Extraction of Uranium (VI) with Triton X-100/Tween-40/D2EHPA/ $BMIMMeSO_4$: Factorial Design Optimization from Cloud Point

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ABSTRACT: *This work reports the Uranyl (UO_2^{2+}) extraction from water by the Triton X-100 / Tween-40 / D2EHPA / $BMIMMeSO_4$ by two aqueous phases or Cloud Point Extraction (CPE). The procedure has been developed to extract uranium (VI) using a mixture of non-ionic surfactants: Triton X-100 and Tween-40 in different contexts, and a mixture of lipophilic chelating extracting agent D2EHPA/ $BMIMMeSO_4$. The UO_2^{2+} sample was analyzed by UV-Visible spectroscopy. A mixture of 100 µL of Arsenazo III and 100 µL of UO_2^{2+} in a medium whose pH was equal to 2.0. The interaction product of Arsenazo III with UO_2^{2+} was determined at λ_{max}= 653 nm. Three key variables: initial pH value, ion strength, and initial uranyl concentration have been studied by the 3^3 factorial design methods, in order to find the optimum conditions for uranium (VI) extraction. The temperature, the time, the concentrations of Triton X-100, and Tween-40 were fixed: T =25°C, time = 24 hours, Triton X-100 (8%), and Tween-40 (2%). The optimal extraction of uranium (VI) by Micelle-Mediated Extraction (CPE) procedure was obtained for pH= 3.0, Na_2SO_4 (% w/w) = 9.0 and $[UO_2^{2+}]$ = 5.50 mM. This system has research value and application in wastewater treatment.*

KEYWORDS: *Cloud point extraction; Uranyl ion; Triton X-100; Tween 40; D2EHPA; Design of Experiments (DOE).*

INTRODUCTION

Uranium, a weekly radioactive and toxic metal, is widespread in the environment, found at low levels in soils, waters, and rocks. Its disposal of wastewater is of great importance. In the nuclear industry and mining, uranium and its compounds are potentially toxic [1-4]. This toxicity can be caused by breathing air containing uranium dust or by eating substances contaminated by uranium [5-7]. The uranium separation from its associated components becomes necessary in view of its increased demand. Effective methods are increasingly being developed to separate uranium from the various flux encountered at the various stages of nuclear fuel cycle; although solvent extraction methods are the backbone of the nuclear reprocessing industry. The use of green and sustainable technology requires alternative processes with a lower organic solvent use.

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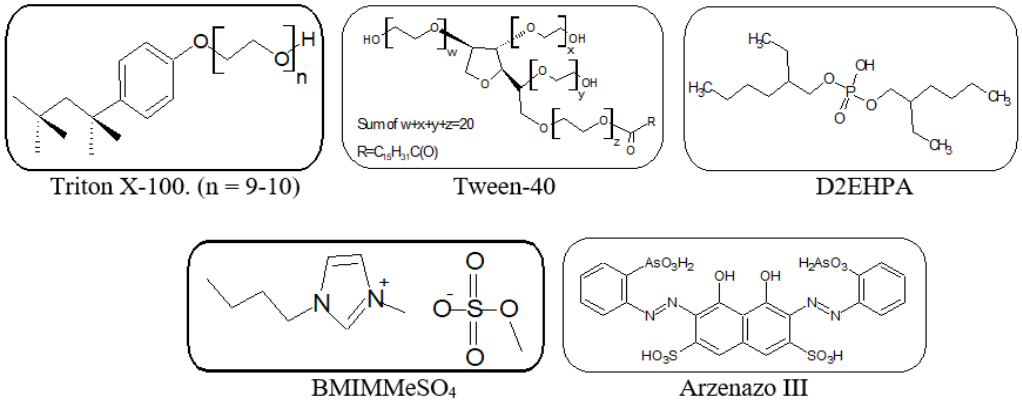

Fig. 1: Structures

To study the extraction of uranium (VI) using different techniques such as solvent extraction which uses large quantities of organic solvents [8], several investigations have been carried out [1,9,10]: ion exchange [11,12], adsorption [13-16], electrochemical membrane separation [8,17], and other techniques [7,18]. For technical and economic reasons, these processes do not respect environmental regulations.

Alternatively, Cloud Point Extraction (CPE) was generally observed in nonionic surfactant micelles solutions when the temperature of the surfactant solution is raised to a certain value [19-23]. This process can be used for the extractive pre-concentration, separation and purification of metal ions, metal chelates, biomaterials and organic compounds [25]. Not requiring the presence of organic diluents is the fact that it is primarily a two-phase aqueous process. High values of concentration factors can be achieved compared to organic solvent extraction. Extraction technology using benign phases for the environment replaces the volatile organic solvents used in conventional solvent extraction technologies. CPE is based on the phase separation phenomenon, exhibited by micelles solutions of nonionic surfactants [24].

Factorial design optimization has proven its usefulness to obtain empirical linear models relating process response to process factors [25,26].

The aim of this work is to study the effect of factorial design on the operating parameters such as the uranyl ions concentration, Na_2SO_4 salt, and initial pH, in order to find the optimum conditions for uranium (VI) extraction. The temperature, the time, the concentrations of Triton X-100 and Tween-40 were fixed: T =25°C, t = 24 hours, Triton X-100 (8%) and Tween-40 (2%).

The influences of uranyl ions concentration, Na_2SO_4 salt, and the initial pH, and their interactions on the extraction yield of uranyl ions were investigated herein using the 3^3 factorial designs.

EXPERIMENTAL SECTION

Reagents

Uranyl acetate dihydrate (390.13g/mol), NaCl 99%, Na_2SO_4 99%, CH_3COONa 99%, $Na_2S_2O_3$ 99%, KBr 99% and KNO_3 99% were supplied from Merck. The nonionic surfactants used in this study were p-octylpolyethylene glycol phenyl ether (Triton X-100 – Fig. 1) having an HLB value of 13.5 and a critical micelle concentration CMC equal to 3.0×10^{-4} M at 25 °C and, polyoxyethylene sorbitan monopalmitate (Tween-40 – Fig. 1) having an HLB value of 15.6 and a critical micelle concentration CMC equal to 2.7×10^{-2} M at 25 °C provided from Biochem Chemopharma and Fluka, respectively. Di-(2-ethylhexyl) phosphoric acid (D2EHPA – Fig. 1) (322.43g/mol) from Fluka and 1-butyl-3-methylimidazolium-methyl sulfate ($BMIMMeSO_4$, 98%- Fig. 1) (250.32g/mol) were obtained from Sigma-Aldrich. 2,2'-(1,8-dihydro-3,6-disulfanonaphthylene-2,7-biazo) bisbenzenearsonic acid (Arsenazo III- Fig. 1) (776.36g/mol). Buffer solution at pH equal to 2.07 prepared by ammonium acetate and hydrochloride acid (37%), were supplied by Merck. Ultrapure water was prepared in the laboratory.

Instruments

The UV-Visible absorbance of solutions was measured using SPECORD 210/Plus UV–Vis spectrophotometer. For pH measurements, pH-ORP-TEMP Bench Meter AD1030 was used. Thermostatic water bath (Thermo-Circulator) preserved at the distinct temperature, was

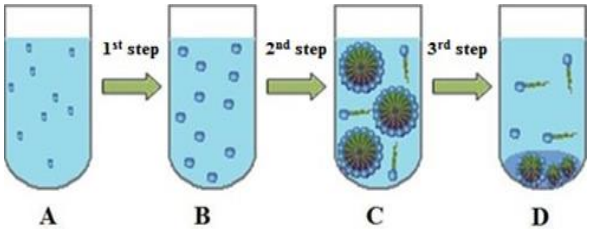

Fig. 2: Principle of cloud point extraction
(A): Solute solution; (B): Formation of complexes after addition of complexing agent;
(C): Trapping of complexes inside micelles; (D): phase separation following the temperature rise.

applied for CPE. The weighing was made with an electronic analytical balance type Carat Series OHAUS Item: PAJ1003. The preparation of ultra-pure water was carried out by the YOUNG LIN distiller. The volumes were collected using micropipettes (SCI LOGEX 100 - 1000 µL).

Extraction procedure of uranyl ions

The CPE extraction operation was based on the following steps (Fig. 2) [29].

The balance established between the two obtained phases depends on certain parameters such as the nature and the concentration of the surfactant, those of the chelating agent, ionic strength, temperature, etc.

CPE is carried out in graduated tubes; the Triton X-100 (8%) and Tween-40 (2%) were mixed as non-ionic surfactants. A mixture of D2EHPA (0.02 g) and $BMIMMeSO_4$ (0.02 g), Na_2SO_4 salt (8%, 9%,10%), and then top up 10 mL with a uranium (VI) solution (10^{-4} M, 5.5 10^{-4} M, 10^{-3}M) after pH adjustment (3,4.5,6). After stirring the mixture, it was allowed to stand at 25°C for 24 hours; the coacervate phase was distinguished from the dilute phase. The latter is a measured by UV-Vis spectrophotometer.

The UO_2^{2+} sample was analyzed by a mixture of 100 µL of Arsenazo III and 100 µL of UO_2^{2+} in a medium whose pH was equal to 2.0. The interaction product of Arsenazo III with UO_2^{2+} was determined at λ_{max}= 653 nm [27-31].

These phenomena are explained as follows: in the first extraction case, uranyl ions were fixed on the negative micelles' surface [13, 14]. But in the second case, the increase in UO_2^{2+} extraction yield in presence of $BMIMMeSO_4$ is due to the formation of big mixed micelles in which UO_2^{2+} was complexed both by D2EHPA anion [32].

The percentage of extracted uranyl ions was determined as (Equation 1):

$$Yield(\%) = \frac{C_i - C_e}{C_i}.100 \quad (1)$$

where C_i and C_e were the initial, and equilibrium UO_2^{2+} concentrations (mol L^{-1}, respectively

RESULTS AND DISCUSSION

Factorial design study

The present study deals with the optimization of the uranium (VI) extraction.

The regression equation of matrice was represented by the following expression (Eq. 2):

$$E(\%) = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_{12}X_1X_2 + a_{13}X_1X_3 + a_{23}X_2X_3 + a_{123}X_1X_2X_3 + a_{11}{X_1}^2 + a_{22}{X_2}^2 + a_{33}{X_3}^2 \quad (2)$$

In our investigations, a series of 27 tests were conducted using a 3^3 factorial experience plan, varying three key variables: pH value (X_1), ion strength (X_2), and initial uranyl concentration (X_3). Three levels of variation for each parameter were considered and summarized in (Table 1) [32].

As a result, 27 experiments with all possible combinations of variables were conducted at room temperature to which three center points were added to estimate the error. The results of the uranyl extraction process were expressed in terms of extraction efficiency, considered to be the response function in the process studied. These results are summarized in Table 2.

Preliminary observations show that extraction yields according to the parameters of the experiment reach values of 72.2 to 99.4% under certain operating conditions. From Table 2, it already appears that the highest yield extraction value (99.4%) was obtained for a minimum pH value, an average initial uranyl concentration, and an average Na_2SO_4 (w/w %).

Xj = 1 to 3: a reduced variable which takes two values: –1 (low level) and + 1 (high level); low level = 2 (low value – mean)/range; high level = 2 (high value – mean)/range; mean = (high value + low value)/2; range = (high value–low value).

Model calculation and refinement

The Uranium (VI) extraction model was performed based on 27 measured values, using the second-order

Table 1: Factor levels used in the 3^3 factorial experiment designs at T = 25 °C

Factors	Symbol of coded variables	Low level (-1)	Medium level (0)	High level (+1)
pH	X_1	3	4.5	6
Na_2SO_4 (w/w %)	X_2	8	9	10
$[UO_2^{2+}] \cdot 10^4$ (mol L^{-1})	X_3	1	5.5	10

Table 2. Experimental data

Experiment N°	Factor levels			Reduced values			Response function Extraction yield (%)
	pHi	Na_2SO_4 (w/w%)	$[UO_2^{2+}].10^4$(mol L^{-1})	X_1	X_2	X_3	
1	3	8	1	-1	-1	-1	95.4
2	3	8	5.5	-1	-1	0	94.3
3	3	8	10	-1	-1	+1	85.9
4	3	9	1	-1	0	-1	76.5
5	3	9	5.5	-1	0	0	99.4
6	3	9	10	-1	0	+1	84.0
7	3	10	1	-1	+1	-1	91.1
8	3	10	5.5	-1	+1	0	89.9
9	3	10	10	-1	+1	+1	79.8
10	4.5	8	1	0	-1	-1	93.1
11	4.5	8	5.5	0	-1	0	94.8
12	4.5	8	10	0	-1	+1	85.4
13	4.5	9	1	0	0	-1	82.1
14	4.5	9	5.5	0	0	0	89.3
15	4.5	9	10	0	0	+1	86.8
16	4.5	10	1	0	+1	-1	80.3
17	4.5	10	5.5	0	+1	0	91.8
18	4.5	10	10	0	+1	+1	89.1
19	6	8	1	+1	-1	-1	97.3
20	6	8	5.5	+1	-1	0	95.7
21	6	8	10	+1	-1	+1	93.9
22	6	9	1	+1	0	-1	72.2
23	6	9	5.5	+1	0	0	96.3
24	6	9	10	+1	0	+1	83.8
25	6	10	1	+1	+1	-1	80.4
26	6	10	5.5	+1	+1	0	92.8
27	6	10	10	+1	+1	+1	84.4
(28,29,30)[a]	4.5	9	5.5	0	0	0	86.5/89.3/89.0

[a]Three additional tests at the central point (0,0,0) for the calculation of the student's and Fisher's tests, using the normal rule of variance.

Taylor polynomial [33]. The model calculations were performed using non-dimensional or reduced values of these variables, each of which varied over three levels. The following mathematical model shows the values of coefficients of the model, supposed to describe the individual effects of parameters, with their possible interactions.

The Student's t-test was carried out on coefficients of Equation (3) by analyzing the repeated values shown in Table 2.

With a view to reproducibility, it is necessary to verify whether this model describes with precision the studied process by determining which coefficients could be neglected, using Student's *t*-test and Fisher's test [34,35].

Table 3: Model adequacy tests and variance analysis

Characteristic	Symbol/equations	Values
Parameternumber	P	3
Levelnumber	L	3
Number of experimental attempts	N	27
Number of tests at (0, 0, 0) point	n	3
Model variance	ν	2
Averageyield at (0,0,0) point	$Y_0 = \sum Y_{oi}/3$	88.3
Random variance	$S^2 = \Sigma (Y_{oi} - Y_0)^2/v$	2.34
Square root of variance	S	1.53
Risk factor (chosen arbitrary)	α	0.05 (95%)[a]
Student's *t*-test factor	t_ν	4.3[b]
Average error on the coefficient value	$\Delta a_i = \pm t_{\nu,\alpha/2} S/N^{0.5}$	±1.26
Number of remaining coefficients	R	6[c]
Model response at (0,0,0)	$a_0(y_{000})$	90.76
Discrepancy on average yield Error on average yield discrepancy	$d = y_0 - y(0,0,0) = y_0 - a_0$ $\Delta d = \pm t_{\upsilon,\alpha/2} S(1/N + 1/n)^{0.5}$ with N=27& n=3	2.50 4.00
Average yield for the 27 attempts	$y_m = \sum y_i/27$	88.4
Residual variance	$S_r^2 = \sum (y_i - y_m)^2/(N - R)$	59.83
Degrees of freedom	ν_1	2
Residual degrees of freedom	ν_2	5
ObservedFisher's test	$F_{obs} = S_r^2/S^2$	25.51
Fisher-Snedecorlaw	F_{α,ν_1,ν_2}	5.78[d]

The suitability of the model strongly depends on the precision of the experiment. In the current experience, the main errors come from volume and weight measurements.

For this purpose, three additional tries of the central point (0,0,0) are demanded to estimate the average error in the value of every coefficient, based on the random variance. The calculations made are summed up in Table 2.

$$E(\%) = 90.76 + 0.031X_1 - 3.12X_2 + 0.263X_3 - 1.21X_1X_2 + 2.11X_1X_3 + 1.83X_2X_3 + 1.146X_1X_2X_3 + 0.46{X_1}^2 + 4.13{X_2}^2 - 8.179{X_3}^2 \quad (3)$$

So, with a 95% trust (i.e., α= 0.05), and for two variances (i.e., for three experiments at the central point), one assessed the value of $t_{v,1-\alpha/2}$ as being equal to 4.3.

As a result, in it (1 − α) level, the range of trust for all estimated coefficients to be using 27 runs (N = 27), will be $\Delta a_i = \pm$ 1.2673 at 95% trust (Table 3). According to Student's *t*-tests, it results in that $|\Delta a_i| < |a_i|$ for a_1 a_3, a_{12}, a_{11}, and a_{123}. Consequently, these coefficients should be removed from the mathematical model because they show a significant effect on the response function, being shaded by their mean error. Therefore, the final form of the polynomial model that describes the extraction of uranyl ions was in the following Equation (4).

a. α= 5% was arbitrary chosen. In this case, one regarded that a 95% confidence may be satisfactory;

b. Student tables with two degrees of freedom at a 95% confidence, tcrit (2; 0,05);

c.After removing the less significant coefficients; d.See Fisher-Snedecor tables.

$$E(\%) = 90.76 - 3.12X_2 + 2.11X_1X_3 + 1.83X_2X_3 + 4.132{X_2}^2 - 8.179{X_3}^2 \quad (4)$$

This model was supposed to accurately fit the extraction process of uranyl investigated herein. Thus in the vicinity of the expected optimal parameters values, it appears that only the individual effect pH and Na_2SO_4 influence the extraction positively. But the quadratic effect of Uranyl concentration influences negatively the extraction.

The individual effects and interactions of the parameters were discussed based on the sign and the absolute

Table 4: Coefficients and their corresponding effects upon yield extraction of Uranium (VI)

Variable	Model		Expected effect on the yield extraction
	Coefficient	Value	
X_0=1	a_0	90.76	High average extracting capacity of uranium (VI)
X_2	a_2	-3.12	Weak detrimental individual effect of X_2
X_1 X_3	a_{13}	+2.11	(++) Favorable binary interaction of X_1 and X_3
X_2 X_3	a_{23}	+1.83	(++) Favorable binary interaction of X_2 and X_3
X_2^2	a_{22}	+4.13	(++)Favorable quadratic interaction of X_2
X_3^2	a_{33}	-8.17	(- -) Slight and flat maximum with respect to X_3

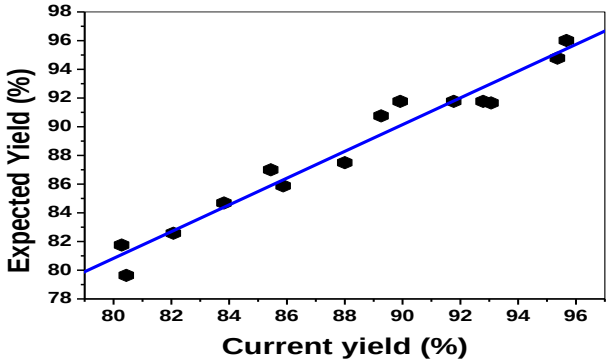

Fig. 5: The expected and current response plot of uranium (VI) extraction

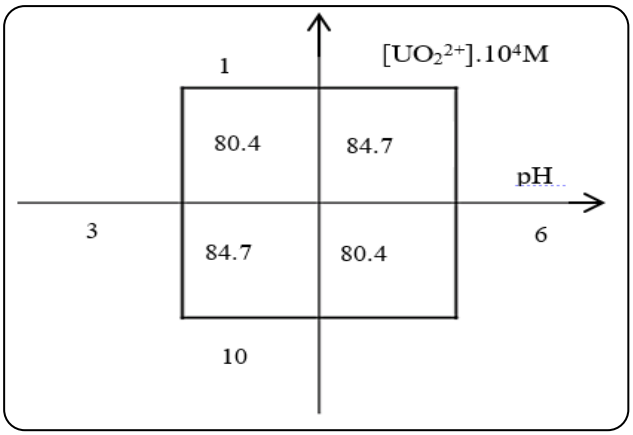

Fig. 3. Factorial interaction between pH and Uranium (VI) concentration (X_1X_3)

value of each coefficient. These coefficient characteristics will define the strength of the corresponding effect involved and how it acts when extracting the yield (favorable or detrimental), respectively (Table 4).

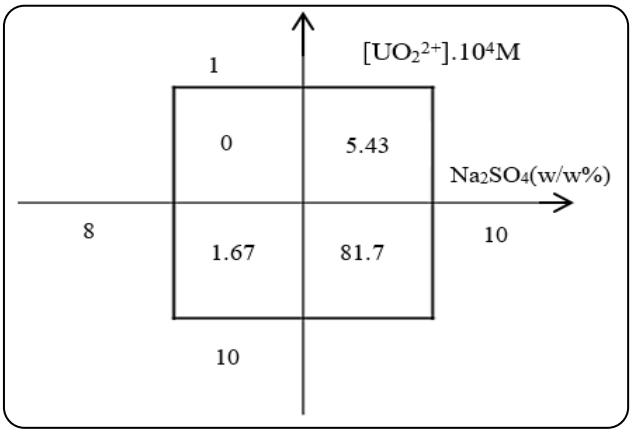

Fig. 4: Factorial interaction between ionic strength and Uranium (VI) concentration (X_2X_3)

pH value (X_1), ion strength (X_2), and initial uranyl concentration (X_3)

Interpretation

The effect of individual variables and interactional effects can be estimated from the above Equation (4). According to the equation of the model, it is clear that individual operating variables concentration of Na_2SO_4 (w/w %) and UO_2^{2+} concentration has a net negative effect on uranium extraction. Whereas the interaction between pH of solution and concentration of UO_2^{2+} and the interaction between Na_2SO_4 (w/w %) and UO_2^{2+} concentration have a net positive effect. A positive than negative value for the concentration of Na_2SO_4 (w/w %) indicate that the measured value of adsorbed metal amount increased and decreased as the factor was changed from its first level to its second level respectively. This optimization showed that the best conditions were obtained for pH = 3.0, Na_2SO_4 (% w/w) = 9.0 and [UO_2^{2+}] = 5.50 mM with extraction yield of 99.4 % in one step. For these optimal values, the experiment carried out gave an extraction yield of 98.1%. The difference was 1.3%.

The interaction between pH and the concentration of uranium (VI) (X_1X_3) and the interaction between the concentration of Na_2SO_4 (w/w %) and concentration of uranium (VI) (X_2X_3) are plotted in Fig.s 3 & 4. As can be seen in Fig. 4, for the interaction (X_1X_3) at the (+1) and (-1) for each factor in the same time, show a high extraction of uranium 84.70 %. Also, the Fig. 4 show a higher extraction of (X_2X_3) 91.6 % at the (-1) and (-1) for each factor.

Fig. 5 shows the relationship between expected and current values of uranium (VI) removal from solutions

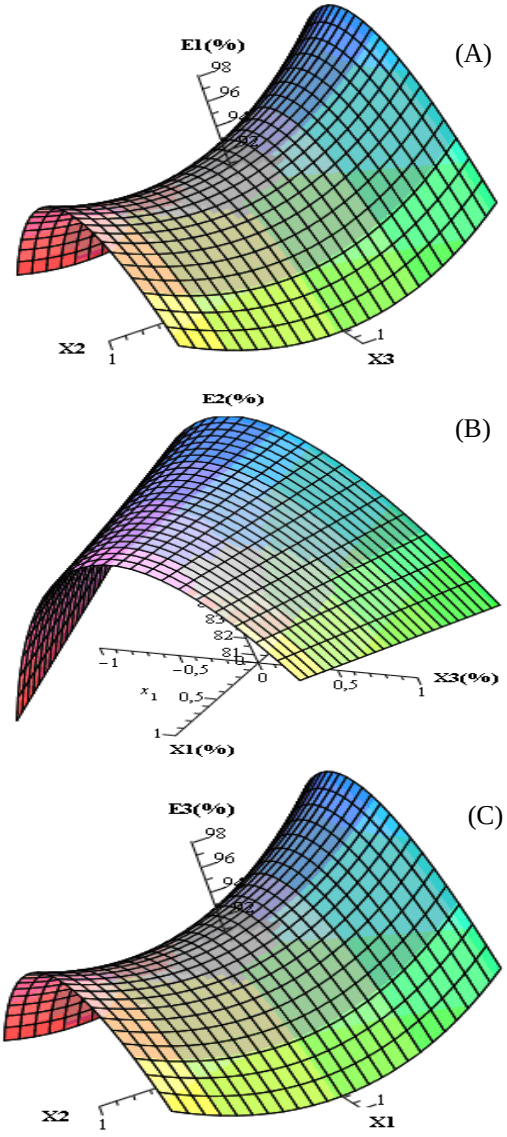

Fig. 6: 3D representation of the yield extraction (%) of uranium (VI): at fixed pH (A), at fixed Na_2SO_4 (w/w %) (B) & at fixed UO_2^{2+} concentration (C)

using non-ionic surfactants and a mixture of lipophilic chelating extracting agent D2EHPA/ $BMIMMeSO_4$. The current data are the original measure of uranyl concentration in the solution that was estimated experimentally using Equation (1).

The expected values were generated using Equation (3). The fairly moderate value of the correlation coefficient R^2 (0.9800) was obtained between the experimental and expected response (Fig. 5). It could be due to cover a wide range of process variables in a limited number of experiences and/or the contribution of non-significant terms in the Equation (3). The shape of the response surface was plotted three times by fixing successively the three parameters at the central values. The vicinity around these central values is supposed to include the optimum, and the resulting 3-D representations of the response function, as illustrated by Fig. 6.

CONCLUSIONS

Extraction of UO_2^{2+} ions in aqueous solution was investigated using cloud point extraction by a mixture of using a mixture of non-ionic surfactants Triton X-100 and Tween-40, and a mixture of extracting agent D2EHPA/ $BMIMMeSO_4$ from aqueous solution. The use of ionic liquids $BMIMMeSO_4$, characterized by this wide range, has various advantages such as environmental respect.

3^3 factorial designs were employed to determinate the factors that would influence the extraction of uranium (VI). The most significant effect for uranium (VI) uptake is ascribed to interaction between pH of solution and concentration of uranium (VI) then the interaction between Na_2SO_4 (w/w %) and uranium (VI) concentration. This optimization showed that the best conditions were obtained for pH = 3.0, Na_2SO_4 (% w/w) = 9.0 and $[UO_2^{2+}]$ = 5.50 mM with extraction yield of 99.4 % in one step.

The results show that uranium (VI) was extracted significantly in a single CPE extraction under optimal conditions and the polynomial models developed here can provide a valuable basis for industrial-scale applications as the wastewater treatment**.**

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