VI), this result from 2-(4-chlorophenyl)-8,9-dihydro-7Hpyrazolo[1,5-a]quinazolin-6-one, which considered as multi-dentate agent with many donor atoms<sup>[30]</sup>. The characterization of this ligand was carried out by elemental analysis, FT IR, NMR, Ms and <sup>13</sup>C. Also this aims to evaluate the potential use of 2-(4-chlorophenyl)-8,9-dihydro-7Hpyrazolo[1,5-a]quinazolin-6-one as ligand in the liquid liquid extraction of U (VI), as well as to determine the optimum extraction conditions (pH, O/A ratio, initial Uranium concentration, organic concentrations and contact time), kinetics of the extraction experiments and case study.

## EXPERIMENTAL

### Reagent and solutions

Several reagents were used in this study. These are mainly; 1,3-cyclohexanedione and piperidine purchased from *Across Organics Co.(Belgium)*. 5-amino-1H-pyrazole and dimethyl formamide- dimethylacetal (DMF-DMA) obtained from *Merck Co.*, Germany. Dimethyl formamide and piperidine purchased from *Aldrich Chemical Co.* Ethanol and carbon tetrachloride were BDH reagents. The uranium standard stock solution (1000 ppm) was prepared from uranium acetate by dissolving the appropriate amounts of solid salt

in de-ionized water.

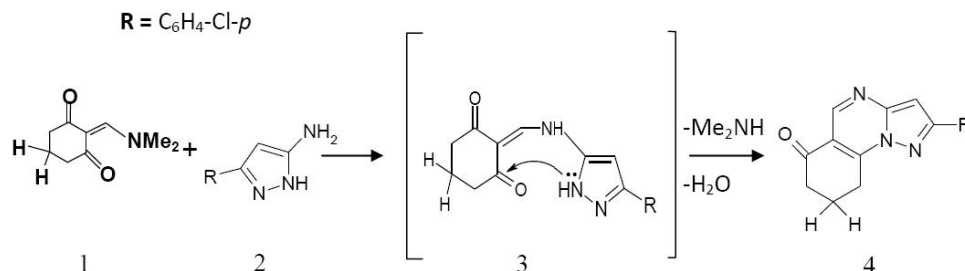
### Instrument

All melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. The infrared spectra were recorded in potassium bromide disks on a pye Unicam SP 3300 and Shimadzu FT IR 8101 PC infrared spectrophotometers. The NMR spectra were recorded on a Varian Mercury VXR-300 NMR spectrometer. <sup>1</sup>H spectra were run at 300 MHz while <sup>13</sup>C spectra were run at 75.46 MHz in deuterated chloroform (CDCl<sub>3</sub>) or dimethyl sulphoxide (DMSO-d<sub>6</sub>). Chemical shifts were related to that of the solvent. Mass spectra were recorded on a Shimadzu GCMS-QP 1000 EX mass spectrometer at 70 e.V. Elemental analyses were carried out at the Microanalytical Center of Cairo University.

### Synthesis of the extractant

To a mixture of 2-((dimethylamino) methylene) cyclohexane-1,3-dione (10mmol) (DMAMC) (1) was treated with substituted 5-amino-1H-pyrazole (10mmol) (AP) (2), in refluxing ethanol for 30 min, in the presence of catalytic amount of piperidine. The solid product was filtered off, washed with ethanol and recrystallized from proper solvent to afford the corresponding 2-(4-Chlorophenyl)-8,9-Dihydro-7H-pyrazolo[1,5-a]quinazolin-6-one<sup>[31]</sup> (4) in 90% yield, (Scheme 1). The structure of compound (CPDHPQ) established on the basis of their elemental analyses and spectral data.

The formation of the product (CPDHPQ) is assumed to take place *via* an initial *Michael* addition of the exocyclic amino group in the aminopyrazole (AP) to the  $\alpha,\beta$ -unsaturated moiety in the enamindione (1) (DMAMC), to yield the corresponding acyclic non-insoluble intermediate (3) which undergo cyclization and aromatization into the final product (4) (CPDHPQ).



Scheme 1

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### Extraction experiments

The extraction test was performed using 2-(4-Chlorophenyl)-8,9-dihydro-7H-pyrazolo [1,5a] quinazolin-6-one as extracting agent. This substance was first dissolved in carbon tetrachloride with solid to liquid ratio of about 0.1g/100 ml this solution will be marked as CPDHPQ, and then it was tested for uranium extraction from aqueous solution. The optimum extraction conditions including contact time, uranium concentrations, pH, organic concentrations and aqueous to organic ratio were experimentally investigated. About 10 ml from CPDHPQ was added to round bottom glass bottles of 50 ml capacity with 5 ml of uranium solution of desire concentration (50-1000 mg/L) and (1-5) pH range. The flasks were capped and placed

on a mechanical shaker at room temperature and the samples were taken at predetermined intervals (5-60 min), with shaking the organic phase was separated from the aqueous phase. The amount of extracted uranium was determined by complexing U (VI) with Arsenazo III<sup>[32]</sup>, where it ion measured in the organic phase by the difference between the uranium concentration in the aqueous phase before and after extraction.

### Leach liquor sample

The studied leach liquor (Case study) prepared from the processing of the geologic ore sample collected from G. El Sella area, Eastern Desert. Egypt. The chemical specification of the studied leach liquor reveals its significantly enriched in U, SO<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub> and Al (TABLE 1).

TABLE 1 : Leach liquor chemical composition

Constituents	U	Fe <sub>2</sub> O <sub>3</sub>	SO <sup>2-</sup>	Th <sup>4+</sup>	Cu	Al <sup>3+</sup>	Na <sup>+</sup>	P <sub>2</sub> O <sub>5</sub>	Ni <sup>2+</sup>
g/L	0.28	1.82	4.1	0.006	0.013	2.9	0.98	0.345	0.82

## RESULTS AND DISCUSSION

### Analysis and characterization of CPDHPQ

The analytical specification of the extractant revealed

that, it was synthesized efficiently and rapidly in good yield (90%), with melting point 231-232°C (ethanol). The structure of the complexing agent was identified and characterized by IR, NMR, Ms, NMR<sup>13</sup>C, (TABLE 2).

TABLE 2 : Chemical structure and characterization of synthesized CPDHPQ

Product	CPDHPQ
Formula	C <sub>16</sub> H <sub>12</sub> ClN <sub>3</sub> O
Elemental analysis	Calcd
	Found
<sup>1</sup> H NMR (DMSO-d <sub>6</sub> )	δ 2.27 (m, 2H, CH <sub>2</sub> ), 2.66 (t, 2H, CH <sub>2</sub> ), 3.45 (t, 2H, CH <sub>2</sub> ), 7.37 (s, 1H, CH), 7.54-8.09 (m, 4H, Ar H), 8.79 (s, 1H, CH).
MS (m/z):	297 (M <sup>+</sup> ), 275, 51.
IR (KBr) ν <sub>max</sub> /cm <sup>-1</sup>	1694 (C=O), 1655(C=N), 1605 (C=N).
NMR <sup>13</sup> C	134.3 (C-Cl), 129.3 (2CH), 128.9 (2CH), 135.1 (C), 155.6 (C=N), 92.5 (CH), 149.4 (C), 172.4 (C), 25.3 (CH <sub>2</sub> ), 21.2 (C), 38.4 (CH <sub>2</sub> ), 196.8 (C=O), 119.5 (C), 156.5(CH).

\* Analyzed in Cairo university (Micro analysis lab.).

### Extraction of uranium by CPDHPQ

The extraction experimental results are expressed in terms of pH, contact time, extraction yield (Y) as follow:

$$Y(\%) = \frac{m_i - m_f}{m_i} \times 100$$

Where m<sub>i</sub> is the initial mass of uranium in aqueous phase; m<sub>f</sub> is the mass of uranium after extraction.

### Effect of pH on uranium extraction

The effect of solution pH was investigated in the pH range of 1-5, where about 10 ml from CPDHPQ was contacted with 5 ml from uranium aqueous solution (200 ppm concentration) at room temperature for about 25 minutes, then the aqueous solution separated from the organic one and uranium concentration was measured (Figure 1).

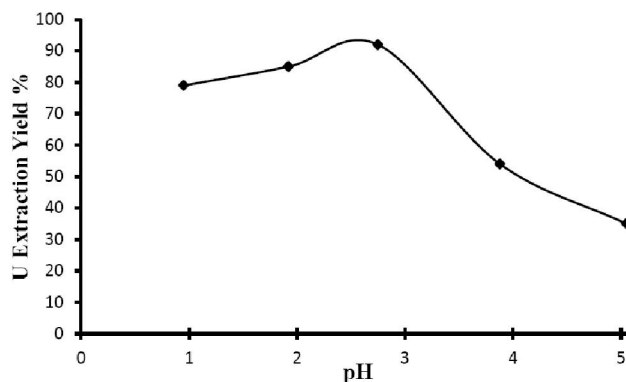


Figure 1 : Effect of pH on uranium extraction efficiency

From the obtained results (Figure 1), it is clear that the solution pH has an important role in the extraction yield, where it increases in the pH range between 1-3 attaining a maximum value at pH 2.5. Then the extraction efficiency decreased with further increase in pH. This is may be due to that the hydrolysis of uranyl ions take place as the pH varies from 1 to  $3.0 \pm 0.1$  (availability of free uranium ions). When pH increases over to  $3.0 \pm 0.1$ , uranium exist in hydrolyzed form and the following ionic species  $\text{UO}_2^{2+}[(\text{UO}_2)_2(\text{OH})_2]^{2+}$  dimer,  $[(\text{UO}_2)_3(\text{OH})_{25}]^+$  trimer. The complexes formed in aqueous solution lead to the precipitation stage<sup>[33]</sup>.

### Effect of initial uranium concentration

The dependence of the extraction capacity of CPDHPQ on the initial concentration of uranium ions [ $m_1$ ] at room temperature was represented in (Figure 2). The obtained results reveal that extraction yield increased steadily with metal ion concentration till uranium concentration of 200 mg/l. This is related to the increase in the concentration gradient, which acts as a driving force for the adsorption process, and then the increase in extraction yield becomes less significant at [ $m_1$ ] > 200 mg/L.

### Effect of O/A ratio

The effect of O/A ratio was investigated within the range from 1:1 to 5:1, the solution pH adjusted at pH 2.5 for about 25 min at room temperature and uranium concentration equal 200 ppm. The separation of aqueous solution from the organic phase and the determination of uranium concentration are illustrated in (Figure 3). From the obtained data, it is quite clear that the O/A ratio has a positive effect on uranium extraction where the maximum CPDHPQ extraction efficiency obtained

at O/A ratio 2:1 then the efficiency decrease with the increase in the ratio, so 2:1 is set to be the optimum O/A.

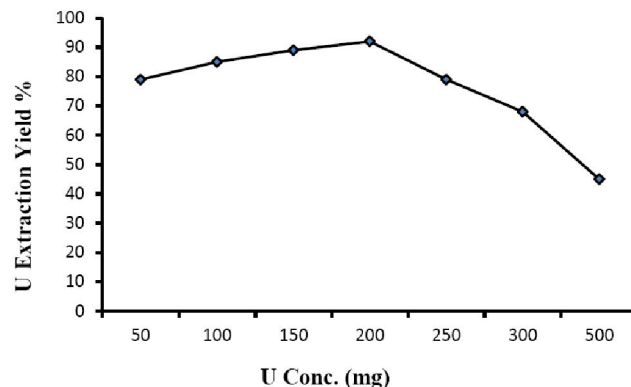


Figure 2 : Effect of initial uranium concentration on the extraction efficiency of CPDHPQ

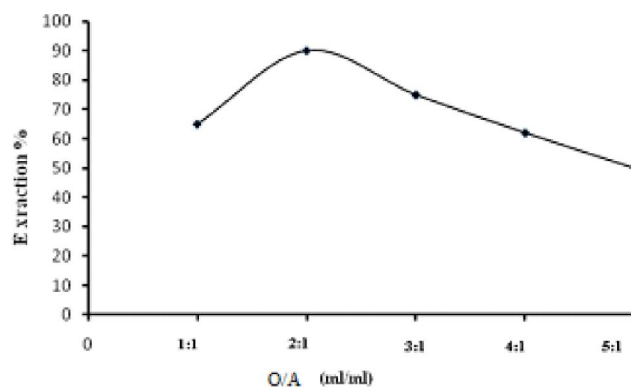


Figure 3 : Effect of O/A ratio on uranium extraction by CPDHPQ

### Effect of the extractant's concentration

To study this factor, the concentration of the synthesized extractant CPDHPQ in carbon tetrachloride was varied from 0.005% up to 0.2% whereas the other extraction conditions were fixed as an O/A ratio of 2/1, shaking time 25 min, at PH 2.5 and with working uranium concentration equal 200 ppm. From the obtained results shown in (Figure 4), it is clear that as the synthesized extractant CPDHPQ concentration increased, the extraction efficiency of the uranium gradually increased until reached 90% uranium at 0.05% concentration and above which no further extraction occurred.

In the meantime, it would be possible to determine the molar ratio of the used extractant CPDHPQ with the extracted uranium through plotting the log values of the distribution coefficient and the extractant CPDHPQ concentration. Using the obtained data, it was thus possible to obtain a straight line as shown in (Figure 5) and

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its slope attained 1.07. It can thus be inferred that the attained CPDHPQ/uranium molar ratio would be 2/1. The involved reaction can thus be visualized as follows:

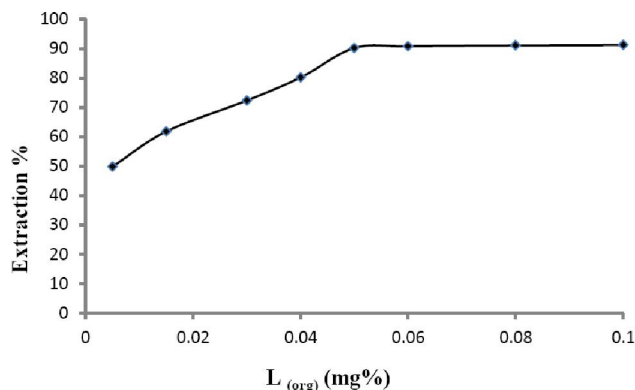


Figure 4 : Effect of the extractant's concentration (CPDHPQ)

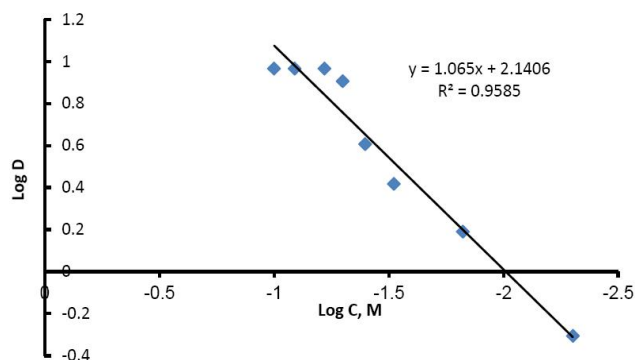


Figure 5 : Distribution coefficient of uranium (D) as a function of organic concentration in carbon tetrachloride for the used leach liquor

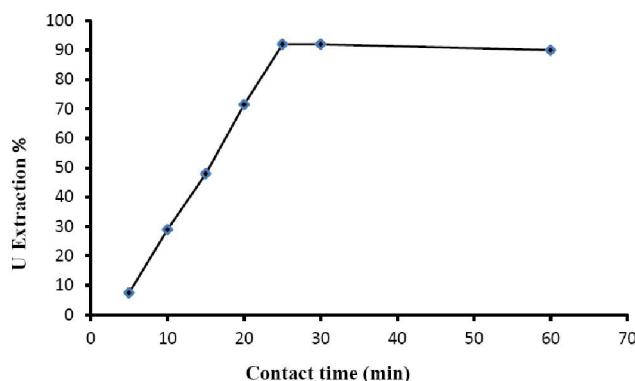


Figure 6 : Effect of contact time on uranium extraction efficiency by CPDHPQ

### Extraction kinetics of metal ions

The effect of contact time was determined in the range of 5-60 minutes. In these experiments about 10ml from 2-(4-Chlorophenyl)-8,9-dihydro-7H-pyrazolo [1,5a] quinazolin-6-one ligand contacted with 5 ml from

uranium aqueous solution (200 ppm concentration) at room temperature. The aqueous solution was then separated from the organic phase in which the uranium concentration was determined and the data were shown in (Figure 6). From the data plotted in (Figure 6), it is clear that the extraction efficiency of the metal ions using 2-(4-Chlorophenyl)-8,9-dihydro-7H-pyrazolo [1,5a] quinazolin-6-one ligand showed that the extraction efficiency of U(VI) increased till it reached equilibrium after approximately 25 minutes and then remained constant (E= 92%).

### Determination of rate constants for the extraction of metal ions

The rate constants for the extraction of metal ions were determined using equation:

$$\ln [M^{2+}]_t = k t \ln [M^{2+}]_0$$

where  $[M^{2+}]_0$  and  $[M^{2+}]_t$  represent the initial concentration and the concentration at time t of the metal ion in aqueous solution, respectively. K is the extraction rate constant.

For pseudo-first-order reactions, the plot of  $\ln [M^{2+}]_t$  vs time, results in a straight line with the slope corresponding to  $-k$ <sup>[33]</sup>. The extraction rate constants for the metal ions were calculated from the slope of the linear plots (Figure 7), the value obtained was 0.0399.

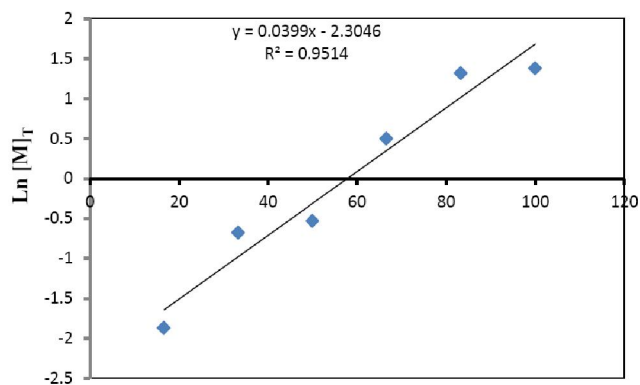


Figure 7 : Pseudo-first-order kinetic model for the extraction of metal ions

### Case study

A case study was performed to evaluate the ability of 2-(4-Chlorophenyl)- 8, 9-dihydro-7H-pyrazolo [1,5-a] quinazolin-6-one as solvent extraction of uranium (VI). The used sample was performed from Inshas Pilot Plant Unit. The uranium concentration in the sample was 0.28 g/L as mentioned in (TABLE 1).



The application of the organic compound was performed under the following conditions; pH 2.5 and at room temperature with O/A ratio of 2/1 and uranium concentration < 200 ppm (the used sample solution was diluted with distilled water and the uranium concentration was about 140 ppm). About 50 ml from the used sample contacted with 25ml from the organic solution for about 25 min, then the aqueous phase was separated and the uranium concentration was 35 ppm (aqueous phase). Then the fresh leach liquor solution contacted again with the organic phase and the uranium was determined in the aqueous phase after separation, this process was repeated three times. The uranium concentration (aqueous phase) was 60, 82 and 98 ppm respectively. The obtained result reveals that 2-(4-Chlorophenyl)-8, 9-dihydro-7H-pyrazolo [1,5-a] quinazolin-6-one has a potential ability to uranium extraction.

### Mechanism of uranium metal extraction

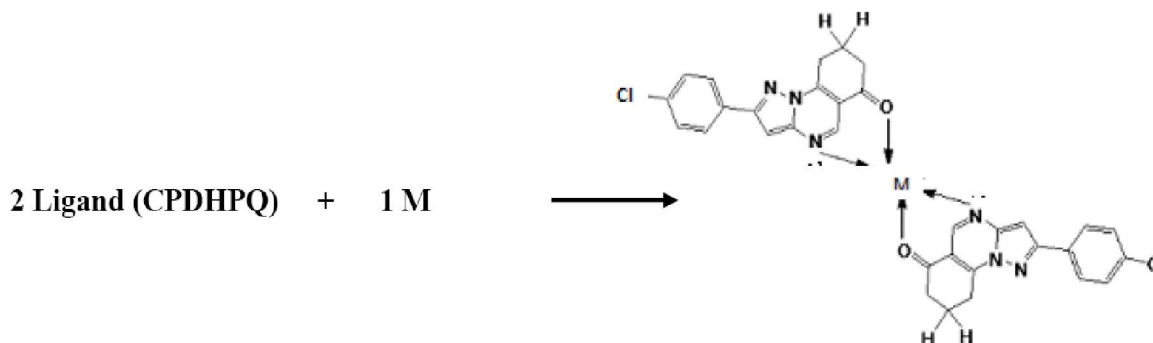
The organic phase was subjected to IR analysis and the result is presented in (TABLE 3). From the IR analysis, the mechanism of uranium extraction by 2-(4-Chlorophenyl)-8,9-dihydro-7H-pyrazolo[1,5-a]quinazolin-6-one will be discussed in the following section. This analysis included the prepared 2-(4-Chlorophenyl)-8,9-dihydro-7H-pyrazolo[1,5-a]quinazolin-6-one extractant in CCl<sub>4</sub> before U extraction freshly prepared (free-state) as well as after their extraction (loaded-extractants) as shown in (TABLE 3). From the obtained results, it has been realized that some characteristic peaks representing the major groups of the studied extractant as the aliphatic C-H, C=O and C=N groups have sharp intensity that turned to medium intensity after the extraction experiments. This

TABLE 3 : Infrared spectra of the fresh and loaded synthesized CPDHPQ extractant

Major groups	CPDHPQ	
	Extractant cm <sup>-1</sup> (vs)	After extraction cm <sup>-1</sup> (m)
Aliphatic		
C – H	2962.5	2922.38
C = O	1694.0	1735.54
C = N	1655.0	1659.02
C = N	1605.0	1608.49

vs: very strong; m: moderate

indicates that the studied extractant are able to form complexes with uranium ion in the leach liquor. Accordingly, the sharp C=N peak at 1655.0 cm<sup>-1</sup> and the C=O peak at 1694.0 cm<sup>-1</sup> present in the extractant ligand spectra decreased before extraction but increased after extraction (TABLE 3). Accordingly, the C=N peak at 1659.02 cm<sup>-1</sup> and the C=O peak at 1735.54 cm<sup>-1</sup>; a matter which is most probably due to the formation of the metal complex. It is thus possible to mention that the synthesized extractant; namely 2-(4-Chlorophenyl)-8,9-dihydro-7H-pyrazolo[1,5-a]quinazolin-6-one can be considered as multi-dentate agent with many donor atoms. The latter exhibits a good affinity toward uranium ions in the leach liquor. It can thus be cited that the U metal ion has most probably been complexed to the extractant through binding to the nitrogen and oxygen atoms in acidic media of the extraction step. It is clearly evident that the formed complex between the uranium metal and the ligand would take place by the reaction of oxygen and nitrogen atoms<sup>[34,35]</sup> in a manner to form the six membered ring which is more stable and more planar and not be steric with oxygen so producing more yield in 2-(4-Chlorophenyl)-8,9-dihydro-7H-pyrazolo[1,5-a]quinazolin-6-one complex. The mechanism can be represented as follows:



Ligand: 2-(4-Chlorophenyl)-8,9-dihydro-7H-pyrazolo[1,5-a]quinazolin-6-one; M: Uranium metal.

Scheme 2

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### CONCLUSION

As expected, the extraction of uranium from the studied sample using the extractant ligand CPDHPQ was mainly controlled by several optimized conditions. The amount of the extracted uranium ions reached a maximum value at pH 2.5 and O/A of 2.1. The suggested extraction mechanism was performed through the coordination of U metal ion to the ligand via nitrogen and oxygen atoms within the acidic media of the extraction step. Also, It is clear that the formed complex between the uranium metal and the ligand would take place by the reaction of oxygen and nitrogen atoms form the six membered ring which is more stable and more planar and not be steric with oxygen so producing more yield in pyrazolo quinazolin - 6 - one.

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