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PARAMETRIC AND THERMODINAMIC STUDY OF URANYL ION EXTRACTION BY ORGANOPHOSPHORIC RESIN

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Abstract **— This study is focused on the solid liquid extraction of uranyl ions by a solid extractant which is an phosphonated-hyperbranched material synthesized from polyethyleneimine (PEI) (Lupasol family).The effects of several parameters (contact time; pH, metal concentration, quantity of adsorbent, ionic strength, and temperature) are studied in order to determine the optimal extraction conditions.**

The kinetic study showed that for a time equal to 40min the yield reaches its maximum value 90%, this value increases for an initial value of pHi equal to 5.8. The process is in agreement with the Langmuir model and in agreement with pseudo-second order kinetics. The study of the diffusion mechanisms revealed the preponderance of the diffusion by chemical reaction, the effect of salt addition shows us that the best yield is with the addition of KSCN. For the thermodynamic results, the reaction is endothermic, the disorder increases during the extraction, and on the other hand, the sorption is spontaneous.

Key words: Extraction, Uranyl, Phosphonated hyperbranched materials, Polyethyleneimine.

I. INTRODUCTION

In this last period the accumulation of rare earths provokes an increase in the concentration of these in human beings, animals and also in the soil, because of the daily rejects of the producing industry[1]. We are interested in uranium, which is a heavy, radioactive metal, while the uranyl ion is soluble and presents greater risks of chemical toxicity, because it is easily transported to the kidneys, the most vulnerable organ in living beings[2].

Uranyl is an element that belongs to the actinide family, its separation from associated elements is coveted because of its increased demand in the nuclear industries. The industrial activities produce a variety of wastewater which contains a lot of pollutants resulting in dangerous consequences for the living being and the environment, several methods of elimination and separation of rare earths have been tested by researchers such as, membrane filtration, chemical precipitation, electrochemical treatment and solvent extraction, coagulation [3], but unfortunately these techniques require a lot of money and materials, so we are obliged to use ecologically and economically favorable methods[4], such as sorption by an organophosphorus resin functionalized based on polyethyleneimine PEI [5]. The aim of this research is to extract the maximum of uranyl ions and also carried out an experimental study to validate the performance of this extractant used by kinetic and thermodynamic aspect taking into account the operating parameters such as contact time, concenrtation, pH and temperature.

II. EXPERIMENTAL PART

A. REAGENTS

The uranyl solution is prepared at 10-2 M from Uranyl acetate $UO_2(CH_3COO)_2$, $2H_2O$ supplied by Fluka. The other solutions were prepared by dilution of the stock solution.Arsenazo III for UV-Visible analysis, hydrochloric acid (37%), nitric acid (70%), sodium hydroxide, potassium chloride, thiocyanate and cyanide are supplied by SIGMA ALDRICH.The functionalized resin is an organophosphorus polymer, produced on the basis of polyethyleneimine (Lupasol G20), commercially available from BASF.

B. APPARATUS

The extraction of Uranyl ion by organophosphorus resin « PEIP » was performed with a stirring plate (Haier model), the separation of the phases was effected by SIGMA 2-6E centrifuge. The samples containing uranyl were analyzed by spectrophotometer (Analytik Jena Specord 210 Plus) using Arzenazo as complexing agent [6]. For the PH measurements it was carried out from a PH-meter, using a combined electrode mark (Adwa). For the thermodynamic study a magnetic stirrer (RCT Basic IKAMAG Stirrer with ETS-D5 Temperature Controller) was used. Weighing was done on an electronic analytical balance (KERN ABS).

C. EXTRACTION PROCEDURE

In a batsh reactor 0.03g of the functionalized resin is mixed with 5ml of the uranyl solution at known concentrations, the separation of the resin is made by filtration, the filtrate is then

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analyzed by UV-visible spectrophotometry in the presence of Arzenazo(III) [7].

The analysis of the Uranyl ions is done by introducing a volume of 100 µL of the uranyl solution to be analyzed with 100 µL of the Arzenazo solution (10-3M) and 2mL of the buffer solution (pH =2.1), the Arzenazo (III) reacts with the Uranyl ions to give a pink complex which absorbs at a wavelength of about 665nm [8]. The removal efficiency; is the percentage of UO_2^{+2} ion absorbed on the organophosphorus is determined from the concentrations of the metal before and after extraction (equation 1).

$$R(\%) = 100 \times \frac{Ci-Cf}{Ci} \text{.....Eq 1}$$

The determination of the amount absorbed by the resin is given by the following expression (equation 2) :

$$qt\ (mg/g) = \frac{Ci-Cf}{m} \times V \text{.....Eq 2}$$

With:
C_i : the initial concentration of the Uranyl (before extraction)
C_f : the final concentration of Uranyl (after extraction)
(C_i and C_f in mol/L).
R : the extraction yield in (%).
q : the amount absorbed (mg/g).
M : the mass of the resin (g).
V : the volume of the Uranyl solution (L).

III. RESULTATS ET DISCUSSION

A. *EFFECT OF STIRRING RATE*

The speed of agitation showed a medium effect on the sorption of Uranyl ions, we varied the speed of agitation from 0 to 700 rpm and found that the extraction yield is low when working without agitation, and when the speed is 100 rpm the yield is 60%, this value increases to 300 rpm has an extraction yield is 87% and at this stage it became stable. As shown in the following graph (Fig. 01).

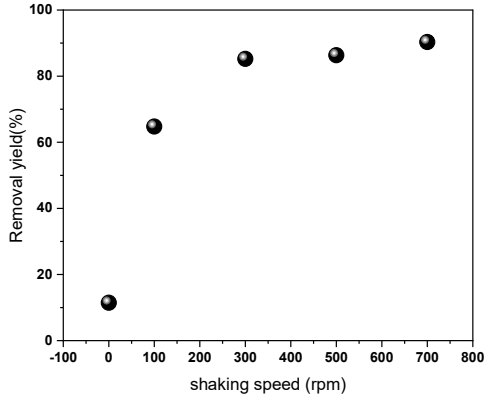

Fig.1 variation of the extraction yield according to the stirring rate.

B. *EFFECT OF CONTACT TIME*

The equilibrium time was studied by mixing the resin with two uranyl solutions for different concentrations (10^{-3}M and 5.10^{-4}M) for 180min.From Fig. 02, we can observe that the retention capacity of the UO_2^{+2}ions by the resin increases rapidly with the increase of the contact time, the equilibrium is reached about 40mn. The graph can be separated into three stages:

1st stage: the kinetics of sorption is very fast this speed is due to the concentration gradient, the availability of functional sites on the surface of the resin.
2nd stage: the kinetics of sorption becomes very slow this is due to the presence of diffusional limitations and the appearance of several mechanisms of sorption.
3rd stage: in this step the sorption reaches the equilibrium.

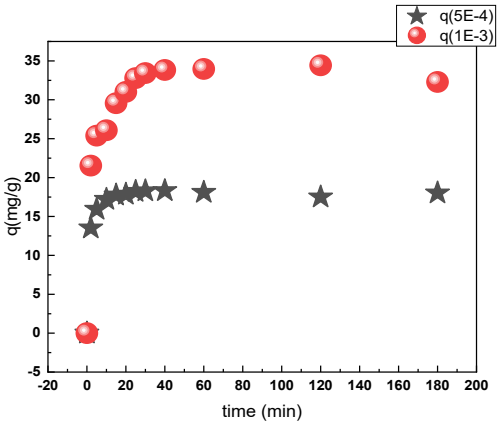

Fig.2 variation of the quantity absorbed of uranyl ions as a function of time

The sorption kinetics of UO_2^{+2}ions by organophosphorus resin is described using standard kinetic models such as the pseudo first and second order equations [9].
The linear pseudo first-order form is expressed in equation 03:

$$Ln(q_e-q_t) = \ln(q_e) - K_1 \text{ .....Eq 03}$$

The linear form of pseudo first order is given by equation 04:

$$\frac{t}{qt} = \frac{1}{K2qe^2} + \frac{t}{qe} \text{.....Eq 04}$$

qe and qt are the amounts of Uranyl adsorbed by the resin at equilibrium and time t, respectively (mg g^{-1})
k_1 is the first order adsorption rate constant (min^{-1}), k_2 is the pseudo-second order adsorption rate constant ($g.mg^{-1}min^{-1}$).

TABLE I
PRESENTATION OF THE ORDERS OF THE REACTION

Metal	Pseudo first order	Pseudo second order
Uranyl	K_1=0,168 Q_e = 6,82 R^2 = 0,962	K_2=0,087 Q_e=18,86 **R^2 = 0,997**

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Following the results obtained for a concentration of the uranyl ion equal to 5.10^{-4}M we notice that the model of the pseudo-second order is the model which represents more accurately the experimental results, which indicates that we have a chemistry-sorption.

C. *EFFECT OF PH*

The sorption of UO_2^{+2} ion by the PEIP resin has been studied at different pH values from 1 to 8. For pH values below 3.5, in a medium rich in H^+ proton, there is a competition between the metal ions and the H^+ proton, the extraction of Uranyl ions is less favorable in this range. On the other hand, in a medium with pH values between 4 and 8 (the most negative sites are increasingly available) [10], and it becomes more efficient through the formation of complexes and also because of the electrostatic attraction between the metal and the active sites of the resin.

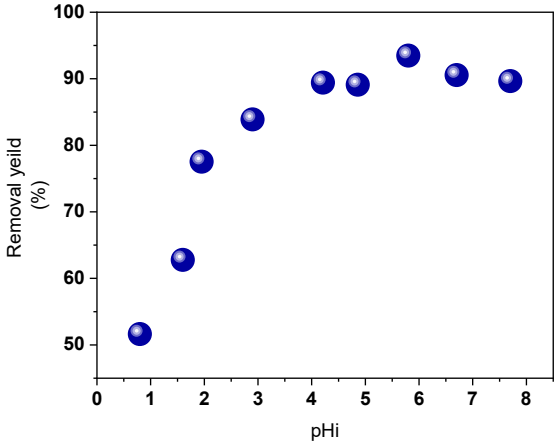

Fig.3 variation of the yield according to the initial pH.

D. *EFFECT OF TEMPERATURE*

The determination of the thermodynamic parameters requires a complete study on the effect of temperature.

This effect is carried out by mixing 0.03g of the resin with 5mL of the Uranyl solution, of concentration 5.10^{-4}M during an equilibrium time which is 40min, by varying the temperature from 12°C to about 50°C. Fig. 04 shows the variation of the extraction yield as a function of temperature.

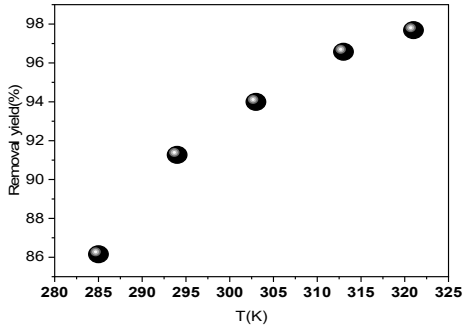

Fig.4 : Variation of extraction efficiency as a function of temperature.

Thermodynamic parameters such as free energy change (ΔG), enthalpy changes (ΔH) and entropy (ΔS) are calculated using the following equations[11]:

$$\Delta G° = \Delta H° - T\Delta S° \quad \text{.....Eq 05}$$

$$\Delta G° = -RT \ln (D) \quad \text{.....Eq 06}$$

$$\ln(D) = -\frac{\Delta H°}{R} \times \frac{1}{T} + \frac{\Delta S°}{R} \quad \text{.....Eq 07}$$

R : the constant of gas (8.314 J/K mol)
T : the absolute temperature (K°)

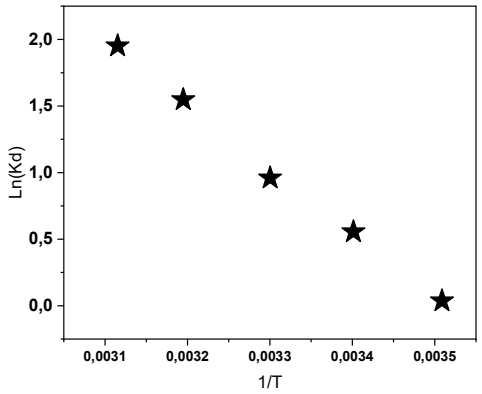

Fig.5 :variation of Ln(Kd) as a function of (1/T).

TABLE II
PRESENTATION OF THERMODYNAMIC RESULTS

T	Kd (l/g)	ΔG (KJ.mol^{-1})	ΔH (kJ/mol)	ΔS (kJ/mol)
285	1,036	-76,54		
294	1,741	-80,23	40,31	0,41
303	2,609	-83,92		
313	4,699	-88,02		
321	7,039	-91,3		

The table II presents the thermodynamic results, we can clearly see that the variation of enthalpy ΔH is positive which indicates that the reaction is endothermic, even for the entropy is positive which shows that the disorder increases during the extraction, on the other hand the free enthalpy is negative this means that the sorption is spontaneous on the other hand, ΔG decreases the sorption of Uranyl ions by PEIP is favored at higher temperatures [12].

E. *EFFECT OF SALT*

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To study the effect of salt several salts (of sodium, potassium, cyanide, nitrate ...) were added to the aqueous phase of the same concentration (1mol/L).
Fig. 06 shows the efficiency of sorption of Uranyl ion with various salts in aqueous solution.

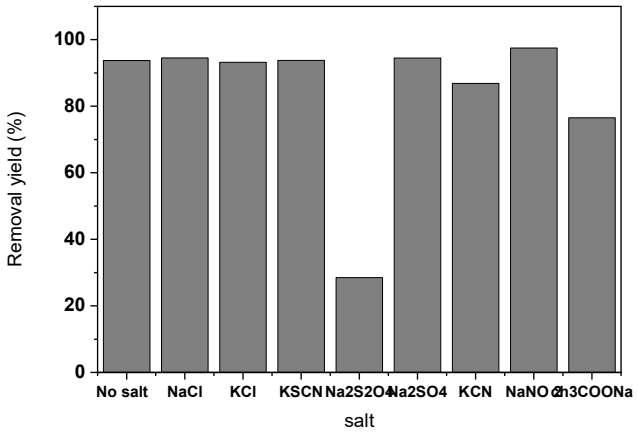

Fig.6 Variations of the extraction yield according to the added salt.

The effect of salt addition on Uranyl sorption the best yield was obtained with KSCN and the lowest yield was obtained with $Na_2S_2O^{-4}$.

F. *EFFECT OF THE INITIAL CONCENTRATION*

The study of the variation of the initial concentration of Uranyl by 0.03g of absorbent, calls for the realization of several experiments. The amount of Uranyl absorbed per unit mass increases with the increase of the concentration of the metal as shown in Fig. 07.

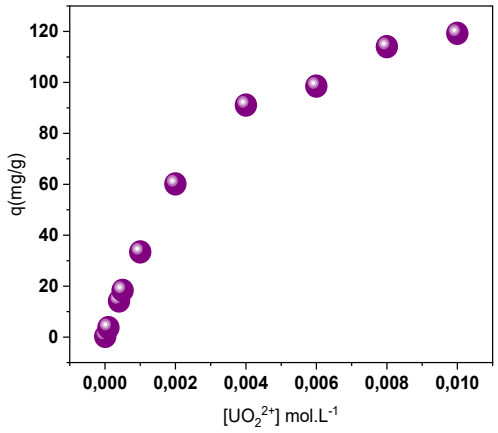

Fig.7 Sorption isotherm of Uranyl on organophosphorus resin as a function of initial metal concentration (V=5mL m=0.03g Θ= 300tpm).

For the study of the mechanism of sorption two models were applied, Langmuir and Freundlich their equations are respectively, 8 and 9 [13].

$$\frac{Ce}{qe} = \frac{1}{Klqm} + \frac{Ce}{qm} \text{.....Eq 08}$$

$$\text{Ln (qe)} = \text{Ln } (K_F) + n\text{Ln (Ce)}\text{.....Eq 09}$$

From which:
C_e: the equilibrium concentration of uranyl (mg L^{-1}).
q_e : the amount of uranyl adsorbed on the organophosphorus resin (mg g^{-1}).
k_L : the Langmuir adsorption constant (L mg^{-1}).
q_{max} : the maximum amount of uranyl that can be adsorbed.
k_F : the Freundlich adsorption constant.
n : the constant which indicates the capacity and the intensity of the adsorption respectively.

The results are expressed in the following table:

TABLE III
PRESENTATION OF SORPTION ISOTHEMS

Métal	Langmuir	Freundlich
UO^{2+}	K_L= 250	K_F=12581,17
	Q_m=200 mg/g	1/n=0,907
	R^2= **0,991**	R^2=0,981

The modeling of the sorption isotherms of Uranyl ions by the organophosphorus was carried out by the two models Langmuir, Freundlich; following the coefficients of correlations the model of Langmuir is the most adequate model to describe this process.

J. *ELUTION STUDY*

In order to study the elution behavior of uranyl (UO^{2+}_2) from the organophosphorus polymer, experiments were carried out using different eluting agents, in this work the eluting agents used are the three acids HCl, H_2SO4, and HNO_3 of concentration one mole per liter.
The elution yields were calculated using the following expression (Equation 10) :

$$R\ (\%) = 100 \times (C_{elution})/(C_i - C_f) \text{ ……..Eq 10}$$

With:
$C_{elution}$: the concentration of Uranyl after the acid treatment (mol/L)

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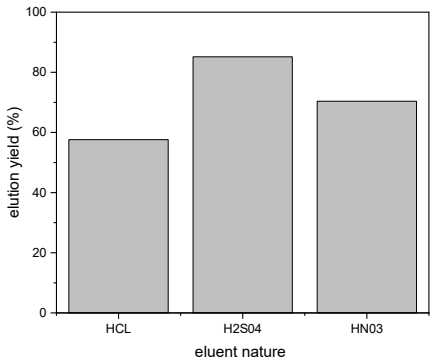

Fig.8 Effect of the nature of the eluent on the elution of Uranyl.

The elution procedure was done as follows: the resin was saturated with metal, and mixed with 5ml of the eluting acid for a time of 3h, according to the following figure (Fig. 08) the best eluent is the sulfuric acid with a yield more than 85%.

IV. CONCLUSION

In this study the liquid-solid extraction of UO_2^{2+}ions is performed with an organophosphorus resin based on polyethyleneimine (PEI), several parameters were studied to describe this extraction, the contact time, the effect of concentration, the pH, the salt effect, and the temperature. The equilibrium time was 40min for a maximum sorption capacity of uranyl ions equal to 18.29 mg/g, the optimal yield of the extraction is reached at a pH value equal to 5.8 also this extraction is favored in high temperatures. Desorption study can be performed with sulfuric acid, better than hydrochloric and nitric acid.

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