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Statistical optimization of process parameters for the extraction of chromium(VI) from pharmaceutical wastewater by emulsion liquid membrane

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ABSTRACT

Response surface methodology (RSM) is used to optimize the process parameters for the extraction of chromium from aqueous solution of waste sodium dichromate recovered from the pharmaceutical industry wastewater using emulsion liquid membrane technique. The liquid membrane used was composed of kerosene oil as the solvent, Span-80 as the surfactant and potassium hydroxide as internal reagent and Aliquat-336 as carrier. The process parameters, namely feed concentration, pH, internal reagent concentration and surfactant concentration on the extraction of chromium were optimized using Box-Behnken design. The optimum conditions for the extraction of chromium(VI) were: feed concentration (223.55 ppm), pH (2.73), internal reagent concentration (0.72 N) and surfactant concentration (1.91%, w/w). At the optimized condition the maximum chromium extraction was found to be 97.57%.

1. Introduction

Response surface methodology (RSM) is an advanced tool, now a days commonly applied involves three factorial designs giving number of input (independent) factors and their corresponding relationship between one or more measured dependent responses. RSM is advantageous over conventional methods available and it includes less experiment numbers. It is suitable for multiple factor experiments and searches for common relationship between various factors towards finding the most suitable conditions for the processes. In this method, linear or quadratic effects of experimental variables construct contour plots and a model equation fitting the experimental data. This facilitates the determination of optimum value of factors under investigation and prediction of response under optimized condition. 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, etc. [1–6]. It has also been used to determine the optimal values for process parameters such as pH, temperature, aeration, feeding rates in various processes [7–9].

The emulsion liquid membrane (ELM) separation technique has been regarded as an emerging technology with considerable potential for a variety of applications. Many studies have been carried out using ELM for the recovery of metal ions [10,11], phenol [12], organic acids [13], sephalexin from dilute solution [14], aniline [15] and bioactive materials [16]. Recovery of dye from aqueous solutions has been studied by emulsion liquid membrane [17]. 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.

The strong release of heavy metals into the environment by several industries has made their recovery from wastewater, a major topic of research in wastewater treatment. The most toxic metals

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are aluminium, chromium, iron, cobalt, nickel, copper, zinc, cadmium, mercury, and lead. The major industries that contribute to water pollution by chromium are mining, leather tanning, textile dyeing, electroplating, aluminium conversion coating operations, plants producing industrial inorganic chemicals and pigments, and wood preservatives. Chromium bearing wastewater resulted from all these industries must be disposed off after treatment. Although some works on this particular aspect are available [18–21], 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 feed concentration, pH, internal reagent concentration and surfactant 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

2.1. Experimental design and procedure

A full factorial design, which includes all possible factor combinations in each of the factors, is a powerful tool for understanding complex processes for describing factor interactions in multifactor systems. RSM is an empirical statistical technique employed for multiple regression analysis by using quantitative data obtained from properly designed experiments to solve multivariate equations simultaneously. An orthogonal 2^4 Box-Behnken design (BBD) with five replicates at the center point, all in duplicates, resulting in a total of 29 experiments were used to optimize the chosen key variables for the extraction of chromium. The purpose of the center points is to estimate the pure error and curvature.

The experiments with different feed phase concentration (100, 200, and 300 ppm), pH (1, 3 and 5), internal reagent concentration (0.2, 0.6 and 1 N), surfactant concentration (1, 2 and 3%, w/w) were employed simultaneously covering the spectrum of variables for the percentage extraction of chromium in the Box-Behnken design. In order to describe the effects of feed concentration (X_1), pH (X_2), internal reagent concentration (X_3), and surfactant concentration (X_4) on percentage of chromium extraction, batch experiments were conducted. The coded values of the process parameters were determined by the following equation.

$$x_i = \frac{X_i - X_0}{\Delta x} \tag{1}$$

where x_i is the coded value of the ith variable, X_i is 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 2 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

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

where Y is the predicted response, β_i, β_j, and β_{ij} are coefficients estimated from regression, they represent the linear, quadratic and cross products of $x_1, x_2, x_3, \ldots$ 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 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(VI).

Independent variable	Range and levels		
	−1	0	+1
Feed concentration, X_1 (ppm)	100	200	300
pH, X_2	1	3	5
Internal reagent concentration, X_3 (N)	0.2	0.6	1.0
Surfactant concentration (%, w/w)	1	2	3

Table 2
Box-Behnken design matrix along with predicted and experimental values of percentage extraction of chromium.

Run no.	X_1	X_2	X_3	X_4	%Extraction of chromium	
					Experimental	Predicted
1	0	−1	0	1	85.50	85.52
2	−1	−1	0	0	71.60	70.83
3	0	0	1	−1	97.50	98.34
4	0	0	−1	1	88.61	89.94
5	0	1	−1	0	77.11	83.88
6	0	0	0	0	96.82	96.81
7	0	0	1	1	95.62	97.30
8	1	−1	0	0	74.31	79.78
9	0	−1	0	−1	91.01	90.42
10	0	1	1	0	89.89	85.96
11	0	0	0	0	96.78	96.81
12	1	0	−1	0	78.02	75.03
13	1	0	1	0	90.19	88.77
14	1	1	0	0	70.09	73.07
15	−1	0	0	−1	73.21	75.30
16	1	0	0	1	79.63	78.48
17	0	0	0	0	96.85	96.81
18	−1	1	0	0	66.51	67.47
19	−1	0	−1	0	78.89	77.15
20	1	0	0	−1	85.29	86.60
21	0	−1	−1	0	86.28	82.42
22	0	0	0	0	96.82	96.81
23	0	0	0	0	96.80	96.81
24	−1	0	0	1	79.82	79.46
25	0	1	0	−1	89.80	85.60
26	0	0	−1	−1	92.30	92.82
27	0	−1	1	0	90.31	93.26
28	0	1	0	1	88.10	85.52
29	−1	0	1	0	76.50	76.33

X_1—feed concentration (ppm); X_2—pH; X_3—internal reagent concentration; X_4—surfactant concentration.

2.2. 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 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 and poly-butyl succinimide (1.5 wt%) as membrane strengthening agent. Aliquat-336 (2%, v/v) was used as carrier. The internal reagent was potassium hydroxide. 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 was then dispersed (at 210 rpm) in the external aqueous phase containing solutes (Cr^{6+} = 100–300 ppm as feed in the form

Table 3
Analysis of variance (ANOVA) for response surface quadratic model for the percentage extraction of chromium using Aliquat-336 as carrier.

Source	Coefficient factor	Sum of squares	d.f.	Mean square	F	P-value, prob > F
Model	96.81	2375.25	14	169.66	32.50	<0.0001[a]
X_1	2.58	80.08	1	80.08	15.34	0.0015[a]
X_2	−1.46	25.55	1	25.55	4.89	0.0441[a]
X_3	3.23	125.45	1	125.45	24.03	0.0002[a]
X_4	−0.99	11.66	1	11.66	2.23	0.1572
X_1X_2	0.22	0.19	1	0.19	0.036	0.8517
X_1X_3	3.64	53.00	1	53.00	10.15	0.0066[a]
X_1X_4	−3.07	37.64	1	37.64	7.21	0.0178[a]
X_2X_3	2.19	19.14	1	19.14	3.67	0.0762
X_2X_4	0.95	3.63	1	3.63	0.70	0.4184
X_3X_4	0.45	0.82	1	0.82	0.16	0.6980
X_1^2	−16.07	1675.08	1	1675.08	320.92	<0.0001[a]
X_2^2	−9.01	527.00	1	527.00	100.96	<0.0001[a]
X_3^2	−1.42	13.17	1	13.17	2.52	0.1345
X_4^2	−0.78	3.93	1	3.93	0.75	0.4000
Residual		73.08	14	5.22		
Lack of fit		73.07	10	7.31	10746.04	<0.0001[a]
Pure error		0.00272	4	0.00068		
Cor total		2778.33	28			

S.D.: 2.28; R^2: 0.9702; mean: 85.52; adj R^2: 0.9403; C.V.%: 2.67; pred R^2: 0.8281; adeq precision: 18.810.
[a] Significant variable.

of sodium dichromate) in the mixer-settler for 30 min. During this period, the solute transport occurs through the membrane phase in to 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 in the UV wave length range.

3. Results and discussion

The effect of process variables like feed concentration, pH, internal reagent concentration and surfactant concentration on the extraction of chromium(VI) was investigated using response surface methodology according to Box-Behnken design. The batch runs were conducted in BBD designed experiments to visualize the effects of independent factors on responses. The coded values of the test variables and the experimental results of percentage extraction of chromium using Aliquat-336 are presented in Table 2. Multiple regression analysis of the experimental data yielded the following regression equation for the percentage extraction of chromium.

$$Y_1 = 96.81 + 2.58\,X_1 - 1.46\,X_2 + 3.23\,X_3 - 0.99\,X_4 + 0.22\,X_1X_2 + 3.64\,X_1X_3 - 3.07\,X_1X_4 + 2.19\,X_2X_3 + 0.95\,X_2X_4 + 0.45\,X_3X_4 - 16.07\,X_1^2 - 9.01\,X_2^2 - 1.42\,X_3^2 - 0.78\,X_4^2 \quad (3)$$

where Y_1 is the percentage extraction of chromium using Aliquat-336, X_1 is the feed concentration, X_2 is the pH, X_3 is the internal reagent concentration and X_4 is the surfactant concentration. The value of regression coefficient ($R^2 = 0.9702$) 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 3 shows the analysis of variance (ANOVA) model for the percentage extraction of chromium using Aliquat-336. ANOVA is required to test the 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 (32.50) and a very low probability value ($P \le 0.0001$). The lack of fit F-value of 10746.04 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 0.8281 is in reasonable agreement with the adjusted R^2 of 0.9403. "Adequate Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Here the ratio of 18.810 indicates an adequate signal.

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 0.0500 indicate model terms are significant. In this case $X_1, X_2, X_3, X_1^2, X_2^2, X_1X_3$, and X_1X_4 are significant model terms. Values greater than 0.10 indicate the model terms are not significant. This implies that the linear effects of feed concentration ($P = 0.0015$), pH ($P = 0.0441$) and internal reagent concentration ($P = 0.0002$) are more significant. Table 3 also indicate that the square effects of feed concentration and pH and interactive effects of feed concentration and internal reagent concentration ($P = 0.0066$) and feed concentration and surfactant concentration ($P = 0.0178$) 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

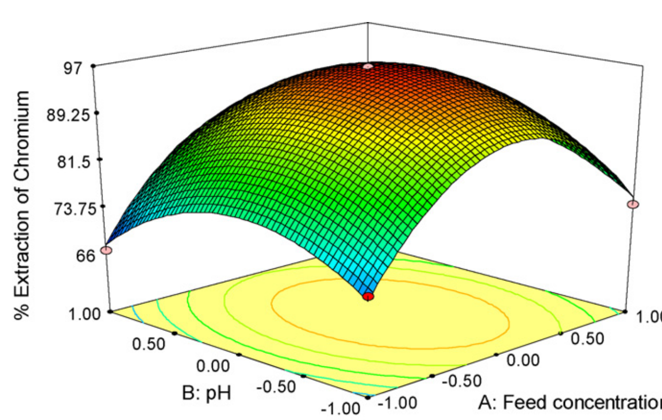

Fig. 1. The 3D plot showing the effects of feed concentration, pH and their mutual interaction on extraction of chromium by ELM.

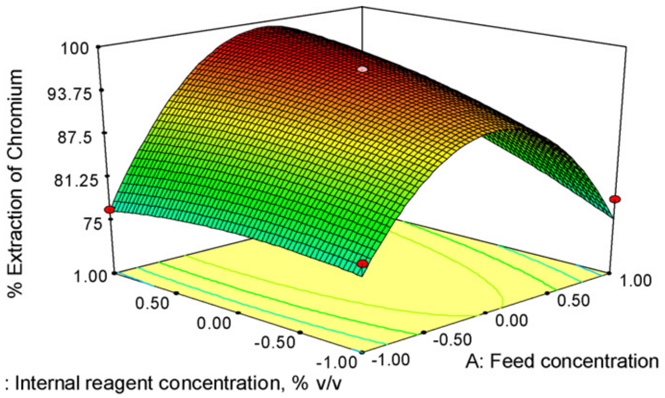

Fig. 2. The 3D plot showing the effects of feed concentration, internal reagent concentration and their mutual interaction on extraction of chromium by ELM.

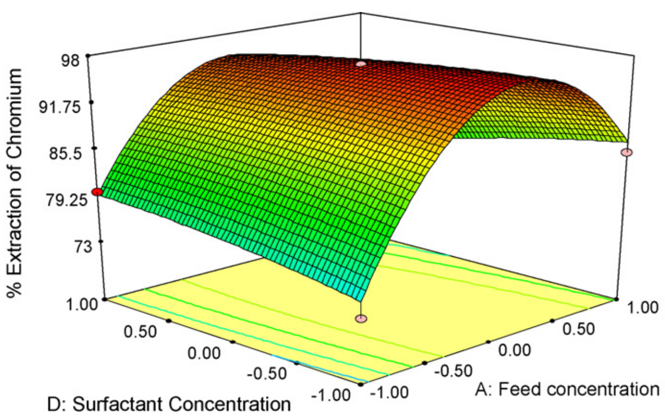

Fig. 3. The 3D plot showing the effects of feed concentration, surfactant concentration and their mutual interaction on extraction of chromium by ELM.

be easily obtained. The response surface curves for extraction of chromium by ELM using Aliquat-336 is shown in Figs. 1–6. 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 lies within the range; feed concentration: 210–240 ppm, pH: 2.5–3.0,

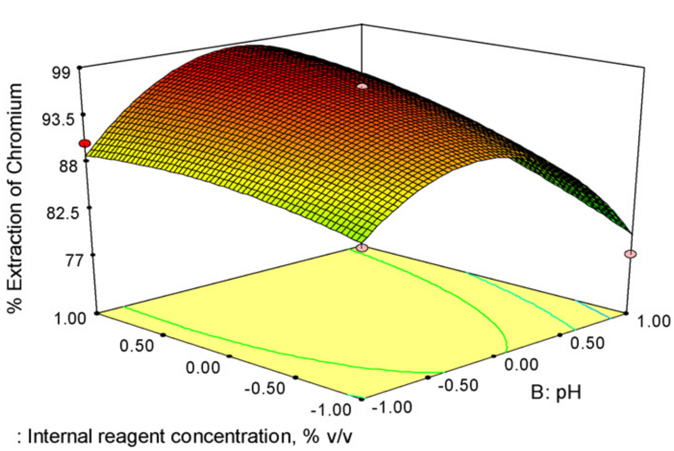

Fig. 4. The 3D plot showing the effects of pH, internal reagent concentration and their mutual interaction on extraction of chromium by ELM.

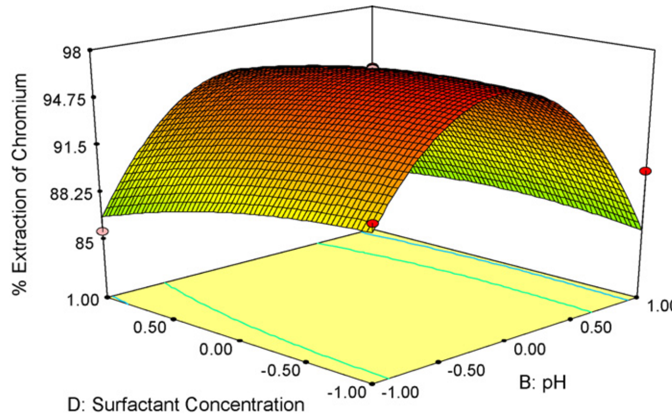

Fig. 5. The 3D plot showing the effects of pH, surfactant concentration and their mutual interaction on extraction of chromium by ELM.

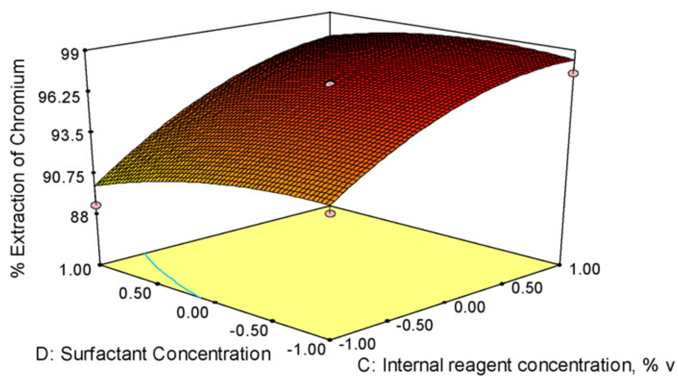

Fig. 6. The 3D plot showing the effects of internal reagent concentration, surfactant concentration and their mutual interaction on extraction of chromium by ELM.

internal reagent concentration: 0.5–0.8 N and surfactant concentration: 1.5–2 N.

The sequential quadratic programming in MATLAB 7 is used to solve the second-degree polynomial regression Equ. (3). The optimum values of test variables in coded units are $X_1 = 0.2355$, $X_2 = -0.1335$, $X_3 = 0.2986$, and $X_4 = -0.0919$. They are converted into uncoded units for the actual values and the optimum values of the test variables were: feed concentration (223.55), pH (2.73), internal reagent concentration (0.72 N) and surfactant concentration (1.91%, w/w). Under the optimal condition the maximum predicted efficiency was 97.57%.

4. Conclusion

Due to the increasing economic relevance of removal of chromium, this study was conducted in an attempt to optimize the process parameters and to study the linear, square and interactive effects of process parameters like a feed concentration, pH, internal reagent concentration and surfactant concentration on the extraction of chromium by emulsion liquid membrane. Box-Behnken design was used to find the optimum process conditions for the extraction of chromium. From the results it was found that the linear effects of feed concentration, pH, internal reagent concentration, the square effects of feed concentration, pH and interactive effects of feed concentration and internal reagent concentration, and feed concentration and surfactant concentration had very significant influence on the extraction of chromium. The optimum conditions for the extraction of chromium are: feed concentration—223.55 ppm, pH—2.73, internal reagent concentration—0.72 N and surfactant concentration—1.91% (w/w).

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