Comparative Study Of Uranium(VI) Extraction Between Lewatit TP 260, Polyethyleniminephenylphosphonamidic Acid & Diaminotriphosphonic Acid Grafted Polystyrene Divinyl Benzene Resins

Omar Abderrahim[1], Mohamed Amine Didi*[1], Abdelhakim Kadous[1], Didier Villemin[2]

[1]Laboratory of Separation and Purification Technologies, Department of Chemistry, Tlemcen University, Box 119, Tlemcen-Algeria.

[2] Laboratoire de Chimie Moléculaire et Thioorganique, UMR CNRS 6507, INC3M, FR 3038, ENSICAEN & Université de Caen, 14050 Caen, France

ABSTRACT

Phosphonic complexing moiety was covalently linked to polyethyleneimine liquid resin and to polystyrene divinyl-benzene polymer. This stable extractor of metal ions was tested and compared to another commercial phosphorus resin, Lewatit TP 260 in disodium form, in the sorption of uranyl ions from aqueous solutions. Batch study was carried out to optimize various process parameters such as pH of aqueous phase, time contact, initial concentration of uranyl ions, ion strength and temperature. The results showed that polyethyleniminephenylphosphonamidic acid could exchange uranyl better at high acidity (pH≈1.5) whereas diaminotriphosphonic acid grafted polystyrenedivinyl benzene adsorbs uranyl effectively at low acidity (pH≈3.5). The overall sorption capacities for UO_2^{2+} ions were found to be 39.66, 41.76 and 58.33 $mg.g^{-1}$ with polyethylenimine- phenylphosphonamidic acid, diaminotriphosphonic acid grafted polystyrenedivinyl benzene and Lewatit TP 260 resins, respectively. The adsorption behavior of uranyl on diaminotriphosphonic acid grafted polystyrenedivinyl benzene followed Freundlich isotherm. In the case of the Lewatit TP 260 resin, it followed suitably a Langmuir isotherm. Thermodynamic parameters showed the adsorption of an endothermic process and spontaneous nature at higher temperature.

Keywords - Lewatit TP 260, Phosphonic sorbent, phosphonamidic acid, solid phase extraction, uranyl ions.

I. INTRODUCTION

During the past decades, the separation and purification of uranium has gained considerable importance with the increasing demand for this element [1]. Various kinds of separation and preconcentration methods such as liquid – liquid, liquid – solid extraction, … etc have been used.[2-6] Among these, the liquid – solid extraction method is presently considered most promising. There are a variety of inorganic and organic adsorbents and/or ion exchanger developed so far. These resins should have high thermal and chemical stability as well as the possibility of regeneration repeatedly. The most chelate forming resins are characterized by reactive functional group P and O donor atoms and capable of coordinating to uranium ions [7]. Many researches have been published investigating the extractive properties of various phosphorus resins toward uranyl ions [8]. The effect of many parameters like pH, contact time, amount of the resin, concentration of the uranyl ions in aqueous phase, ionic strength, presence of foreign ions were investigated to find out the metal uptake characteristics of the resins [8, 9]. The present work deals with the preparation of phosphonic acid group covalently linked to polyethylenimine or to polystyrene divynil-benzene and reports the sorption of uranyl ions by this sorbents and another one commercialised by Fluka (Lewatit TP 260 in disodium form). The effect of contact time, pH, concentration of uranyl ions, ion strength and temperature on the efficiency of these phosphonic resins in sorption of uranyl ions, in batch process, is reported.

II. EXPERIMENTAL

A. Instrumentation

Infrared spectra were recorded on a Perkin-Elmer Spectrum One equiped with ATR accessory. Absorbencies were measured using Perkin-Elmer-Lambda 800 UV-Vis spectrophotometer. pH measurements were taken on a potentiometer Consort C831. ^{13}C {-^{1}H}, ^{31}P {-^{1}H} and ^{1}H NMR spectra were measured on a Bruker AC 250 working at 250 MHz in D_2O /Na_2CO_3 solution and Elemental analyses were carried out on a Thermoquest CHNS analyzer.

B. Reagents

P, P – dichlorophenylphosphine oxide ($C_6H_5P(O)Cl_2$), chloromethyl styrene-divinylbenzene copolymer (S-3% DVB), Lewatit TP 260 resin (fig. 1 and table 1), toluene, diethyleme amine and acetone were supplied by Fluka. Polyethylenimine (Lupasol WF) is commercially available from BASF with ratio of prim.: sec.: tert. amines (1: 1.07: 0.77) and a molecular weight (M_w) of 750 000. Arzenazo III {3,6-bis[(2-arzonophenyl)azo]-4,5-dihydroxy-2,7-naphthalene disulphonic acid}, uranyl nitrate hexahydrate, uranyl acetate dehydrate, potassium nitrate, sodium acetate, sodium chloride, sodium sulfate and sodium nitrate were purchased from Merck. Hydrochloride acid (36%), nitric acid (65%) and phosphorus acid were purchased from Reidel de Haen.

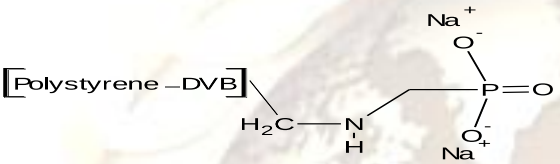

Fig.1. Structure of Lewatit TP 260

Table 1: Physical and chemical characteristics of Lewatit TP 260 cation exchange resin.

Characteristics		Value	Units
Ionic form as shipped	Di-Na^+	-	-
Bead size	> 90%	0.4 - 1.25	mm
Effective size		0.55 ±	mm
Shipping		770	$g.L^{-1}$
Density		1.2	$g.mL^{-1}$
Water		59 – 61	%
Total	Hydrogen	2.3	$Eq.L^{-1}$
Volume change	$Na^+ >> H^+$	-25	max.%
Stability	temperature	-10 – 85	°C
	pH range	0 – 14	
Storability	of product	2	min.
	temperature	-20 – 40	°C

C. Synthesis and characterisation of new functionalized resins

1. diaminotriphosphonic acid grafted polystyrenedivinyl benzene resin

The new sorbent, DiAminoTriPhosphonic Acid grafted Polystyrene DiVinyl Benzene resin (DATPA), was synthesized from commercially available chloromethyl styrene- divinylbenzene copolymer (S-3% DVB) according to the Moedrizer-Irani reaction (Fig. 2) [10].

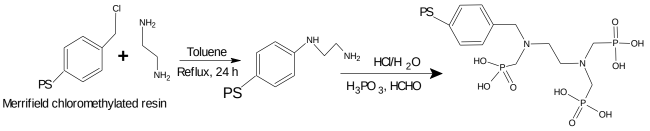

Fig. 2: Scheme of DATPA resin synthesis, PS: polystyrene polymer

The presence of phosphonic acid group was confirmed by the appearance of absorption bands at 920 cm^{-1} (P=O) and 2400 cm^{-1} (P-OH). The experimental CHNP analysis data of DATPA-PS-DVB was C (%):57.44, H(%): 6.39, N(%): 7.00 and P(%): 4.95.

2.Synthesis of polyethyleneiminephenylphosphonamidic acid

The new PolyEthylenIminePhenylPhosphonAmidic Acid resin (PEIPPA) was synthesized by reaction between commercially available polyethylenimine (Lupasol WF, primary and secondary amine) and P, P – dichlorophenylphosphine oxide ($C_6H_5P(O)Cl_2$) (Fig. 3).

The structure of the final complexing agent was identified and characterized by FTIR spectroscopy. The spectra showed the expected characteristic bonds for P-OH group (2341, 2324 and 1044 cm^{-1}) P=O at 1136 cm^{-1} and NH at 1593 and 750 cm-1, as matched to the proposed structure (Fig. 3) [11].

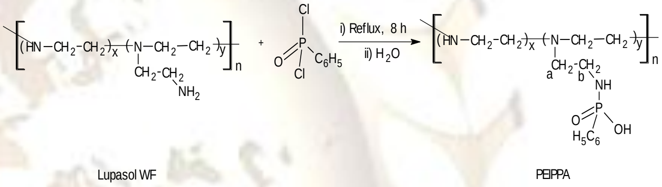

Fig. 3: Scheme of PEIPPA synthesis from Lupasol WF

D. Sorption procedure

The new grafted resins and the commercial one have been investigated in liquid-solid extraction of uranyl cation from aqueous solution. An accurately weighed mass of resins was separately added to 5 mL of uranyl solution (with known concentration and fixed pH) in a 50 mL glass flask. The mixture is subjected to vigorous stirring for a determined time, then, the aqueous phase was separated from the functionalized resin by filtration. The uranyl concentrations in the aqueous phase were determined, before and after extraction spectrophotometrically with Arzenaso III at pH 2 [12]. The absorbance of Arzenazo III - uranium (VI) complex was measured at 651 nm.

III. RESULTS AND DISCUSSION

A. Effect of pH on the uptake of uranyl ion

The modifying resins have an O=P-OH, a nitrogen atom and/or -NH group. This makes it suitable for complex formation with uranyl ion. Comparing the behaviour of these three resins towards the uranyl ion, in aqueous phase, at initial pH values ranging from 1.4 to 6.0 (Fig. 4) shows that for the PEIPPA extractant, the retention of U(VI) is high in acidic solutions and increases by decreasing the pH and the maximum uptake (31.09 $mg.g^{-1}$) was attainted at initial pH = 1.5. [13]. For the other resins (DATPA and Lewatit TP 260), the retention of U(VI) increases with the pH from 1.5 to 3.5, then the adsorption capacity decreases at pH higher than 4.5. Uptake of uranyl (37.45 mg.g^{-1}) is higher for DATPA resin at pH=3.5.

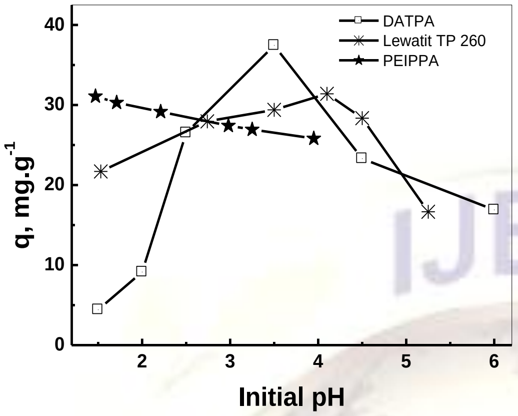

Fig. 4: Effect of solution pH for efficient extraction of uranyl ion

B. Adsorption kinetics

Figure 5 shows the change of the uptake of uranyl ion from his aqueous solution at the natural pH as a function of time by resins PEIPPA, DATPA-PS-DVB and Lewatit TP 260.
The uptake values of Lewatit TP 260 and PEIPPA were higher than that of DATPA-PS-DVB resin.

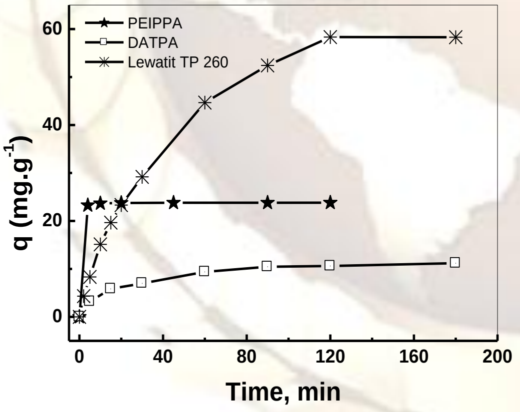

Fig. 5: Effect of stirring time on the adsorption of uranyl on the resins

It is seen that the uptake increases rapidity with the PEIPPA, only 30 minutes are required for the attainment of equilibrium. For Lewatit TP 120 and DATPA-PS-DVB, the uptake continued to increase even after 30 minutes, and becomes constant after 120 minutes and 180 minutes, respectively.

The kinetics of uranyl adsorption on these three ion exchangers resins followed the first order rate expression given by Lagergren, equation 1 [14]:

$$Log_{10}(q_e - q_t) = Log_{10}q_e - \frac{kt}{2.303} \qquad (1)$$

where q_t and q_e are the amount of U(VI) adsorbed at time, t and equilibrium time, respectively, and k is the sorption rate constant of Lagergren equation. Linear plot of log (q_e – q_t) versus t (Fig. 2) shows the applicability of the above equation for PEIPPA, DATPA-PS-DVB and Lewatit TP 260 resins. The sorption rate constant values, calculated from the slope of the linear plots and the correlation coefficients of the linear plots is 0.7255 min^{-1} are given in table 2.

Table 2: Sorption rate constant values and the correlation coefficients.

resin	PEIPPA	DATPA	Lewatit TP 260
Equilibrium time (min)	30	180	120
K, (min^{-1})	0.7255	0.0259	0.0254
r	0.9949	0.9940	0.9960

C. Sorption capacity

The sorption capacity of functionalized resin was determined by equilibrating 0.1 g of the resin with 5 mL of uranyl ion solutions at different concentrations. The amount of uranyl ion needed for saturation was obtained as follows (eq. 2):

$$q(mg.g^{-1}) = \frac{(C_0 - C_e)}{W} \times V \times 238.02 \qquad (2)$$

where C_0 and C_e denote the initial and equilibrium concentrations of U(VI) in the aqueous phase (mol L^{-1}), V is the volume of the aqueous phase (5 mL), W is the weight of grafted resin (0.100 g) and 238.03 is the molar weight of Uranium (g.mol^{-1}). The experimental capacity obtained for PEIPPA, DATPA and Lewatit TP 260 resins are 39.66, 41.76 and 58.33 mg/g, respectively.

D. Adsorption isotherm

The adsorbed amounts of uranyl on resins have been determined as a function of the metal concentration in the supernatant at the equilibrium state and ambient temperature (25±2 °C). Two models were tested, the Langmuir and Freundlich. The Langmuir treatment [15] is based on the assumption that (i) maximum adsorption corresponds to saturated monolayer of adsorbate molecules on the adsorbent surface, (ii) the energy of adsorption is constant and (iii) there is no transmigration of adsorbate in the plane of the surface.

$$\frac{Ce}{q_e} = \frac{1}{q_0 b} + \frac{Ce}{q_0} \qquad (3)$$

The Freundlich equation was also applied to the adsorption. The Freundlich equation is basically empirical but is often useful as a means of data description. It generally agrees quite well compared to Langmuir equation and experimental data over a moderate range of adsorbate concentrations. The Freundlich isotherm is represented by equation 4:

$$\log q_e = \log K_F + \left(\frac{1}{n}\right)\log C_e \qquad (4)$$

where C_e is the equilibrium concentration (mg l^{-1}), q_e the amount adsorbed at equilibrium and q_0 and b are Langmuir constants related to adsorption capacity and energy of adsorption, respectively. K_F and n are the Freundlich constants characteristic of the system. KF and n are indicators of adsorption capacity and adsorption intensity, respectively.

In case of PEIPPA resin, the non linear plot of C_e/q_e versus C_e and $\log q_e$ versus Log C_e show that adsorption not obeys Langmuir and Freundlich models. Deviation from linearity indicated the presence of multi-model interaction [16].

With DATPA, the plot of log q_e versus log C_e (Fig. 6) is linear and the constants K_f and n were found to be 1.537 and 1.418, respectively. The value of $1 < n < 10$ shows a favourable adsorption of uranyl onto this resin. The correlation coefficient for the Freundlich plot was found to be 0.997 indicating a better fit of the experimental data compared to Langmuir plot (0.995).

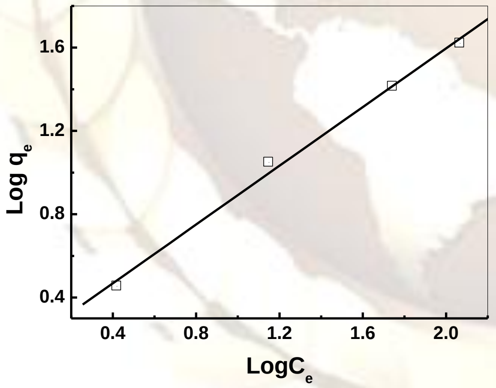

Fig. 6: Freundlich plot for the adsorption of U(VI) on DATPA resin

With Lewatit TP 260, the linear plot of C_e/q_e versus C_e shows that adsorption obey Langmuir adsorption model (Fig.7). The correlation coefficient for the linear regression fits of the Langmuir plot was found to be 0.9996. q_0 and b determined from the Langmuir plot were found to be 63.371 mg g^{-1} and 0.0165g mg^{-1} respectively.

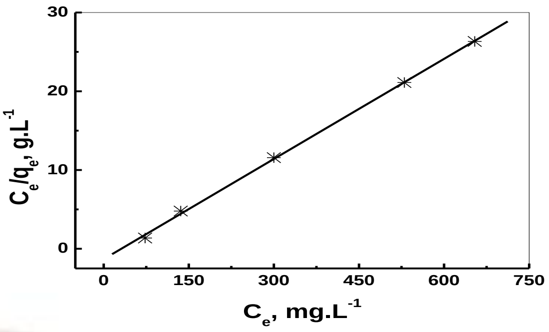

Fig. 7: Langmuir plot for the adsorption of U(VI) on Lewatit TP 260 resin

E. Effect of the extractant to analyte ratio

Figure 8 shows the recovery of uranyl ion as a function of resin/UO_2^{2+} ratio (g/mmol). It can be observed that the recovery increased with increase in the resin/UO_2^{2+} ratio in both cases due to the increasing amount of resins available for uranyl complexation. The recovery of uranyl by Lewatit TP 260 and DATPA-PS-DVB are higher than with PEIPPA and in both cases recovery does not change at resin/UO_2^{2+} ratio higher than 20/1.

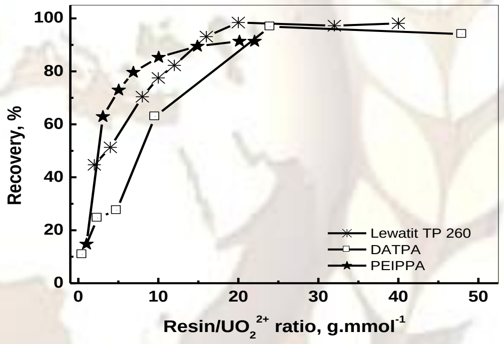

Fig. 8: Effect of the uranyl to resins ratio on the recovery
of uranyl

F. Effect of electrolyte on uranyl ion extraction

Sodium salts are the major component in soil and sediment samples, a study to ensure a good tolerance for this electrolyte for quantitative uranyl extraction becomes essential [17]. For this study an amounts of resins were stirred with increasing NaCl concentration. It is evident from Fig. 9:

- That for PEIPPA resin, there is a small positive effect on increasing NaCl concentration from 0 to 0.1 mol.L^{-1}
- That for DATPA-PS-DVB, there is no effect on extraction efficiency in interval concentration [0 - 0.01 mol.L^{-1}]. However, a negative trend was observed at salt concentration higher than 0.01 mol.L^{-1}. This can be attributed to the formation of more stable anionic chloro-complex formation in aqueous solution and/or to the screen effect of Na^+ which affects the diffusion of ions within the resin.

- That for Lewatit TP 260, we observe the decrease of recovery; this could be due to the formation of more stable anionic chloro-complex formation in aqueous solution and/or to the screen effect of Na^+ which affects the diffusion of ions within the resin.

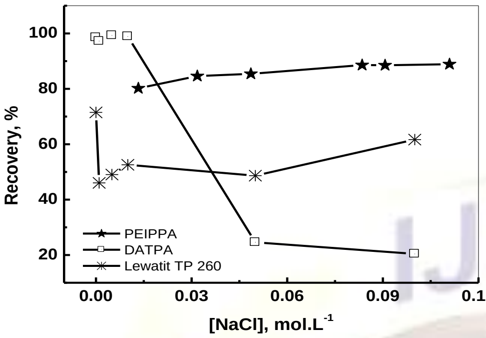

Fig. 9: Effect of NaCl concentration on the extraction of U(VI) with grafted resins

G. Effect of temperature on extraction equilibrium

The effect of temperature on the sorption of uranium (VI) ions was studied**.** Different thermodynamic parameters were computed using equations 5, 6 and 7.

$$\Delta G = \Delta H - T\Delta S \qquad (5)$$

$$\Delta G = -RTLnK_d \qquad (6)$$

$$LogK_c = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \qquad (7)$$

where ΔH, ΔS, ΔG, and T are the enthalpy, entropy, Gibbs free energy, and temperature in Kelvin, respectively. The values of equilibrium ratio (K_c), was calculated at each temperature using the relationship 8.

$$K_c = \frac{F_e}{1-F_e} \qquad (8)$$

where F_e is the fractional attainment of equilibrium at time t, obtained by the expression $F_e = q/q_m$, where q_m is the maximum adsorption capacity at optimal conditions.

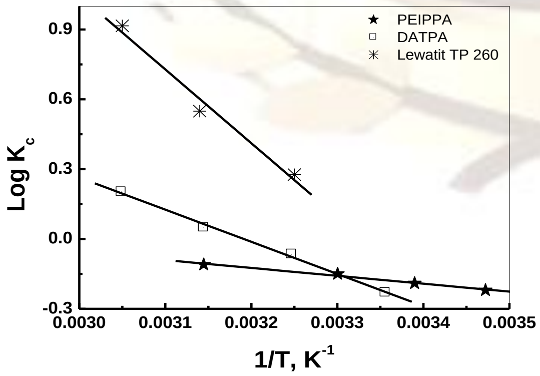

Fig. 10. *Variation of equilibrium ratio (Kc) with temperature for the sorption of U(VI) ions onto resins*

The plot of log K_c vs 1/T is a straight line, as shown in Fig. 10, with correlation coefficient r = 0.9980. The numerical values of ΔH, ΔS are computed from the slope and intercept of the graph are given in Table 3. The negative value of Gibbs free energy for the sorption of UO_2^{2+} by the Lewatit TP 260 as shown in Table 3 indicates the spontaneous nature of sorption from bulk or aqueous phase, while decrease ΔG values with increasing temperature in case of PEIPPA and DATPA indicate that the sorption is better at high temperature. Positive values of ΔH of all sorbents reflect the endothermic sorption behavior.

Table 3: Thermodynamics parameters for sorption process of UO_2^{+2} on the resins

Sorbent	T, K	ΔG, kJ.mol^{-1}	ΔH, kJ.mol^{-1}	ΔS, J.mol^{-1}.K^{-1}	r
PRIPPA	288	1.20	+6.49	+18.37	0.992
	295	1.07			
	303	0.92			
	318	0.65			
DATPA	298	1.30	+26.45	+84.40	0.998
	308	0.45			
	318	-0.39			
	328	-1.23			
	308	-4.57			
Lewatit TP 260	318		+61.74	+215.3	0.989
		-6.72			
	328	-8.88			

The increase in entropy favors the stability of the sorbed complex via covalent interaction type chemisorption. The main source of this entropy gain may be due to the rupturing of the hydration zone formed around a central metal atom in mother liquid to a great extent and direct interaction of U(VI)-Functional group complex of resins results in net positive entropy effect [18].

IV. CONCLUSION

Two new type of ion exchange polymers based on the commercially available polyethylenimine polymer (Lupasol WF) and Merrifield resin were developed in this study.

This new phosphonated ion-exchangers obtained and another commercialized by Fluka are used as support material for UO_2^{2+} sorption from aqueous solution in batch process. The extraction efficiency for the extraction of uranium by these sorbents was determined as a function of various parameters such as time contact, pH, uranyl initial concentration, extractant to uranium ratio, NaCl concentration and temperature. The results showed that:

- The sorbent PEIPPA was the fastest to reach the sorption equilibrium (t=30 min)
- The sorption capacity of 58.33 mg.g^{-1} was obtained by the Lewatit TP 260, where as for

DATPA and PEIPPA it were only 41.76 and 39.66 mg.g^{-1}, respectively.

- The presence of ions (Na^+, Cl^-) do not affect the selectivity of PEIPPA for UO_2^{2+}, but with DATPA and Lewatit TP 260 the extraction was found to decrease with increase in NaCl concentration,

- The PEIPPA sorbent is more suited for the sorption of uranyl from acidic solution (pH≈1.5) while DATPA can be used at moderate pH (pH≈3.5).

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