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Optimization of process parameters for the extraction of chromium (VI) by emulsion liquid membrane using response surface methodology

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ABSTRACT

The emulsion liquid membrane technique was used for the extraction of hexavalent chromium ions from aqueous solution of waste sodium dichromate recovered from the pharmaceutical industry wastewater. The liquid membrane used was composed of kerosene oil as the solvent, Span-80 as the surfactant and potassium hydroxide as internal reagent. Trioctyl amine and Aliquat-336 were used as carriers. The emulsion stability was carried out at different surfactant concentration, agitation speed and emulsification time. Statistical experimental design was applied for the optimization of process parameters for the extraction of chromium by emulsion liquid membrane. The effects of process parameters namely, agitation speed, membrane to emulsion (M/E) ratio and carrier concentration on the extraction of chromium were optimized using a response surface method. The optimum conditions for the extraction of chromium (VI) using response surface methodology for Trioctyl amine were: agitation speed – 201.369 rpm, M/E ratio – 0.5887% (v/v) and carrier concentration – 4.0932% (v/v) and for Aliquat-336: agitation speed – 202.097 rpm, M/E ratio – 0.5873% (v/v) and carrier concentration – 3.9211% (v/v). At the optimized condition the maximum chromium extraction was found to be 89.2% and 96.15% using Trioctyl amine and Aliquat-336, respectively.

1. Introduction

Emulsion liquid membrane (ELM) is an improved solvent extraction technique that has found its application in separation of organic acids and bases, pharmaceutical separations, extraction of fructose and treatment of industrial wastewaters containing a wide range of toxic contaminants such as phenol [1–7]. This technique offers some advantages in comparison to common liquid–liquid extraction such as improvement of kinetics, selectivity of species to be removed and decreasing the necessary volume ratio of organic phase to aqueous feed solution. Further, it is characterized by simplicity and high efficiency. Besides these advantages, ELM processes allow very high mass transfer rates due to a large surface area within the emulsion globules and internal droplets. The ELM process is expected to become increasingly important in hydrometallurgical operations. This advanced extraction technique has a very good commercial potential. The ELM process contains a three-phase dispersion system, which consists of a stripping phase encapsulated by a membrane phase (organic phase), which in turn contains the extractant in an organic diluent together with a surfactant to stabilize the emulsion droplet. Thus the ELM process involves simultaneous extraction and stripping in one step. Metallic solutes present in lean solution form a complex with the extractant. The complex formed then diffuses through a membrane phase to a stripping phase interface from where it is stripped into the bulk of the encapsulated stripping phase. The volume of stripping zone liquid is very small compared to that of the aqueous feed phase, thereby resulting in concentration of chromium (VI). The concentrated chromium (VI) from the strip phase can be recovered by breaking the emulsion. Liquid membrane technique has been widely applied by researchers in various areas of separation and extraction, of which heavy metal ions are of particular interest [8–11].

RSM provides important information regarding the optimum level of each variable along with its interactions with other variables and their effects on product yield. It reduces the number of experiments without neglecting the interaction among the parameters. This multivariate approach also improves statistical interpretation possibilities, and evaluates the relative significance of several affecting factors even in the presence of complex interactions. RSM is widely used for multivariable optimization studies in several biotechnological processes such as optimization of media, process conditions, catalyzed reaction conditions, oxidation, production, fermentation, biosorption of metals, etc. [12–18]. It has also been used to determine the optimal values for process parameters such as pH, temperature, aeration, feeding rates in various processes [19–22].

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Chromium is considered as one of the highly toxic heavy metal, which is commonly used in a number of industrial applications such as mining, leather tanning, textile dyeing, electroplating, aluminium conversion coating operations, production of industrial inorganic chemicals and pigments, and wood preservatives. Chromium bearing wastewater resulting from all these industries must be disposed off after treatment. Emulsion liquid membrane separation technique provides a potentially powerful technique for the removal of chromium (VI) ions from the wastewater [23–29]. Although some works on this particular aspect are available, comprehensive and detailed studies on the interaction between process variables are yet to be carried out. So, in this work, an attempt was made to optimize the process parameters such as agitation speed, membrane to emulsion (M/E) ratio and carrier concentration using statistical experiment design and to study the linear, square and interactive effects of process parameters on extraction of chromium (VI) from pharmaceutical wastewater by ELM.

2. Materials and methods

The characteristics of sodium dichromate recovered from pharmaceutical industry wastewater were analyzed according to the procedure given in APHA [30]. The constituents of the liquid membrane used in this study were: Kerosene oil as the solvent and Span-80 as surfactant to stabilize water-in-oil emulsions. Aliquat-336 (tricaprylmethylammonium chloride or methyltrioctylammonium chloride) and Trioctyl amine were used as carriers. The internal reagent was potassium hydroxide (0.1N). Since, the success of ELM largely depends on its stability, stable emulsion formulation was found experimentally. The organic phase initially contains 0.25–1.75% (v/v) surfactant, carrier and the rest solvent. The mixture is then stirred at different speeds ranging from 2500 to 5000 rpm with various emulsification times from 0.2 to 1 h to optimize the process conditions for obtaining stable emulsion.

2.1. Experiments

A glass mixer-settler, 12.5 cm diameter fitted with a stop-cock for easy sampling and a variable speed turbine impeller was used for batch extraction. The primary emulsion (W/O) was prepared by gradually dripping KOH solution into the oil phase in a beaker by high speed stirring at around 4500 rpm for about 30 min. The resultant milky white emulsion (40 ml) was then dispersed at 150 rpm, in the external aqueous phase (200 ml) containing solutes (Cr (VI) as feed in the form of sodium dichromate) in the mixer-settler for 30 min. During this period, the solute transport occurs through the membrane phase into the internal stripping phase where it is concentrated. The treated sample was then separated from the emulsion and filtered before analyzing for chromium, using a UV spectrophotometer at 540 nm.

2.2. Experimental design and procedure

An orthogonal 2^3 factorial central composite experimental design with 6 star points ($\alpha = 1.68$) and 6 replicates at the center point, all in duplicates, resulting in a total of 20 experiments were used to optimize the chosen key variables for the extraction of chromium. The experiments with different agitation speeds of 70, 140, 210, 280 and 350 rpm, M/E ratio 0.2, 0.4, 0.6, 0.8 and 1.0% (v/v) and five different carrier concentration 2, 3, 4, 5 and 6% (v/v) were employed simultaneously covering the spectrum of variables for the percentage extraction of chromium in the Central Composite Design. In order to describe the effects of agitation speed (X_1), M/E ratio (X_2) and carrier concentration (X_3) on percentage of chromium extraction, batch experiments were conducted. The coded values of the process parameters were determined by the following equation:

$$x_i = \frac{X_i - X_0}{\Delta x} \quad (1)$$

where x_i is the coded value of the ith variable, X_i the uncoded value of the ith test variable and X_0 is the uncoded value of the ith test variable at center point.

The range and levels of individual variables were given in Table 1. The experiment design was given in Table 3 along with experimental data and predicted responses. The percentage extraction of chromium is the response. The regression analysis was performed to estimate the response function as a second-order polynomial:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i^2 + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \beta_{ij} X_i X_j \quad (2)$$

where Y is the predicted response, β_i, β_j, β_{ij} are coefficients estimated from regression, they represent the linear, quadratic and cross-products of x_1, x_2, x_3 on response.

A statistical program package Design Expert 7.1.5, was used for regression analysis of the data obtained and to estimate the coefficient of the regression equation. The equations were validated by the statistical tests called the analysis of variance (ANOVA) analysis. The significance of each term in the equation is to estimate the goodness of fit in each case. Response surfaces were drawn to determine the individual and interactive effects of test variable on percentage extraction of chromium. The optimal values of the test variables were first obtained in coded units and then converted to the uncoded units.

Table 1
The levels of different process variables in coded and un-coded form for the extraction of chromium.

Independent variable	Range and levels				
	$-\alpha$	−1	0	1	α
Agitation speed (X_1, rpm)	70	140	210	280	350
M/E ratio (X_2, % v/v)	0.2	0.4	0.6	0.8	1.0
Carrier concentration (X_3, % v/v)	2	3	4	5	6

3. Results and discussion

The initial characteristic of sodium dichromate recovered from the pharmaceutical industrial effluent is studied and is given in Table 2. The pH of the sodium dichromate is between 1.2 and 1.5. The acidic nature of the effluent is because of oxidation of the Ibu-aldehyde to Ibu-acid by using the oxidizing agent such as concentrated sulphuric acid and sodium dichromate powder. The used sodium dichromate is removed and recovered as sodium dichromate from the wastewater. The diluted solution is corrosive, black in colour and odourless.

Table 2
Characterization of waste sodium dichromate.

Parameter	Values
pH	1.2–1.5
Specific gravity	1.7–1.8
Odour	Odourless
$Cr_2O_7^{2-}$	90–93%
SO_4^{2-}	5–8%
HCO_3	2–3%

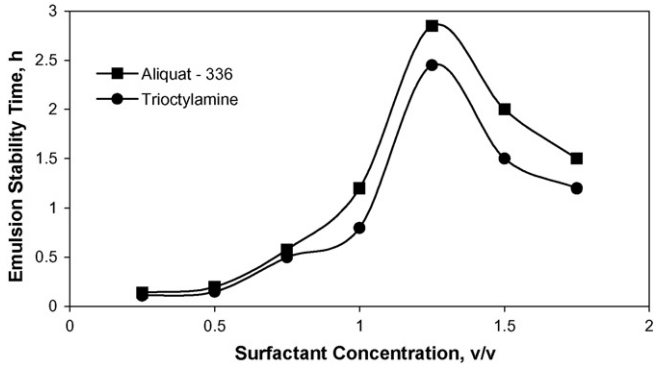

Fig. 1. Effect of surfactant concentration on emulsion stability for both carriers.

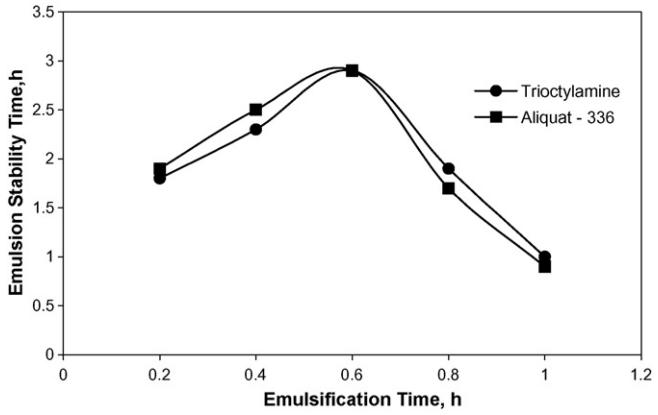

Fig. 2. Effect of emulsification time on emulsion stability for both carriers.

3.1. Emulsion stability

The emulsion stability is studied by varying the parameter like surfactant concentration, agitation speed and emulsification time. From Figs. 1 to 3, it is observed that increase in surfactant concentration (up to 1.25% (v/v)), emulsion time (up to 0.4 h) and agitation speed (up to 4500 rpm) increases the stability of emulsion. Further increase in those conditions reduces the stability time. From the experiments, the stable emulsion is formed at: surfactant concentration, 1.25% (v/v); emulsion time, 30 min and agitation speed, 4500 rpm.

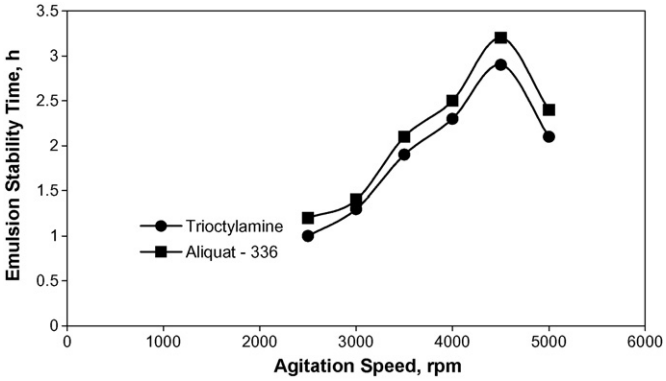

Fig. 3. Effect of agitation speed on emulsion stability for both carriers.

3.2. Optimization of process parameters for the extraction of chromium using Trioctyl amine carrier

The coded values of the test variables and the experimental results of percentage extraction of chromium using Trioctyl amine are presented in Table 3. Multiple regression analysis of the experimental data yielded the following regression equation for the percentage extraction of chromium:

$$Y_1 = 89.20 - 1.96 \times X_1 - 0.90 \times X_2 + 1.47 \times X_3 - 3.10 \times X_1 \times X_2 - 0.58 \times X_1 \times X_3 + 2.59 \times X_2 \times X_3 - 9.43 \times X_1^2 - 5.82 \times X_2^2 - 3.24 \times X_3^2 \quad (3)$$

where Y_1 is the percentage extraction of chromium using Trioctyl amine, X_1 is the agitation speed, X_2 is the M/E ratio, X_3 is the carrier concentration. The value of regression coefficient ($R^2 = 0.9628$) is closer to one indicates that the correlation is best suited in predicting the values for the extraction system and the predicted values are found to be closer to the experimental results.

Table 4 shows the ANOVA model for the percentage extraction of chromium using Trioctyl amine. ANOVA is required to test the

Table 3
Central Composite Design matrix along with predicted and experimental values of percentage extraction of chromium.

Run no.	X_1	X_2	X_3	Trioctyl amine		Aliquat-336	
				Experimental	Predicted	Experimental	Predicted
1	0.00000	0.00000	0.00000	89.05	89.19	96.10	96.15
2	0.00000	1.68179	0.00000	70.30	71.24	76.90	77.97
3	−1.00000	1.00000	−1.00000	69.40	70.23	75.60	76.66
4	0.00000	0.00000	0.00000	89.08	89.19	95.98	96.15
5	1.00000	1.00000	−1.00000	62.10	61.27	69.20	68.06
6	0.00000	0.00000	−1.68179	79.10	77.56	85.90	84.34
7	−1.00000	−1.00000	1.00000	66.30	69.93	73.00	76.66
8	0.00000	0.00000	0.00000	89.02	89.19	96.10	96.15
9	0.00000	−1.68179	0.00000	79.10	74.25	86.20	81.57
10	1.00000	−1.00000	−1.00000	72.20	69.93	79.10	81.6
11	−1.00000	−1.00000	−1.00000	68.40	71.01	75.90	78.12
12	0.00000	0.00000	1.68179	84.90	82.50	90.80	88.78
13	0.00000	0.00000	0.00000	89.06	89.19	96.05	96.15
14	−1.00000	1.00000	1.00000	78.99	79.51	85.90	85.92
15	−1.68179	0.00000	0.00000	68.98	65.82	75.30	72.38
16	1.68179	0.00000	0.00000	59.99	59.23	66.60	65.96
17	1.00000	1.00000	1.00000	68.05	68.23	74.50	74.8
18	0.00000	0.00000	0.00000	89.05	89.19	96.10	96.15
19	0.00000	1.68179	0.00000	70.30	71.24	76.90	77.97
20	−1.00000	1.00000	−1.00000	69.40	70.23	75.60	76.66

X_1: agitation speed (rpm); X_2: M/E ratio; X_3: carrier concentration.

Table 4
Analysis of variance (ANOVA) for response surface quadratic model for the percentage extraction of chromium using Trioctyl amine as carrier.

Source	Coefficient factor	Sum of squares	DF	Mean square	*F*	*P*-value Prob > *F*
Model	89.20	1906.53	9	211.84	28.78	<0.0001[a]
X_1	−1.96	52.43	1	52.43	7.12	0.0235[a]
X_2	−0.90	11.01	1	11.01	1.50	0.2494
X_3	1.47	29.57	1	29.57	4.02	0.0729
$X_1 \times X_2$	−3.10	77.13	1	77.13	10.48	0.0089[a]
$X_1 \times X_3$	−0.58	2.69	1	2.69	0.37	0.5589
$X_2 \times X_3$	2.59	53.77	1	53.77	7.31	<0.0222[a]
X_1^2	−9.43	1281.96	1	1281.96	174.17	<0.0001[a]
X_2^2	−5.82	488.16	1	488.16	66.32	<0.0001[a]
X_3^2	−3.24	151.20	1	151.20	20.54	<0.0011[a]
Residual		73.60	10	7.36		
Lack of Fit		73.58	5	14.72	3763.90	<0.0001[a]
Pure error		0.020	5	0.00391		
Cor total		1980.14	19			

Std. Dev.: 2.71; R^2: 0.9628; mean: 76.57; Adj R^2: 0.9294; C.V. %: 3.54; Pred $R^{2:}$: 0.7180; Adeq precision: 15.624.
[a] Significant variable.

significance and adequacy of the model. The mean squares are obtained by dividing the sum of squares of each of the two sources of variations, the model and the error variance, by the respective degrees of freedom. The fishers variance ratio *F*-value = (Sr^2/Se^2) is the ratio of the mean square owing to regression to the mean square owing to error. It is the measure of variation in the data about the mean. Here the ANOVA of the regression model demonstrates that the model is highly significant as evident from the calculated *F*-value (28.78) and a very low probability value (P = <0.0001). It is also observed that the coefficient for squared effect is highly significant (P = <0.0001) when compared with the individual and interactive effect. The Lack of Fit *F*-value of 3763.90 implies the Lack of Fit is significant. There is only a 0.01% chance that a "Lack of Fit *F*-value" this large could occur due to noise. The Pred R^2 of 0.7180 is not as close to the Adjusted R^2 of 0.9294 as one might normally expect. This may indicate a large block effect or a possible problem with model and/or data. Things to consider are model reduction, response tranformation, outliers, etc. "Adequate Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Here the ratio of 15.624 indicates an adequate signal. A plot of experimental and RSM predicted values is shown in Fig. 4 and the deviation is found to be less than 5%.

The *P*-values are used as tool to check the significance of each of the coefficients, which in turn, may indicate the patterns of the interaction among the variables. Larger the magnitude of *T* and smaller the value of *P* indicate that the corresponding coefficient is more significant. Values of "Prob > *F*" less than 0.05 indicate model terms are significant. In this case $X_1, X_3, X_1^2, X_2^2, X_3^2, X_1X_2, X_2X_3$ are significant model terms. Values greater than 0.10 indicate the model terms are not significant. This implies that the linear effects of agitation speed (P < 0.0235) and carrier concentration (P = 0.0729) are more significant. Table 4 also indicate that the square effects of agitation speed, M/E ratio and carrier concentration and interactive effects of agitation speed and M/E ratio (P = 0.0089) and M/E ratio and carrier concentration (P = 0.0222) had very significant influence on the extraction of chromium using emulsion liquid membrane.

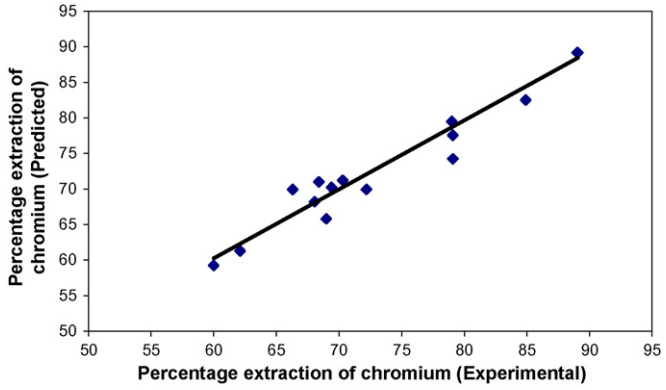

Fig. 4. Comparison of experimental and RSM predicted values for the extraction of chromium using Trioctyl amine carrier.

3.3. Optimization of process parameters for the extraction of chromium using Aliquat-336 carrier

The coded values of the test variables and the experimental results of percentage extraction of chromium using Aliquat-336 are given in Table 3. Multiple regression analysis of the experimental data yielded the following regression equation for the percentage extraction of chromium.

$$Y_2 = 96.15 - 1.91 \times X_1 - 1.07 \times X_2 + 1.32 \times X_3 - 3.02 \times X_1 \times X_2 - 0.63 \times X_1 \times X_3 + 2.68 \times X_2 \times X_3 - 9.54 \times X_1^2 - 5.79 \times X_2^2 - 3.39 \times X_3^2 \quad (4)$$

where Y_2 is the percentage extraction of chromium using Aliquat-336, X_1 is the agitation speed, X_2 is the M/E ratio, X_3 is the carrier concentration. The value of regression coefficient (R^2 = 0.9664) is closer to one indicates that the correlation is best suited in predicting the values for the extraction system and the predicted values are found to be closer to the experimental results.

Table 5 shows the ANOVA model for the percentage extraction of chromium using Aliquat-336. From the ANOVA of the regression model, the calculated *F*-value (31.98) and very low probability value (P = <0.0001) shows that this model is highly significant. The "Lack of Fit *F*-value" of 5447.00 implies the Lack of Fit is significant. There is only a 0.01% chance that a "Lack of Fit *F*-value" this large could occur due to noise. The Predicted R^2 of 0.7433 is in reasonable agreement with the Adjusted R^2 of 0.9362. Adequate Precision measures the signal to noise ratio. A ratio greater than 4 is desirable, hence the ratio of 16.468 indicates an adequate signal. A plot of experimental and RSM predicted values is shown in Fig. 5 and the deviation is found to be less than 5%.

It is also observed that the coefficient for squared effect is highly significant (P = <0.0001) when compared with the individual and interactive effect. In this study $X_1, X_3, X_1^2, X_2^2, X_3^2, X_1X_2, X_2X_3$ are significant model terms. This implies that the linear effects of agitation speed (P = 0.0217) and carrier concentration (P = 0.0890) are more significant. Table 4 also indicate that the square effects of agitation speed, M/E ratio and carrier concentration and interactive effects of agitation speed and M/E ratio (P = 0.0080) and M/E ratio and car-

Table 5
ANOVA for response surface quadratic model for the percentage extraction of chromium using Aliquat-336 as carrier.

Source	Coefficient factor	Sum of squares	DF	Mean square	*F*	*P*-value Prob > *F*
Model	96.15	1934.06	9	214.90	31.98	<0.0001[a]
X_1	−1.91	49.62	1	49.62	7.38	0.0217[a]
X_2	−1.07	15.70	1	15.70	2.34	0.1574
X_3	1.32	23.83	1	23.83	3.55	0.0890
$X_1 \times X_2$	−3.02	73.21	1	73.21	10.89	0.0080[a]
$X_1 \times X_3$	−0.63	3.13	1	3.13	0.47	0.5107
$X_2 \times X_3$	2.68	57.25	1	57.25	8.52	<0.0153[a]
X_1^2	−9.54	1311.10	1	1311.10	195.13	<0.0001[a]
X_2^2	−5.79	483.21	1	483.21	71.91	<0.0001[a]
X_3^2	−3.39	165.26	1	165.26	24.60	<0.0006[a]
Residual		67.19	10	6.72		
Lack of Fit		67.18	5	13.44	5447.00	<0.0001[a]
Pure error		0.012	5	0.002467		
Cor total		2001.25	19			

Std. Dev.: 2.59; R^2: 0.9664; mean: 83.37; Adj R^2: 0.9362; C.V. %: 3.11; Pred R^2: 0.7433; Adeq precision: 16.468.
[a] Significant variable.

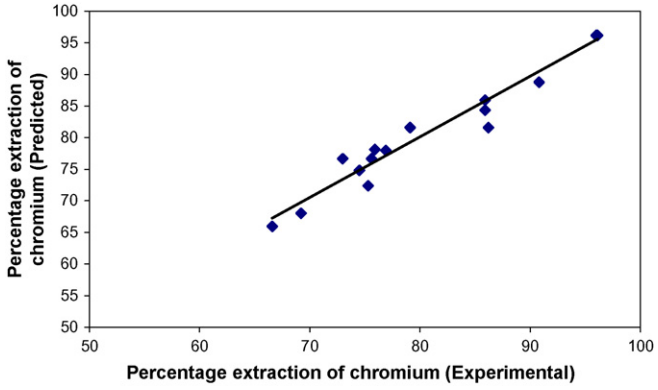

Fig. 5. Comparison of experimental and RSM predicted values for the extraction of chromium using Aliquat-336.

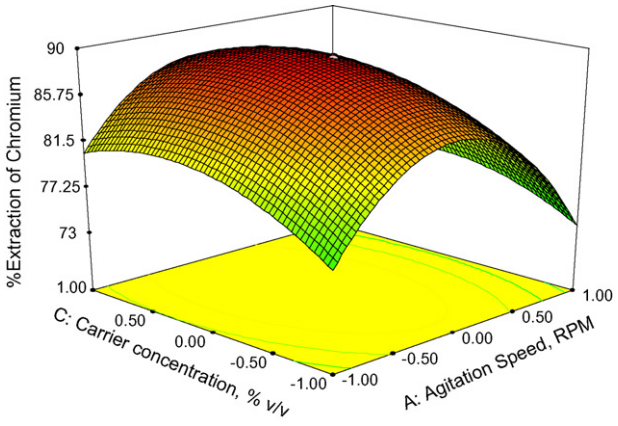

Fig. 7. The 3D plot showing the effects of agitation speed, carrier concentration and their mutual interaction on extraction of chromium by ELM using Trioctyl amine as carrier.

rier concentration ($P = 0.0153$) had very significant influence on the extraction of chromium using emulsion liquid membrane.

The response surface curves are plotted to understand the interaction of the variables and to determine the optimum level of each variable for maximum response. The circular nature of the contour signifies that the interactive effects between the variables are not significant and the optimum values of the test variables cannot be easily obtained. The response surface curves for extraction of chromium by ELM using Trioctyl amine and Aliquat-336 are shown in Figs. 6–11. Each 3D plot represents the number of combinations of the two-test variable. The maximum percentage removal of chromium is indicated by the surface confined in the smallest curve of the plot with the other variable maintained at zero levels. It is evident from the elliptical nature of the contours that the interaction between the individual variables is significant. The studies of the contour plot also reveal the best optimal values of the process conditions for both the carriers and are; agitation speed: 180–220, M/E ratio: 0.4–0.6, and carrier concentration: 3–5.

The sequential quadratic programming in MATLAB 7 is used to solve the second-degree polynomial regression Eqs. (3) and (4). The

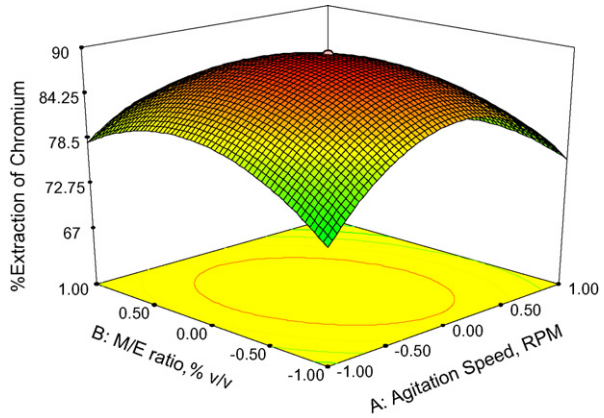

Fig. 6. The 3D plot showing the effects of agitation speed, M/E ratio and their mutual interaction on extraction of chromium by ELM using Trioctyl amine as carrier.

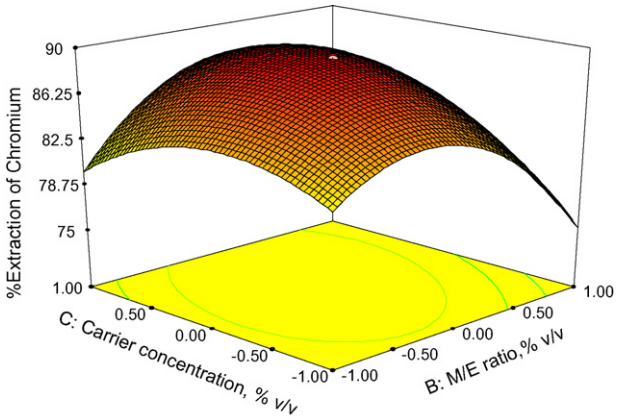

Fig. 8. The 3D plot showing the effects of M/E ratio, carrier concentration and their mutual interaction on extraction of chromium by ELM using Trioctyl amine as carrier.

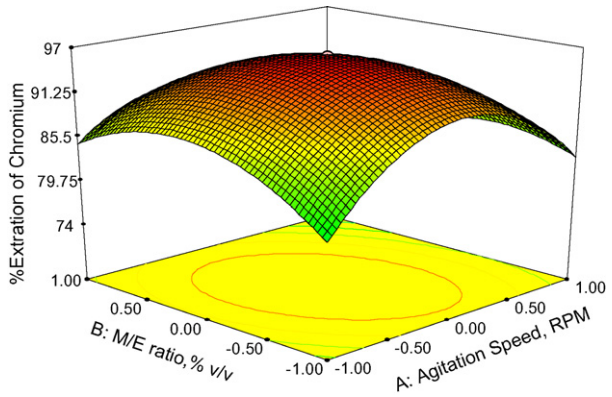

Fig. 9. The 3D plot showing the effects of agitation speed, M/E ratio and their mutual interaction on extraction of chromium by ELM using Aliquat-336 as carrier.

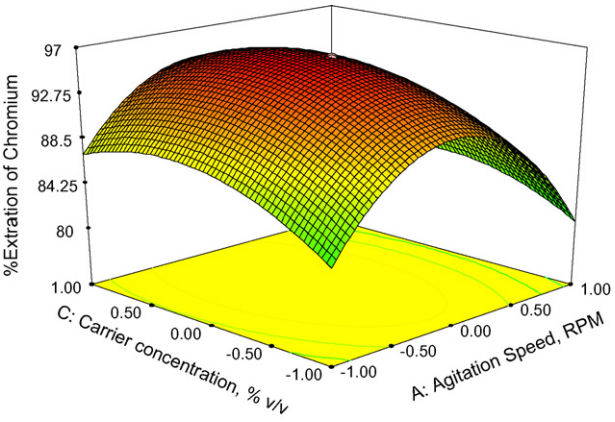

Fig. 10. The 3D plot showing the effects of agitation speed, carrier concentration and their mutual interaction on extraction of chromium by ELM using Aliquat-336 as carrier.

optimum values of test variables in coded units are $X_1 = -0.1233$, $X_2 = -0.0565$, $X_3 = 0.0932$ for Trioctyl amine and $X_1 = -0.1129$, $X_2 = -0.0636$, $X_3 = 0.0789$ for Aliquat-336. They are converted into uncoded units for the actual values and the optimum values of the test variables were: agitation speed – 201.369 rpm, M/E ratio – 0.5887% (v/v) and carrier concentration – 4.0932% (v/v) for Trioctyl amine and agitation speed – 202.097 rpm, M/E ratio – 0.5873% (v/v) and carrier concentration – 3.9211% (v/v) for Aliquat-336. Under the optimal condition the maximum predicted efficiency was 89.2% and 96.15% for Trioctyl amine and Aliquat-336, respectively.

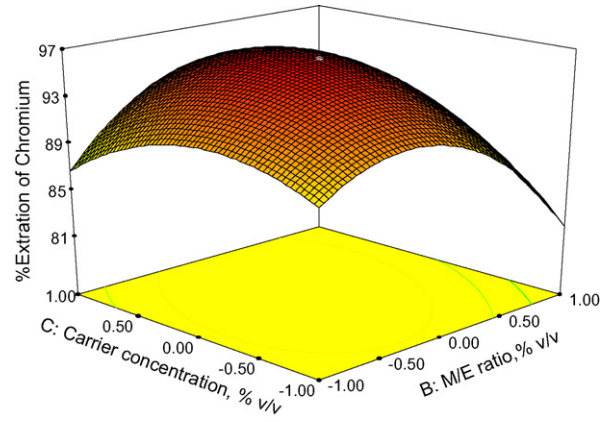

Fig. 11. The 3D plot showing the effects of M/E ratio, carrier concentration and their mutual interaction on extraction of chromium by ELM using Aliquat-336 as carrier.

4. Conclusions

The characteristics of raw waste sodium dichromate sludge recovered from pharmaceutical industry are studied and found that it is highly acidic and contains high dichromate ions. The emulsion stability was carried out by varying surfactant concentration, agitation speed and emulsification time. RSM was used to find the optimum process conditions for the extraction of chromium. The optimum conditions for Trioctyl amine are: agitation speed – 201.369 rpm, M/E ratio – 0.5887% (v/v) and carrier concentration – 4.0932% (v/v) and Aliquat are: agitation speed – 202.097 rpm, M/E ratio – 0.5873% (v/v) and carrier concentration – 3.9211% (v/v). The values predicted by RSM were found to vary with R^2 value of 0.9614 and 0.9124 for Trioctyl amine and Aliquat-336, respectively.

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References

[1] C.C. Wang, A.L. Bunge, Multisolute extraction of organic acids by emulsion liquid membranes—batch experiments and models, J. Membr. Sci. 53 (1990) 71–103.
[2] H. Itoh, M.P. Thien, T.A. Hatton, D.I.C. Wang, Water transport mechanism in liquid emulsion membrane process for the separation of amino acids, J. Membr. Sci. 51 (1990) 309–322.
[3] R. Devulapalli, F. Jones, Separation of aniline from aqueous solutions using emulsion liquid membranes, J. Hazard. Mater. 70 (1999) 157–170.
[4] T. Kumaresan, K.M. Meera Sheriffa Begum, P. Sivashanmugam, N. Anantharaman, S. Sundaram, Experimental studies on treatment of distillery effluent by liquid membrane extraction, Chem. Eng. J. 95 (2003) 199–204.
[5] P.F.M.M. Correia, J.M.R. De Carvalho, Recovery of phenol from phenolic resin plant effluents by emulsion liquid membranes, J. Membr. Sci. 225 (2003) 41–49.
[6] S.C. Lee, H.K. Lee, Development of an emulsion liquid membrane system for extraction of a neutral species, J. Membr. Sci. 264 (2005) 13–19.
[7] M.T.A. Reis, O.M.F. de Freitas, M.R.C. Ismael, J.M.R. Carvalho, Recovery of phenol from aqueous solutions using liquid membranes with Cyanex 923, J. Membr. Sci. 305 (2007) 313–324.
[8] M.T.A. Reis, J.M.R. Carvalho, Recovery of zinc from an industrial effluent by emulsion liquid membranes, J. Membr. Sci. 84 (1993) 201–211.
[9] A.M. Urtiaga, A. Alonso, I. Ortiz, J.A. Daoud, S.A. El-Reefy, S. Perez de Ortiz, T. Gallego, Comparison of liquid membrane processes for the removal of cadmium from wet phosphoric acid, J. Membr. Sci. 164 (2000) 229–240.
[10] R.A. Kumbasar, O. Tutkun, Separation of cobalt and nickel from acidic leach solutions by emulsion liquid membranes using Alamine 300 (TOA) as a mobile carrier, Desalination 224 (2008) 201–208.
[11] M.S. Gasser, N.E. El-Hefny, J.A. Daoud, Extraction of Co(II) from aqueous solution using emulsion liquid membrane, J. Hazard. Mater. 151 (2008) 610–615.
[12] Y.C. Chang, C.L. Lee, T.M. Pan, Statistical optimization of media components for the production of Antrodia cinnamomea AC0623 in submerged cultures, Appl. Microbiol. Biotechnol. 72 (2006) 654–661.
[13] E. Kristo, C.G. Biliaderis, N. Tzanetakis, Modeling of the acidification process and rheological properties of milk fermented with a yogurt starter culture using response surface methodology, Food Chem. 83 (2003) 437–446.
[14] Q.K. Beg, R.K. Saxena, R. Gupta, Kinetic constants determination for an alkaline protease from *Bacillus mojavensis* using response surface methodology, Biotechnol. Bioeng. 78 (2002) 289–295.
[15] L.S.T. Lai, C.C. Pan, B.K. Tzeng, The influence of medium design on lovastatin production and pellet formation with a high-producing mutant of *Aspergillus terreus* in submerged cultures, Process. Biochem. 38 (2003) 1317–1326.
[16] E.L. Soo, A.B. Salieh, M. Basri, Response surface methodological study on lipase-catalyzed synthesis of amino acid surfactants, Process. Biochem. 39 (2004) 1151–1518.
[17] Y.X. Wang, Z.X. Lu, Optimization of processing parameters for the mycelial growth and extracellular polysaccharide production by *Boletus* spp. ACCC 50328, Process. Biochem. 40 (2005) 1043–1051.
[18] B. Preetha, T. Viruthagiri, Application of response surface methodology for the biosorption of copper using *Rhizopus arrhizus*, J. Hazard. Mater. 143 (2007) 506–510.
[19] S. Mannan, A. Fakhrul-Razi, Md.Z. Alam, Optimization of process parameters for the bioconversion of activated sludge by *Penicillium corylophilum*, using response surface methodology, J. Environ. Sci. 19 (2007) 23–28.
[20] C.M. Pan, Y.T. Fan, Y. Xing, H.W. Hou, M.L. Zhang, Statistical optimization of process parameters on biohydrogen production from glucose by *Clostridium* sp. Fanp2, Bioresour. Technol. 99 (2008) 3146–3154.

[21] P.L. Harris, S.L. Cuppett, L.B. Bullerman, Optimization of lipase synthesis by *Pseudomonas fluorescens* by response surface methodology, J. Food Protect. 53 (1990) 481–483.
[22] W.A. Bazaraa, E.E. Hassan, Response surface optimization for the continuous glucose isomerization process, J. Ind. Microbiol. 17 (1996) 100–103.
[23] W.S.W. Ho, T.K. Poddar, New membrane technology for removal and recovery of chromium from wastewater, Environ. Prog. 20 (2001) 44–52.
[24] P. Venkateshwaran, K. Palanivelu, Solvent extraction of hexavelent chromium with tetrabutyl ammonium bromide from aqueous solution, Sep. Purif. Technol. 40 (2004) 279–284.
[25] C.A. Kozlowski, W. Walkowiak, Applicability of liquid membranes in chromium transport with amines as ion carrier, J. Membr. Sci. 266 (2005) 143–150.
[26] S. Chakraborty, S. Datta, P. Bhattacharya, Studies on extraction of chromium (VI) from acidic solution by emulsion liquid membrane, Ind. J. Chem. Technol. 12 (2005) 713–718.
[27] S. Saravanan, K.M. Meera Sheriffa Begum, N. Anantharaman, Removal of hexavalent chromium by emulsion liquid membrane technique, J. Univ. Chem. Tech. Metall. 41 (2006) 333–342.
[28] M. Chiha, M.H. Samar, O. Hamdaoui, Extraction of chromium (VI) from sulphuric acid aqueous solutions by a liquid surfactant membrane (LSM), Desalination 194 (2006) 69–80.
[29] M. Rajasimman, P. Karhtick, Studies on extraction of chromium by emulsion liquid membrane, in: Proceedings of the 60th Annual session of Indian Institute of Chemical Engineers, CHEMCON 2007, Kolkatta, India, 2007.
[30] APHA, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, Washington, DC, 1999.