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Application of response surface methodology for the extraction of chromium (VI) by emulsion liquid membrane

M. Rajasimman [a,*], P. Karthic [b]

[a] Department of Chemical Engineering, Annamalai University, Annamalai Nagar-608002, Tamil Nadu, India
[b] Department of Petrochemical Engineering, Periyar Maniammai University, Tanjore, Tamil Nadu, India

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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 trioctylamine 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 (224.04 ppm), pH (2.76), internal reagent concentration (0.71 N) and surfactant concentration (1.92%, w/w). At the optimized condition the maximum chromium extraction was found to be 92.50%.

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. (Beq *et al.*, 2002; Chang *et al.*, 2006; Kristo *et al.*, 2003; Lai *et al.*, 2003; Soo *et al.*, 2004; Wang and Lu, 2005). It has also been used to determine the optimal values for process parameters such as pH, temperature, aeration, feeding rates in various processes (Harris *et al.*, 1990; Mannan *et al.*, 2007; Pan *et al.*, 2008).

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 (Mikucki and Osseoasare, 1986; Urtiaga *et al.*, 2000), phenol (Zhang *et al.*, 1988), organic acids (Wang and Bunge, 1990), sephalexin from dilute solution (Sahoo and Dutta, 1998), aniline (Devulapalli and Jones, 1999) and bioactive materials (Thien and Hatton, 1988). Recovery of dye from aqueous solutions has been studied by emulsion liquid membrane (Das *et al.*, 2008). 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.

* Corresponding author. Tel.: +91 9842565098.
E-mail address: raja_simms@yahoo.com (M. Rajasimman).

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Table 1
The levels of different process variables in coded and uncoded 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

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 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 (Chakraborty *et al.*, 2005; Chiha *et al.*, 2006; Rajasimman and Karthic, 2007; Saravanan *et al.*, 2006), 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.

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	78.2	79.17
2	−1	−1	0	0	64.3	63.60
3	0	0	1	−1	90.2	90.70
4	0	0	−1	1	81.0	82.51
5	0	1	−1	0	70.9	72.79
6	0	0	0	0	89.2	89.20
7	0	0	1	1	88.5	90.15
8	1	−1	0	0	67.8	68.81
9	0	−1	0	−1	83.6	83.27
10	0	1	1	0	82.2	82.77
11	0	0	0	0	89.2	89.20
12	1	0	−1	0	70.9	68.58
13	1	0	1	0	82.8	87.67
14	1	1	0	0	63.7	66.41
15	−1	0	0	−1	65.7	67.82
16	1	0	0	1	73.0	71.64
17	0	0	0	0	89.2	89.20
18	−1	1	0	0	59.2	60.20
19	−1	0	−1	0	71.3	69.67
20	1	0	0	−1	78.6	79.69
21	0	−1	−1	0	79.2	79.39
22	0	0	0	0	89.2	89.20
23	0	0	0	0	89.2	89.20
24	−1	0	0	1	72.4	72.07
25	0	1	0	−1	81.9	78.17
26	0	0	−1	−1	85.4	85.76
27	0	−1	1	0	83.1	81.97
28	0	1	0	1	80.9	78.47
29	−1	0	1	0	69.9	69.15

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

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 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.

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

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

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

Source	Coefficient factor	Sum of squares	DF	F	P-value Prob > F
Model	89.20	2286.19	14	39.07	<0.0001[a]
X_1	2.86	98.04	1	23.46	0.0003[a]
X_2	−1.45	25.23	1	6.04	0.0277[a]
X_3	3.14	118.44	1	28.34	0.0001[a]
X_4	−0.95	10.83	1	2.59	0.1298
$X_1{*}X_2$	0.25	0.25	1	0.060	0.8103
$X_1{*}X_3$	3.40	46.24	1	11.06	0.0050[a]
$X_1{*}X_4$	−3.07	37.82	1	9.05	0.0094[a]
$X_2{*}X_3$	1.85	13.69	1	3.28	0.0918
$X_2{*}X_4$	1.10	4.84	1	1.16	0.3001
$X_3{*}X_4$	0.68	1.82	1	0.44	0.5198
X_1^2	−15.70	1599.70	1	382.74	<0.0001[a]
X_2^2	−8.74	495.68	1	118.59	<0.0001[a]
X_3^2	−1.23	9.80	1	2.34	0.1480
X_4^2	−0.69	3.10	1	0.74	0.4034
Residual		58.51	14		
Lack of fit		58.51	10		
Pure error		0.00	4		
Cor total		2344.71	28		

Std. Dev., 2.04; R^2, 0.9750; Mean, 78.29; Adj R^2, 0.9501; C.V.%, 2.61; Pred R^2, 0.8563; Adeq Precision, 20.744.
[a] Significant variable.