Kinetic and Thermodynamic Evaluation of the Uranium (VI) Stripping from Alamine-336 in the Presence of Iron (III)

Mirmohammadi, Seyedeh Leila; Mallah, Mohammad Hassan*[+]; Torkaman, Rezvan; Safdari, Jaber

Material and Nuclear Fuel Cycle Research School, Nuclear Science and Technology Research Institute, PO Box 14155–1339, Tehran, I.R. IRAN

ABSTRACT: *An economic process was developed via the batch scale for the uranium (VI) stripping in the presence of iron (III) from loaded alamine-336 by ammonium carbonate solution. The optimum conditions were assessed for the uranium (VI) stripping using the central composite design method, which is a subset of response surface methodology. The R-squared, U (VI), and Fe (III) stripping percentages with a value of equal 0.989, 72.61%, and 0.1% were obtained, respectively in the optimum conditions of the U (VI) and Fe (III) stripping from loaded alamine-336. The optimum stripping conditions led to the obtaining of the ammonium carbonate concentration equal to 0.64 mol/L, the phase ratio of 0.8 (O/A), the temperature of 53 ℃, the contact time of 2510 seconds, and the shaking speed of 1100 rpm. Moreover, the stripping kinetics, equilibrium constant, and thermodynamic data were determined to describe the nature of the U (VI) and Fe (III) stripping from loaded alamine-336 by the ammonium carbonate solution. The temperature-dependent data showed that the U (VI) stripping was an endothermic process.*

KEYWORDS: *U (VI); Fe (III); Central composite design (CCD); Ammonium carbonate; Alamine-336.*

INTRODUCTION

Yellow cake is the preliminary demand in the uranium (VI) production as a nuclear fuel material. Numerous processes have been developed and operated to produce the yellow cake from various types of ores. Another procedure is purification from leach liquors. The previous reviews have demonstrated that the Solvent Extraction (SX) and ion exchange (IX) play key roles in the uranium (VI) purification from the leach solutions [1-3]. Furthermore, the solvent extraction is widely used and investigated for the uranium (VI) extraction and stripping to produce of purified uranium (VI) and nuclear fuel with a high grade. Back extraction or stripping is an action performed on loaded organic phase for two objectives, including stripping the desired metals and organic phase recycling. A number of reagents can be applied to strip of uranium (VI) from the loaded amine solvents, such as nitrates, chlorides, sulphates, carbonates, hydroxides and acids [3-7]. Jyothi Rajesh Kumar et al. investigated the U (VI) stripping from the real LOS (0.01 mol/L of alamine-336), which contained approximately 106.7 ppm of U (VI) [6]. The organic phase was stripped by several diverse agents, such as 28% ammonia (NH_3), 30% hydrogen

* *To whom correspondence should be addressed.*
+ E-mail: mmallah@aeoi.org.ir
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peroxide (H_2O_2), nitric acid (HNO_3), thiourea, hydrochloric acid (HCl), sulphuric acid (H_2SO_4), ammonium chloride (NH_4Cl), ammonium carbonate ($[NH_4]_2CO_3$), ammonium nitrate (NH_4NO_3), and ammonium tartrate ($(NH_4)_2C_4H_4O_6$) in the range of 0.5–5.0 mol/L. According to the results, the U (VI) stripping from alamine-336 with purity 98% reached 85.5% with 5.0 mol/L of H_2SO_4 through five stages while HCl and HNO_3 with the same concentration stripped 34% and 32% of U (VI) from the organic phase, respectively. By observing the U (VI) stripping efficiency of the other solutions, it could be concluded that ammonium carbonate (0.5 mol/L) is the best, whereas H_2O_2, thiourea and HNO_3 are the weakest U (VI) stripping agents from the LOS. It should be noted that the U (VI) stripping process from the LOS is carried out in five steps [7-12]. *G. Ramadevi et al.* studied the U (VI) stripping from the loaded organic (2% v/v alamine-336). In the mentioned research, the maximum stripping efficiency of 99% was obtained by the mixture of 1 normal of NaCl and 0.2 normal of H_2SO_4 at the ambient temperature and O/A phase ratio of 1:0.75.

C.A. Morais et al. researched the subject of the U (VI) stripping from the LOS (alamine-336) using $(NH_4)_2SO_4$ and H_2SO_4. The study of the effect of H_2SO_4 concentration on the U (VI) stripping in the range of 2.0-5.0 mol/L indicated that the U (VI) stripping efficiency increased from 24% to 75%. In other words, the U (VI) stripping from loaded alamine-336 by H_2SO_4 should be carried out in a high acid concentration [13].

The U (VI) Stripping from the loaded organic phase (0.006 g/L U_3O_8) by ammonium sulfate is an acceptable process, where pH causes no problem for the system. To achieve 99.9% efficiency in the efficiency of the U(VI) stripping, five countercurrent mixer-settler stripping stages are adequate to create a loaded solution with 33 g/L U_3O_8 [14]. This study includes two sections and describes the development of an economic stripping flow sheet for an amine extractant process, which produces a high-assay U (VI) concentrate virtually free of iron. The main objective of the first section is finding the best stripping agent by investigating the initial agents' concentrations and the phase ratio (O/A). To this end, the Response Surface Methodology (RSM) based on Central Composite Design (CCD) method was employed. RSM is a mathematical model reported to be a significantly useful tool in optimizing the preparation conditions of the U(VI) stripping, application of which is not reported in the literature [15, 19].

The main goal in the second section is evaluating the effect of the operational parameters and their interaction on the U (VI) stripping efficiency from alamine-336 by the selected stripping agent. These operational parameters are the initial stripping agent concentration, the phase ratio (O/A), the shaking speed, the temperature, and the contact time. In all experiments, the recovery rate of iron was also checked. In the following, the limited number of experimental studies carried out on the thermodynamics of the U (VI) stripping from the synthetic LOS by selected stripping agent solution. The thermodynamic parameters (e.g., Gibbs free energy, ΔG [KJ/mol], the entropy, ΔS [J/mol.K], and the enthalpy ΔH [KJ/mol]) in the process of the U (VI) stripping from the loaded alamine-336 were obtained by assessing the effects of the temperature and stripping agent concentration on the distribution coefficient. In addition, the slope analysis method was used to determine the stoichiometry of the stripped species.

EXPERIMENTAL SECTION

Stripping experiments were carried out using a batch procedure in two sections. In this regard, the significance variables affecting on the U (VI) stripping efficiency (%) was assessed by shaking 20 mL of the organic phase containing about 250 ppm UO_2 in a 20 mL of any stripping agents.

Design of experiments using response surface methodology

The experiments in the first section were carried out with two independent parameters such as the stripping agent initial concentration and phase ratio. The range and level of the parameters used in this experimental design were taken from the previous experiments by one variable at a time method that carried out separately on each stripping agent. Table 1 indicates the ranges and levels of the investigated parameters.

In section 2, the CCD method also was applied for assessing the amount of the stripping agent concentration (mol/L) (x_1), the phase ratio (O/A) (x_2), the temperature (°C) (x_3), the shaking speed (rpm) (x_4), and call time (s) (x_5). It should be noted that The CCD is based on the complete and partial factorial designs that be done in two levels (-1, +1). In the CCD method, all variables are divided into five levels ($-\alpha$, -1, 0, +1, $+\alpha$), each of which

Table 1: Independent parameters and their selected ranges in the first section of the experiments.

Variables	Lower bound of concentration (mol/L)	Upper bound of concentration (mol/L)	Lower bound of (O/A)	Upper bound of (O/A)
$(NH_4)_2CO_3$	0.25	2	1:4	2:1
NH_4Cl	0.25	4	1:4	2:1
$(Na)_2CO_3$	0.25	2	1:4	2:1
NaOH	0.5	4	1:4	2:1
NaCl (pH:2.4)	0.5	4	1:4	2:1
H_2SO_4	0.25	4	1:4	2:1
HNO_3	0.5	3	1:4	2:1
HCl	0.5	2	1:4	2:1
$HClO_4$	0.25	2	1:4	2:1

is a code for the variable value. $\pm\alpha$ are the lower and upper levels obtained as follows:

$$\alpha^4 = \pm 2^f \quad (1)$$

Where, f is the number of the desired parameters.

According to this, the CCD method characterize the five levels (-α, -1, 0, +1, +α) for each parameters. For example the middle levels (0) for the stripping agent concentration, phase ratio, temperature, time and shaking speed are 0.75 M, 1.0, 45 ℃, 1815 s and 800 rpm and upper levels(+α) are 1 M, 1.5, 65 ℃, 3600 s and 1500 rpm respectively.

Encoding the variable levels is accomplished by a simple linear transformation of the primary measurement scale. This method is used to calculate the coefficients of a quadratic model for prediction of the U (VI) stripping efficiency. The design matrix of the CCD method for five variables including 50 design tests or experiments was presented in Table 2 along with the corresponding response data.

After carrying out the 50 experiments, a quadratic model was fitted for the response data using the expert design software (version 7.0.0) according to Eq. (2), as follows:

$$Y = \beta_0 - \sum_i \beta_i x_i + \sum_i \beta_{ii} x_i^2 + \sum_{i<j} \sum_i \beta_{ij} x_i x_j \quad (2)$$

Where βi, βii and βij are the coefficients of the linear terms (xi), the quadratic terms (xi^2), and the interaction terms (xi, xj) respectively.

The coefficient of each variable indicates its importance in the model and the modeled response. Accordingly, larger values have a greater effect among the standardized coefficients. In addition, the negative coefficient indicates the opposite effect of the relevant factor on the modeled response. The CCD three-dimensional plots allow researchers to visually review the interactions between variables in the plot and the response [15-22]. The effects of each variable and their interaction were evaluated using the design-expert program. In a model, Analysis of Variance (ANOVA) created important terms for each response, and non-significant statistical terms (P>0.05) were taken from by stepwise selection. In addition, experimental data were used to generate the final model. The interactive effects of the factors are visible from the response surface plots derived from the selected model.

Materials

The organic phase used in this study was prepared from 0.1 mol/L of Alamine-336 diluted in kerosene with isodecanole as a modifier, contacting by leach liquor in the phase ratio 1:1 (characterization of Alamine 336 before and later the uranium (VI) stripping can be determined by equipment's such as fourier transform infrared spectroscopy analysis, scanning electron microscope and energy-dispersive X-ray spectroscopy). Leach liquor was collected from Bandarabbas uranium production in the south of Iran, containing about 250 ppm of U (VI) as UO_2. Inductively coupled plasma-optical emission spectrometer (ICP-OES) was used for the analysis of the leach liquor. The results are presented in Table 3. In addition, all of stripping agents used in this study supplied from Sigma Aldrich (Germany). All sections of the CCD test were carried out

Table 2: The experimental design matrix using the CCD.

Run	Levels					C_S (mol/L)	O/A	T (℃)	N (rpm)	t (s)	%S
1	+2.38	0	0	0	0	1.00	1.0	45	800	1815	0.64
2	+1	+1	+1	-1	+1	0.86	1.2	53	506	2566	0.55
3	0	0	0	0	0	0.75	1.0	45	800	1815	0.67
4	+1	+1	-1	-1	-1	0.86	1.2	37	506	1064	0.37
5	-1	-1	-1	+1	-1	0.64	0.8	37	1094	1064	0.74
6	+1	+1	-1	+1	-1	0.86	1.2	37	1094	1064	0.39
7	+1	-1	-1	-1	-1	0.86	0.8	37	506	1064	0.56
8	-1	+1	+1	+1	-1	0.64	1.2	53	1094	1064	0.78
9	+1	+1	+1	+1	-1	0.86	1.2	53	1094	1064	0.58
10	+1	-1	+1	+1	-1	0.86	0.8	53	1094	2566	0.64
11	+1	-1	+1	+1	-1	0.86	0.8	53	1094	1064	0.61
12	-2.38	0	0	0	0	0.50	1.0	45	800	1815	0.41
13	-1	-1	-1	+1	-1	0.64	0.8	37	1094	2566	0.78
14	-1	+1	+1	-1	-1	0.64	1.2	53	506	1064	0.71
15	0	0	0	0	+2.38	0.75	1.0	45	800	3600	0.70
16	-1	+1	+1	+1	-1	0.64	1.2	53	1094	2566	0.75
17	0	0	-2.38	0	0	0.75	1.0	25	800	1815	0.45
18	-1	-1	+1	+1	-1	0.64	0.8	53	1094	2566	0.86
19	-1	-1	+1	+1	-1	0.64	0.8	53	1094	1064	0.81
20	0	0	+2.38	0	0	0.75	1.0	65	800	1815	0.80
21	0	0	0	0	-2.38	0.75	1.0	45	800	30	0.60
22	-1	+1	+1	-1	+1	0.64	1.2	53	506	2566	0.74
23	0	+2.38	0	0	0	0.75	1.5	45	800	1815	0.63
24	0	0	0	0	0	0.75	1.0	45	800	1815	0.68
25	-1	+1	-1	+1	-1	0.64	1.2	37	1094	2566	0.52
26	-1	-1	+1	-1	-1	0.64	0.8	53	506	2566	0.85
27	-1	+1	-1	+1	-1	0.64	1.2	37	1094	1064	0.49
28	-1	+1	-1	-1	-1	0.64	1.2	37	506	1064	0.45
29	0	0	0	-2.38	0	0.75	1.0	45	100	1815	0.65
30	0	0	0	0	0	0.75	1.0	45	800	1815	0.67
31	0	0	0	0	0	0.75	1.0	45	800	1815	0.68
32	+1	-1	-1	-1	+1	0.86	0.8	37	506	2566	0.57
33	+1	+1	-1	-1	+1	0.86	1.2	37	506	2566	0.36
34	-1	-1	+1	-1	-1	0.64	0.8	53	506	1064	0.80

Table 2: The experimental design matrix using the CCD. (Concentration)

Run	Levels					C_S (mol/L)	O/A	T (°C)	N (rpm)	t (s)	%S
35	0	-2.38	0	0	0	0.75	0.5	45	800	1815	0.74
36	0	0	0	0	0	0.75	1.0	45	800	1815	0.67
37	+1	-1	+1	-1	-1	0.86	0.8	53	506	1064	0.68
38	-1	-1	-1	-1	-1	0.64	0.8	37	506	1064	0.73
39	-1	-1	-1	-1	+1	0.64	0.8	37	506	2566	0.76
40	+1	+1	-1	+1	+1	0.86	1.2	37	1094	2566	0.37
41	-1	+1	-1	-1	+1	0.64	1.2	37	506	2566	0.48
42	+1	+1	+1	-1	-1	0.86	1.2	53	506	1064	0.53
43	0	0	0	+2.38	0	0.75	1.0	45	1500	1815	0.68
44	+1	-1	-1	+1	-1	0.86	0.8	37	1094	2566	0.58
45	+1	-1	-1	+1	-1	0.86	0.8	37	1094	1064	0.49
46	+1	-1	+1	-1	+1	0.86	0.8	53	506	2566	0.70
47	0	0	0	0	0	0.75	1.0	45	800	1815	0.67
48	0	0	0	0	0	0.75	1.0	45	800	1815	0.67
49	+1	+1	+1	+1	-1	0.86	1.2	53	1094	2566	0.56
50	0	0	0	0	0	0.75	1.0	45	800	1815	0.67

Table 3. The chemical composition of the leach liquor measured by ICP-OES.

Material	Concentration (ppm)
Uranium (U)	252.2
Magnesium (Mg)	6009
Manganese (Mn)	1578.3
Aluminum (Al)	1200.1
Iron (Fe)	950.8
Calcium (Ca)	881.4
Copper (Cu)	11.35
Zinc (Zn)	8.05
Thorium (Th)	7.12
Cobalt (Co)	6.13
Nickel (Ni)	3.69
Chromium (Cr)	3.11
Tungsten (W)	2.66
Niobium (Nb)	2.5
Thallium (Tl)	2.46
Scandium (Sc)	2.34
Platinum (Pt)	2.34
Vanadium (V)	1.40
Titanium (Ti)	1.00
Molybdenum (Mo)	0.825
Zirconium (Zr)	0.81
Beryllium (Be)	<0.5

Table 4: The results of primary experiments for the best U (VI) stripping agent selection from Alamine-336 with 2% error limit.

Stripping agents	O/A	Concentration (mol/L)	The predicted %S of U (VI) in DOE	%S of U (VI) from the Synthetic LOS	%S of U (VI) from the Real LOS	%S of Fe(III) from the Real LOS
$(NH_4)_2SO_4$	1.16	0.79	77.67	78. 02	77.54	0.15
NH_4Cl	1.16	0.6	42.18	43.68	41.73	1.28
$(Na)_2CO_3$	1.16	0. 72	54.83	54.08	52.61	3.36
NaOH	1.26	1.33	44.56	44.00	42.94	2.01
NaCl (pH:2.4)	1.41	0.6	34.34	36.06	32.4	4.1
H_2SO_4	1.62	2.62	44.72	45.03	42.57	15.4
HNO_3	1.91	1.01	51.78	48.95	52.64	8.4
HCl	1.16	1.16	22.79	25.01	20.15	3.87
$HClO_4$	2.61	1.01	61.92	64.71	58.41	12.5

using the synthetic organic phase prepared from the contacted of alamine-336 diluted in kerosene by a synthetic sulfuric acid solution containing about 280 ppm of UO_2.

RESULTS AND DISCUSSION

Table 4 indicates the results of the CCD experiments for selecting the best stripping agent.

According to Table 4, ammonium carbonate was selected due to its advantages, including simple operation, economical effectiveness and/or desired product by recycling the strip solution. Moreover, the higher selectivity of the U (VI) stripping, compared to other metals (e.g., iron, molybdenum, and vanadium) is a justified reason to opt the ammonium carbonate as the best stripping agent for further investigations. In the present study, the thermodynamic parameters and stoichiometry of the U (VI) stripping from Alamine-336 by ammonium carbonate solution was evaluated for the first time.

Response surfaces analysis

The regression coefficient of the U (VI) stripping from the synthetic LOS by the ammonium carbonate is presented in Eq. (3). The positive and negative signs before each term show the synergistic and antagonistic effects of the respective variables on the response [20-22]. In addition, the number of variables in a term represents the effect of each variable, meaning that a single variable and the two variables in a term are equivalent to a uni-factor and a double factor effect, respectively. Moreover, the second order term of the variable shows the quadratic effect. In this research, the selected model for responses is the cubic model, which consists of six replicate variables in the central points for determining the experimental error.

$$(\%S)^3 = 0.30 + 0.041x_1 - 0.033x_2 + 0.086x_3 + 0.005x_4 + 0.027x_5 + 0.03x_1x_2 - 0.026x_1x_3 - 0.013x_1x_4 - 0.0071\,x_1x_5 + 0.019x_2x_3 + 0.012x_2x_4 - 0.014x_2x_5 + 0.0023\,x_3x_4 + 0.00092\,x_3x_5 - 0.001x_4x_5 - 0.024x_1^2 + 0.0042x_2^2 - 0.0043x_5^2 - 0.018x_1x_2x_3 + 0.0055x_1x_2x_4 + 0.0038x_1x_2x_5 - 0.0049x_1x_3x_4 + 0.0076x_2x_3x_4 - 0.007x_2x_4x_5 - 0.0064x_3x_4x_5 - 0.055x_1^2x_2 - 0.011x_1^2x_5 - 0.15x_1x_2^2 \quad (3)$$

Where *x1*, *x2*, *x3*, *x4*, *x5* are the initial ammonium carbonate concentration (mol/L), the phase ratio (O/A), the temperature (°C), the shaking speed (rpm), and the contact time (s), respectively.

The correlations between the predicted and empirical values were determined according to the regression coefficient. The variance of proportion in the response is shown by the model (R^2), where R is the amount of variation in the responses. Table 5 illustrates the ANOVA for the cubic model for the U (VI) stripping by indicating the sum of the squares and mean square of each factor. Additionally, the F-value as well as Prob. > F values are shown in the mentioned table. According to the results, ANOVA validated the importance and adequacy of the models.

According to Table 5, the mean square values were obtained by dividing the sum of squares of each of the various sources, the model and error variance

Table 5: The ANOVA for response cubic model of the U (VI) stripping by ammonium carbonate solution.

Source	Sum of Squares	df	Mean Square	F- Value	p-value Prob.> F	
Model	1.110	28	0.039649	277.22	< 0.0001	significant
x_1-Cs	0.019	1	0.018668	130.52	< 0.0001	
x_2-O/A	0.012	1	0.01204	84.18	< 0.0001	
x_3-T	0.322	1	0.322498	2254.88	< 0.0001	
x_4-N	0.001	1	0.001131	7.91	0.0105	
x_5-t	0.008	1	0.008065	56.39	< 0.0001	
$x_1 x_2$	0.029	1	0.028541	199.56	< 0.0001	
$x_1 x_3$	0.022	1	0.021688	151.64	< 0.0001	
$x_1 x_4$	0.006	1	0.005593	39.11	< 0.0001	
$x_1 x_5$	0.002	1	0.001639	11.46	0.0028	
$x_2 x_3$	0.011	1	0.011204	78.33	< 0.0001	
$x_2 x_4$	0.005	1	0.004827	33.75	< 0.0001	
$x_2 x_5$	0.006	1	0.006384	44.64	< 0.0001	
$x_3 x_4$	0.000	1	1.74E-08	0.00	0.9913	
$x_3 x_5$	0.000	1	2.71E-05	0.19	0.6681	
$x_4 x_5$	0.000	1	3.34E-05	0.23	0.6340	
x_1^2	0.034	1	0.0342	239.13	< 0.0001	
x_2^2	0.001	1	0.001026	7.18	0.0141	
x_5^2	0.001	1	0.001049	7.34	0.0132	
$x_1 x_2 x_3$	0.011	1	0.01078	75.37	< 0.0001	
$x_1 x_2 x_4$	0.001	1	0.000968	6.77	0.0167	
$x_1 x_2 x_5$	0.000	1	0.000459	3.21	0.0878	
$x_1 x_3 x_4$	0.001	1	0.000757	5.29	0.0318	
$x_2 x_3 x_4$	0.002	1	0.001831	12.81	0.0018	
$x_2 x_4 x_5$	0.002	1	0.001582	11.06	0.0032	
$x_3 x_4 x_5$	0.001	1	0.001307	9.14	0.0065	
$x_1^2 x_2$	0.025	1	0.025443	177.89	< 0.0001	
$x_1^2 x_5$	0.001	1	0.001018	7.12	0.0144	
$x_1 x_2^2$	0.179	1	0.179293	1253.60	< 0.0001	
Residual	0.003	21	0.000143			
Lack of Fit	0.003	14	0.000194	4.79	0.0223	significant
Pure Error	0.000	7	4.06E-05			
Core Total	1.113	49				

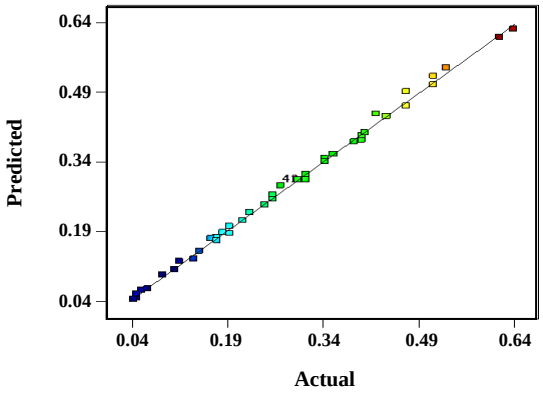


Fig. 1: The predicted values versus the experimental ones for the U (VI) stripping.

by the respective degrees of freedom. The model terms with a value of Prob.> F below 0.05 were considered as significant assets. With respect to the U (VI) stripping, the model F value was 277.22 and Prob. > F value of 0.0001, justifying the model's significance, as can be observed in Table 5. According to the results, all model terms were significant with the exception of CD, CE, and DE. Based on the obtained statistical results, it is evident that the models are suitable in predicting the U(VI) stripping within the range of the studied variables. Furthermore, Fig. 1 indicates the predicted values in comparison with the experimental values of the U(VI) stripping, which indicated the proper matching of the developed models between the process of stripping and responses.

Effects of individual variables and their interactions

According to ANOVA results, the individual effects inflicted on the U(VI) stripping by the ammonium carbonate concentration and the temperature were more superior to the phase ratio (O/A), the contact time and the shaking speed, based on the F-values, which included 130.52 in the ammonium carbonate concentration), 2254.88 in the temperature, 84.18 in the phase ratio (O/A), 56.39 in the contact time, and 7.91 in the shaking speed. The quadratic effect of the ammonium carbonate concentration (F-value of 239.13) was more pronounced, compared to the phase ratio (O/A) (7.18) and contact time (7.34). It shows the relation between the ammonium carbonate concentration and the U (VI) stripping efficiency is not linear. The interaction effects of ammonium carbonate concentration-the phase ratio (O/A), the ammonium carbonate concentration-the temperature, the phase ratio (O/A)-the temperature had a meaningful F-value. Moreover, the interaction effects of the temperature-the contact time, the temperature-the shaking speed, and the shaking speed-the contact time showed significantly low F-values of 1.218E-004, 0.19 and 0.23, respectively. Fig. 2 (a-d) shows the 3D response surfaces, the combined effects of the ammonium carbonate concentration and the phase ratio (O/A) (Fig. 2a), the ammonium carbonate concentration and the temperature (Fig. 2b), the ammonium carbonate concentration and the contact time (Fig. 2c), and the ammonium carbonate concentration and the shaking speed (Fig. 2d) vs U (VI) stripping, respectively. According to Fig. 2a, a higher percentage of the U (VI) stripping was observed with a decrease in the ammonium carbonate concentration from 0.86 to 0.64 mol/L, as well as the decrease in the phase ratio (O/A) from about 1.2 to 0.8. The quadratic effect of ammonium carbonate concentration on the U(VI) stripping efficiency shows that increasing the ammonium carbonate concentration leads to an increase and then a decrease in the U (VI) stripping efficiency. Reduction of the ammonium carbonate concentration prevents the escalation effect of the salting-out on the U (VI) stripping. The salting-out effect reduces the U (VI) stripping efficiency by increasing the amount of the bicarbonate ion. The 3D response surfaces, created to show the two most significant variables (the ammonium carbonate concentration and the temperature) on the U (VI) stripping efficiency, are shown in Fig. 2b, indicating an upsurge in the percentage of the U(VI) stripping at a higher temperature in the range of the ammonium carbonate concentration variable. Increasing the mass transfer by elevation of the temperatures indicated the positive effect of temperature on the U (VI) stripping efficiency. This treatment showed the endothermic reaction between the LOS and ammonium carbonate. Fig. 2 (c and d) indicated the association between the combined ammonium carbonate concentration with the contact time and the shaking speed. It is clear that the contact time and the shaking speed had no significant effect on the U (VI) stripping efficiency. Nonetheless, it is better to consider an optimum contact time and the shaking speed in order to complete this process.

The 3D response surfaces of the interaction between the phase ratio (O/A) and the temperature (constant t:1815 s,

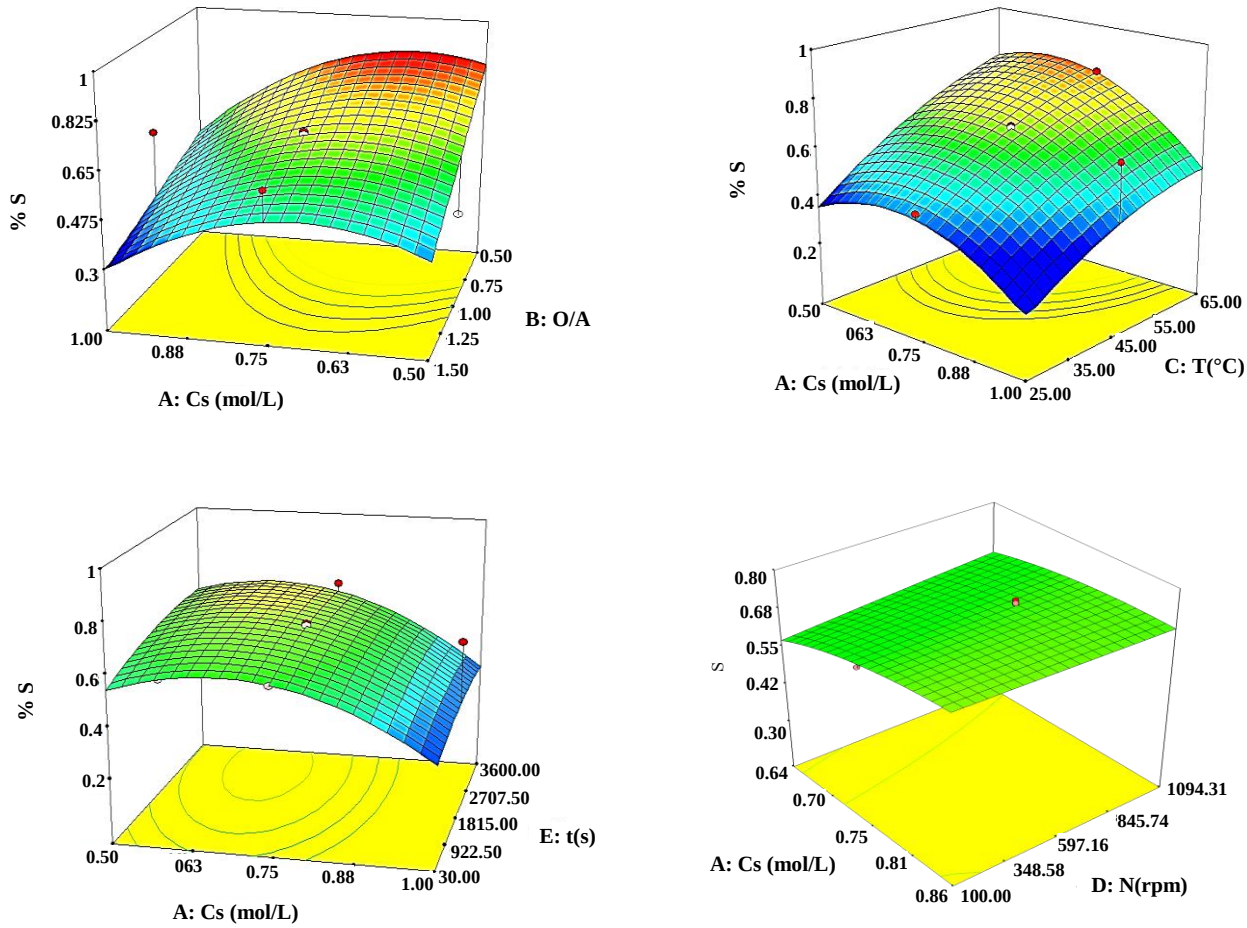


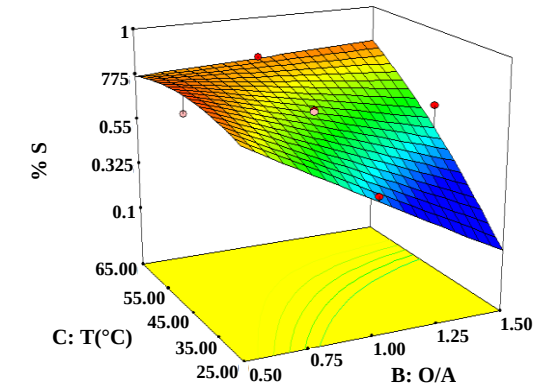
Fig. 2: the three dimensional response surfaces, the combined effects of (a) the ammonium carbonate concentration and the phase ratio (O/A) (at constant t=1815 s, T= 45℃ and N=800 rpm); (b) the ammonium carbonate concentration and the temperature (at constant t=1815 s, O/A= 1 and N=800 rpm); (c) the ammonium carbonate concentration and the contact time (constant N=800 rpm, O/A= 1 and T= 45℃); (d) the ammonium carbonate concentration and the shaking speed at (constant t=1815 s, O/A= 1 and T= 45℃) (d), for U (VI) stripping.

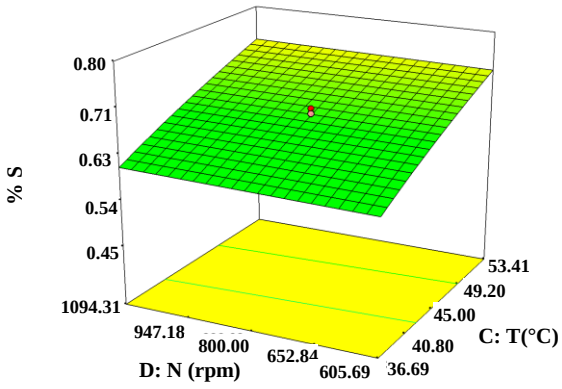
Cs: 0.75 mol/L and N: 800 rpm), the phase ratio (O/A) and the shaking speed (at constant t:1815 s, O/A: 1 and Cs: 0.75 mol/L), the phase ratio (O/A) and the contact time at (constant Cs: 0.75 mol/L, O/A: 1 and T: 45℃) for U(VI) stripping were shown in Fig. 3 (a-c), respectively.

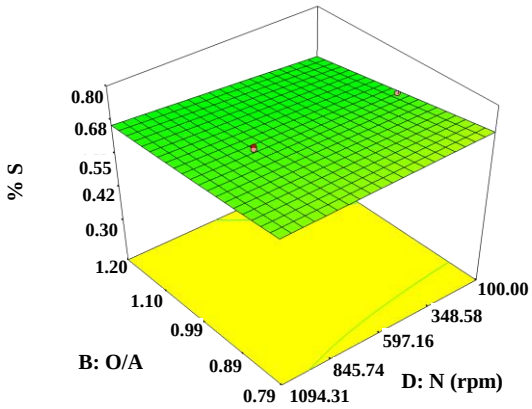
According to Fig. 3, a higher U (VI) stripping efficiency can be obtained by increasing the temperature, shaking speed and time in the range of the phase ratio (O/A). Fig. 3c indicated that the effect of the shaking speed on U (VI) stripping was less than others.

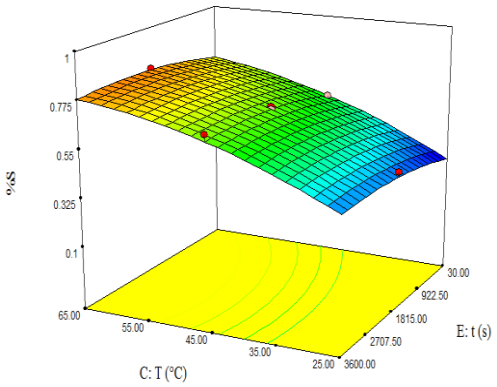
In addition, Fig. 4 (a-c) shows that the 3D response surfaces plot of interaction between the temperature and the contact time (at constant O/A: 1, Cs: 0.75 mol/L and N: 800 rpm), the temperature and the shaking speed (at constant t:1815 s, O/A: 1 and Cs: 0.75 mol/L) and the shaking speed and contact time (at constant Cs: 0.75 mol/L, O/A: 1 and T: 45℃)) for the U(VI) stripping, respectively. In this regard, it was concluded that all of these parameters had positive effects on the U(VI) stripping.

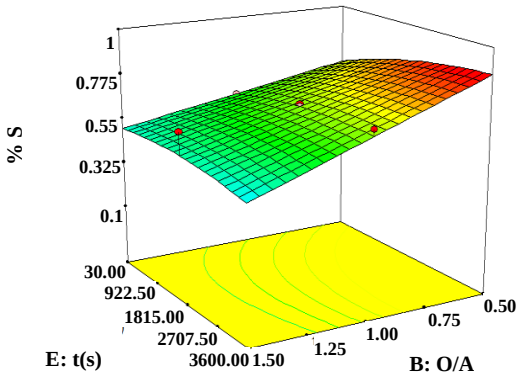
Furthermore, it could be observed from Fig. 4 (a-c) that an increase in the temperature, time and shaking speed led to a higher U (VI) stripping efficiency. Nevertheless, it is obvious that the temperature had the most significant effect on the U (VI) stripping efficiency due to the endothermic reaction between the ammonium carbonate solution and LOS.











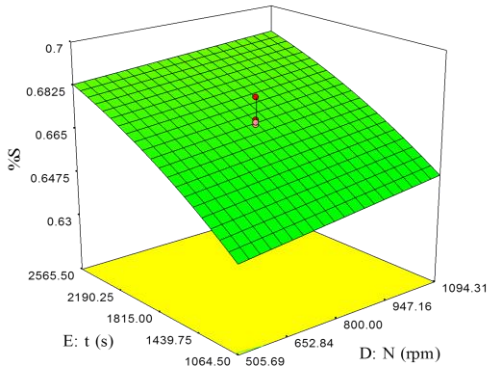


Fig. 3: The three dimensional response surfaces of interaction between (a) the phase ratio (O/A) and the temperature (at constant t=1815 s, Cs= 0.75 mol/L and N=800 rpm); (b) the phase ratio (O/A) and the shaking speed (at constant t=1815 s, O/A= 1 and Cs= 0.75 mol/L); (c) the phase ratio (O/A) and the contact time (at constant Cs= 0.75 mol/L, O/A= 1 and T= 45℃) for U (VI) stripping.

Fig. 4: The three dimensional response surfaces of interaction between (a) the temperature and the shaking speed (at constant t=1815 s, O/A= 1 and Cs= 0.75 mol/L), (b) the temperature and the contact time (at constant O/A=1, Cs= 0.75 mol/L and N=800 rpm); (c) the shaking speed and the contact time (at constant Cs= 0.75 mol/L, O/A= 1 and T= 45℃) for U (VI) stripping.

Table 6: Comparison between the predicted optimal conditions of the DOE and experimental result.

Stripping agent	$(NH_4)_2CO_3$
C_s (mol/L)	0.64
O/A	1
T (℃)	53
t (s)	2565
N (rpm)	1100
% S predicted of U (VI) in DOE	72.61
% S of U (VI) from Synthetic LOS	73.31
% S of U (VI) from Real LOS	72.21
% S of Fe(III) from Real LOS	0.10

Process optimization

In this research, the design-expert software was exploited to optimize the effective parameters on the U(VI) stripping efficiency from the LOS. In the optimization analysis, the target criterion was set as a maximum value for the response [15, 21]. In this respect, the obtained optimum stripping conditions were the ammonium carbonate concentration of 0.64 mol/L, the phase ratio (O/A) of 0.8, the temperature of 53℃, the contact time of 2510 seconds, and the shaking speed of about 1100 rpm with R^2 equal 0.989, as presented in Table 6. It should be noted that the R^2 equal 0.989 indicates the regression predictions perfectly fit the data.

The predicted and experimental values obtained in the optimum conditions were 72.61% and 71.31%, 74.21% for U(VI) stripping from the synthetic and real LOS, respectively, showing an acceptable agreement between the experimental and predicted values of the model. The error obtained from the comparison of these values was relatively small, approximately, 1.3 and 1.6.

Reaction Equation

Organic and aqueous phases were mixed with the same volume of about 10 mL (O/A: 1) in reaction bottles, using a thermostatic water shaking adjusted to 53°C for stripping experiments. After shaking about optimum time, the phases were separated using a separation funnel. The U (VI) and Fe (III) concentrations in the aqueous phase after stripping were determined by the ICP-OES. In addition, the amount of metal ion in the organic phase was obtained by mass balance. The distribution coefficients of the stripping operation (Ds) and the stripping efficiency (%S) were defined as follows: The aqueous samples were analyzed using an ICP-OES and the stripping efficiencies and distribution coefficients were evaluated using the following equation:

$$\%S = 100 \times \frac{D_S \times \frac{[V_{aqueous}]}{[V_{organic}]}}{1 + \left(D_S \times \frac{[V_{aqueous}]}{[V_{organic}]} \right)} \quad (4)$$

where the distribution coefficient, $D_s = \frac{[M_{aqueous}]}{[M_{organic}]}$, that [M] in the present case is the concentration of UO_2 after the stripping process, and $V_{aqueous}$ and $V_{organic}$ are the volumes of the aqueous and organic phases, respectively.

The U (VI) and Fe (III) stripping by ammonium carbonate solution

The larger fraction of the U (VI) and Fe (III) complexes in the sulfate leach liquors was present as $U0_2(S0_4)_3^{4-}$ and $Fe(SO_4)^-{}_2$, which could integrate with $(R_3NH)_2(SO_4)$ to form $[(R_3NH)_4UO_2(SO_4)_3]_{org}$ and $(R_3NH)[Fe\,(SO_4)_2]$, respectively. Therefore, U (VI) and Fe (III) stripping from the LOS by the ammonium carbonate solution can be represented by the Eqs. (5) and (8), respectively [23-25].

$$\left[(R_3NH)_4\,UO_2\,(SO_4)_3\right]_{org} + x\left((NH_4)_2\,CO_3\right)_{aq} \rightleftharpoons \quad (5)$$

$$4\,(R_3N)_{org} + (UO_2(CO_3)_3^{4-})_{aq} + (x-3)(HCO_3^-)_{aq} + 3\,(SO_4^{2-})_{aq} + 2x(NH_4^+)_{aq}$$

$$K_{eq\,U(VI)} = \quad (6)$$

$$\frac{[R_3N]^4 \cdot \left[UO_2(CO_3)_3^{-4}\right]^{\circ} \cdot \left[(HCO_3^-)\right]^{(x-3)} \cdot \left[(SO_4^{-2})\right]^3 \left[(NH_4)\right]^{+2x}}{\left[(R_3NH)_4\,UO_2(SO_4)_3\right]^{\circ} \cdot \left[(NH_4)_2\,CO_3\right]^3}$$

$$= \frac{D_{U(VI)} \cdot [(R_3N)_{org}]^4 . [(HCO_3^-)]^{(x-3)} . [(SO_4^{2-})]^3 . \left[(NH_4)\right]^{+2x}}{\left[\left((NH_4)_2\,CO_3\right)_{aq}\right]^x}$$

$$\log D_{U(VI)} = \log K_{eq\,U(VI)} + x \log\left[(NH_4)_2\,CO_3\right] - \quad (7)$$

$$4 \log[(R_3N)] - (x-3)\log\left[HCO_3^-\right] - 3 \log[SO_4^{(2-)}] - 2x \log[(NH_4)^+]$$

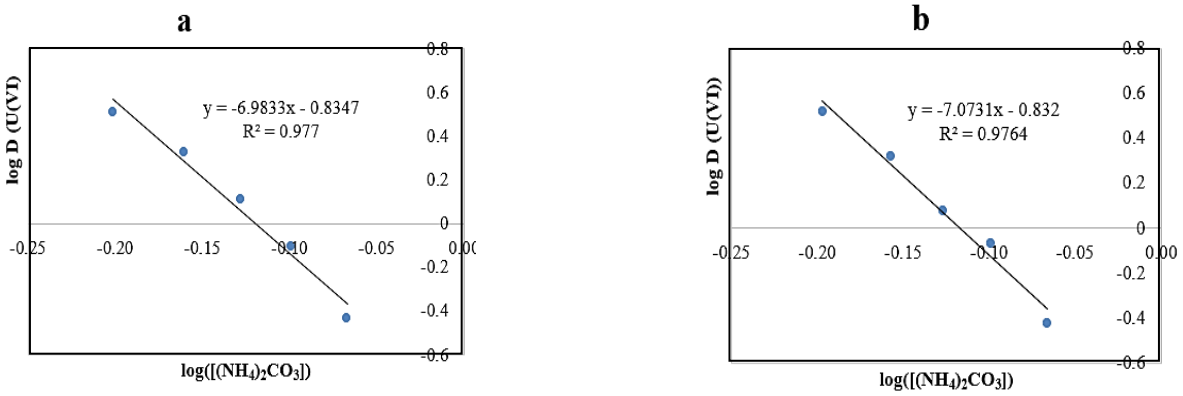


Fig. 5: Log–log relationship between stripping distribution of U (VI) from the real LOS (a) and synthetic LOS (b) with different [(NH4)2CO3].

$$2\left((R_3NH)\left[Fe\,(SO_4)_2\right]\right)_{org} + y\left((NH_4)_2\,CO_3\right)_{aq} \rightleftharpoons \quad (8)$$

$$2\left(R_3NH^+\right)_{org} + 4(SO_4^{2-})_{aq} + \left(Fe_2(CO_3)_3\right)_{aq} +$$

$$(y-3)(CO_3^{2-})_{aq} + 2y(NH_4^+)_{aq}$$

$$K_{eq\,Fe^{3+}} = \quad (9)$$

$$\frac{\left[R_3NH^+\right]^2\cdot\left[Fe_2(CO_3)_3\right]^{\circ}\cdot\left[\left(SO_4^{-2}\right)\right]^4\cdot\left[(NH_4)^+\right]^{2y}\left[\left(CO_3^-\right)\right]^{(y-3)}}{\left[(R_3NH)\left[Fe(SO_4)_2\right]\right]^2\cdot\left[\left((NH_4)_2\,CO_3\right)_{aq}\right]^y}$$

$$= \frac{D_{Fe^{3+}}\cdot\left[\left(R_3NH^+\right)\right]^2\cdot[(SO_4^{2-})]^4\cdot[(NH_4)^+]^{2y}\cdot[CO_3^-]^{(y-3)}}{\left[\left((NH_4)_2\,CO_3\right)_{aq}\right]^y}$$

$$\log D_{Fe^{3+}} = \log K_{eq\,Fe^{3+}} - 2\log[R_3NH^+] - \quad (10)$$

$$(y-3)\log[CO_3^{2-}] - 2y.\log[(NH_4)^+] -$$

$$4\log[SO_4^{2-}] + y\log\left[(NH_4)_2\,CO_3\right)]$$

According to Eq. (5), the coefficient of ammonium carbonate for the U (VI) stripping from the synthetic and real LOS process was equal to the slope of the plot of the logarithmic distribution coefficient of the U (VI) stripping and the equilibrium concentration of the ammonium carbonate solution.

Figs.5a and 5b showed the relationship between the logarithmic distribution coefficient, for the U(VI) stripping from the real (5,a) and the synthetic LOS(5,b), and the equilibrium concentration of ammonium carbonate, respectively.

In this regard, the slope was about seven for the two types of the LOSs. It is confirmed that seven moles of ammonium carbonate was sufficient for complete performing of the reaction when one mole of the complex of U (VI) is stripped. According to Eq. (8), the coefficient of ammonium carbonate for the Fe (III) stripping from the real LOS process was equal to the slope of the plot of the logarithmic distribution coefficient of the Fe (III) stripping and the equilibrium concentration of the ammonium carbonate solution. Fig. 6 demonstrated a log–log-linear plot, slope of which was reported at around four.

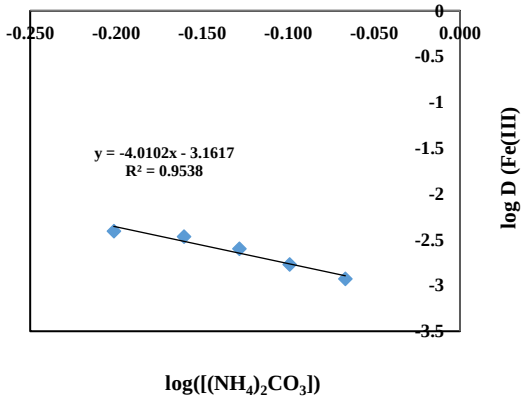


Fig. 6: Log–log relationship between stripping distribution of Fe (III) from the real LOS with different [(NH4)2CO3].

This fact indicated the participation of the four molecules of ammonium carbonate in the Fe (III) species. Based on these results, the U (VI) and Fe (III) can be defined by Eqs. (11) and (12):

$$(R_3NH)_4\,UO_2(SO_4)_3 + 7(NH_4)_2\,CO_3 \rightleftharpoons \quad (11)$$

$$4R_3N + UO_2(CO_3)_3^{4-} + 4HCO_3^- + 3SO_4^{2-} + 14(NH_4)^+$$

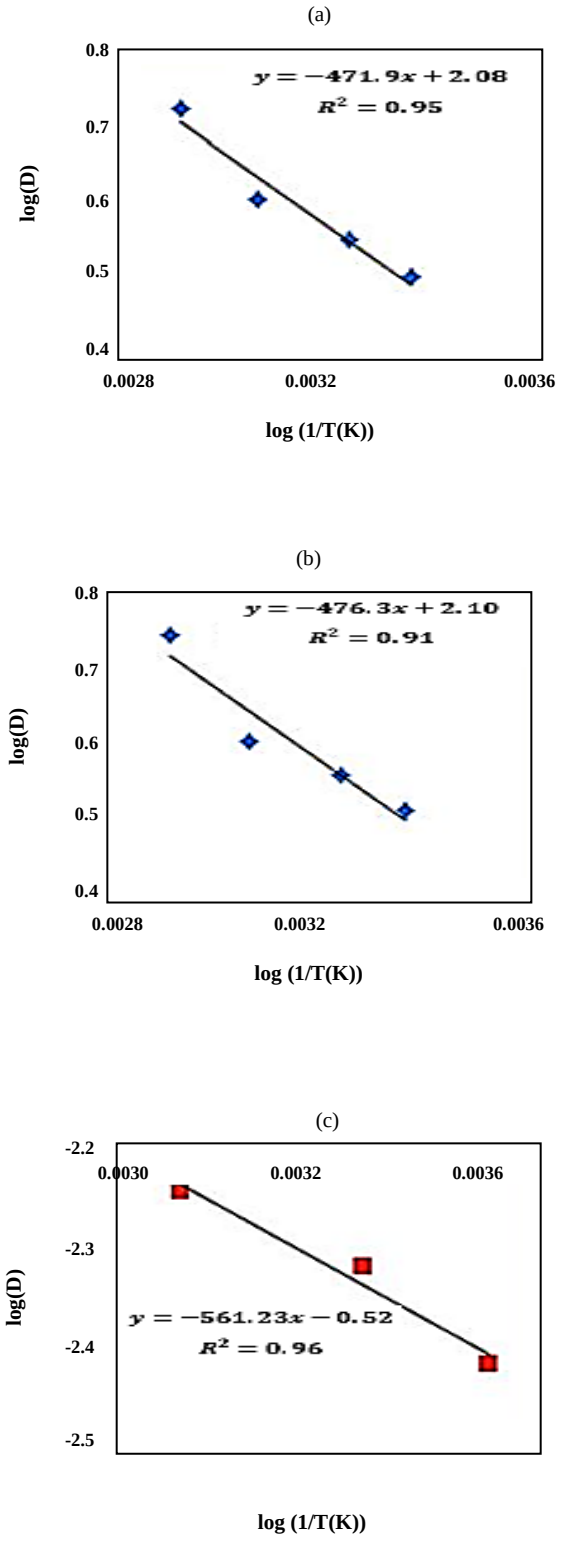


Fig. 7: Variation of stripping distribution of U (VI) from the synthetic LOS (a), U (VI) from the real LOS (b), and Fe (III) from the real LOS (c) vs log 1/T.

$$(R_3NH)[Fe(SO_4)_2] + 4(NH_4)_2CO_3 \rightleftharpoons 2R_3NH^+ + 4\,SO_4^{2-} + Fe_2(CO_3)_3 + CO_3^{2-} + 8\,NH_4^+ \quad (12)$$

Thermodynamic characteristics in the U (VI) and Fe (III) stripping process

The thermodynamic parameters of the studied stripping process have been determined by a series of experiments carried out at the various temperatures ranging from 25 to 60 ºC. The plot of log $D_{U(VI)}$ versus 1/T were shown for the U (VI) stripping from the synthetic and real LOS using ammonium carbonate solution and log $D_{Fe(III)}$ against 1/T for the Fe (III) stripping from the real LOS by the ammonium carbonate solution in Fig. 7.

The thermodynamic parameters of the studied stripping process have been determined by a series of experiments, carried out at various temperatures ranging from 25 to 60 ºC. The value of ΔH was obtained from the slope of the latter plots while the Gibbs free energy, ΔG (KJ/ mol) and the entropy, ΔS (J/mol. K), were calculated for this system using the following Van't Hoff equations:

$$\log D = \frac{-\Delta H}{2.303R}.\frac{1}{T} + C \quad (13)$$

$$\Delta G = -RT \ln K_{eq} \quad (14)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (15)$$

Where R (J/mol. K), T and D_s are the mol/L gas constant, the temperature in Kelvin, and the distribution coefficient, respectively. The calculated values of the thermodynamic parameters for the U (VI) and Fe (III) stripping from synthetic and real LOS were presented in Table 7, respectively. Obviously, the positive value of ΔH for both metal ions showed that the U (VI) and Fe (III) stripping by the ammonium carbonate from real LOS was of an endothermic nature, whereas a decrease in the positive numerical values of ΔG with increasing the temperature indicated that the stripping reaction was not spontaneous. In addition, the negative ΔS parameter suggested the decrease of the system randomness at the liquid-liquid interface during the stripping process.

CONCLUSIONS

Five stripping parameters (the ammonium carbonate concentration (mol/L), the phase ratio (O/A), the temperature (°C), the shaking speed (rpm), and the contact

Table 7: The calculated values of the thermodynamic parameters for U (VI) and Fe (III) stripping from synthetic and real LOS.

System	Equilibrium constants (log K_{eq})	ΔH ($\frac{kJ}{mol}$)	ΔG ($\frac{kJ}{mol}$)	ΔS ($\frac{J}{mol.K}$)
Synthetic LOS (U (VI))	-3.17	9.12	19.82	-32.80
Real LOS (U (VI))	-3.20	9.03	20.01	-33.60
Real LOS (Fe (III))	-8.55	10.74	53.46	-130.80

time (s) were optimized with the aid of CCD for maximizing the U (VI) ion stripping percentage from the LOS. Based on the data analysis, the individual effects of the ammonium carbonate concentration and the temperature on the U (VI) stripping efficiency were superior to the phase ratio (O/A), the contact time and the shaking speed. Meanwhile, the interaction effect of the ammonium carbonate concentration, the phase ratio (O/A), the ammonium carbonate concentration, the temperature and the phase ratio (O/A) were more significant with respect to the U (VI) stripping efficiency. The highest U (VI) stripping percentage of the ammonium carbonate was calculated under the optimum conditions of the ammonium carbonate concentration (0.64 mol/L), the phase ratio (O/A: 0.8), the temperature (53°C), the contact time 2510 s, and the shaking speed of about 1100 rpm with the desirability of 0.99. The experimental data demonstrated an acceptable agreement with the predicted data by the model. The stoichiometric coefficients, equilibrium constants, and thermodynamic parameters for the U (VI) stripping from the synthetic and the real LOS and the Fe (III) stripping from the real LOS were calculated. The reactive U (VI) and Fe (III) stripping by the ammonium carbonate solution were endothermic, as indicated by the positive sign of ΔH.

Nomenclature

U (VI)	Uranium (VI)
Fe (III)	Iron (III)
%S	Stripping Efficiency
D_s	Stripping Distribution Coefficients
LOS	Loaded Organic Solution
C_s	Stripping Agent Concentration
O/A	Organic Phase to Aqueous Phase
CCD	Central Composite Design
DOE	Design of Expert
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometer
R^2	R-Squared
ANOVA	Analysis of Variance
df	Degrees of Freedom
P-value	Probability Value

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