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Box–Behnken modelling of phenol removal from aqueous solution using Emulsion Liquid Membrane

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Abstract - *Response surface methodology (RSM) is used to optimize the process parameters for the removal of phenol from aqueous solution of wastewater using emulsion liquid membrane technique. The liquid membrane used was composed of Xylene as the solvent, SPAN-80 as the surfactant and sodium hydroxide as an internal reagent and optimized using Box–Behnken design. The optimum values for these factors were found to be surfactant concentration 3.29 % (v/v), M/I ratio 1.05 (v/v) and E/E ratio 0.474 (v/v). Under optimal conditions, the model predicted a maximum efficiency of 96.79%. The obtained model is highly significant ($F_{obs} \geq F_{Tabulate}$ and low p-value) with a correlation coefficient of 99.42%. On the other hand, linear, quadratic and interaction terms in this model have the largest statistical effect on the response (confidence level= 99 %).*

Key Words: Response Surface Methodology, Wastewater Box–Behnken design, Emulsion Liquid membrane, Phenol.

1. INTRODUCTION

Phenol is used widely in many industrial processes, such as petroleum refineries, steel plants, and pharmaceutical, coal conversion, chemical and dye industries. They are released in industrial wastewater and domestic water, and may be a threat to human health and aquatic life. Phenols are highly toxic compounds even at low concentrations and the discharge of the wastewater containing phenols is restricted severely and have been listed by US EPA as priority pollutants. Normally, a standard limit of less than 1 ppm is established for the release of phenol; however, several industrial effluents containing phenol concentration up to 6900 ppm. Typical treatment options like biological processes (e.g., activated sludge), activated carbon adsorption, reverse osmosis, ion exchange, coagulation-precipitation, Photo degradation and electro dialysis. However, equipment construction and operation costs could be prohibiting for most of the existing processes especially when these compounds occur at very high concentrations. Removal of phenol from wastewater has been intensively investigated using Emulsion Liquid Membrane (ELM) technique. Phenol removal by ELM has many advantages over other separation methods like high selectivity, extraction – stripping in single stage and low cost of operation. Liquid membrane process incorporates dispersion of an emulsion containing organic membrane and aqueous internal phase in a continuous external phase (W/O/W). The solute penetrates from the external phase to the internal phase through the membrane phase, where it reacts with a stripping agent and converts to a material, which is insoluble in the membrane phase and will be trapped in the internal phase. After the extraction, the emulsion phase is then broken by de-emulsification process and the oil phase is recycled for reusing in the emulsification process [1-11].

Response surface methodology (RSM) is a very useful tool which involves three factorial designs giving number of independent factors and their corresponding relationship between one or more measured dependent responses. RSM uses quantitative data from an appropriate experimental design to determine and then to simultaneously solve multivariate problem. Box–Behnken design is a commonly used protocol of RSM. The advantage of the Box–Behnken design is that only three levels are required to reduce experiments. Furthermore, it is more efficient to arrange and to interpret in comparison than other methods. 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 [12-15].

This study is focused on to study the linear, square and interactive effects and to optimize the process parameters such as Surfactant concentration, membrane to internal phase ratio (M/I) and emulsion to an external phase ratio (E/E) using RSM on removal of phenol from synthetic wastewater by ELM.

2. MATERIALS AND METHODS

2.1 Box-Behnken Design

Box-Behnken was applied to determine the response pattern and then to establish model using Design Expert Software (Stat-Ease Inc.). Three variables used in this study were Surfactant concentration (X_1), M/I ratio (X_2) and E/E ratio (X_3), respectively, with three levels of each variables, while the dependent variable was the phenol removal. The range and levels of individual variables were given in Table 1. An orthogonal 24 Box–Behnken design with five replicates at the center point, all in duplicates, resulting in a total of 17 experiments were used to optimize the chosen key variables for the removal of phenol. The purpose of the center points is to estimate the pure error and curvature. The experiment design was given in Table 2 along with experimental data and predicted responses. The percentage removal of phenol is the response.

Table - 1 Levels of different process variables in coded and un-coded form for phenol removal

Factors	Level		
	-1	0	1
SPAN 80 (%v/v), (X_1)	2	3	4
(M/I), (X_2)	0.50	1.00	1.50
(E/E), (X_3)	0.4	0.5	0.6

Table - 2 Box-Behnken design matrix along with experimental values of phenol removal

Run	Span 80 (X_1)	M/I (X_2)	E/E (X_3)	Phenol removal % (Experimental)	Phenol removal % (Predicted)
1	0	0	0	96.61	96.61
2	-1	0	1	92.73	92.84
3	-1	0	-1	94.36	94.17
4	-1	1	0	92.59	92.62
5	0	1	-1	95.31	95.47
6	0	0	0	96.61	96.61
7	0	1	1	92.68	92.54
8	0	0	0	96.61	96.61
9	1	1	0	94.76	94.71
10	-1	-1	0	93.42	93.47
11	1	-1	0	94.6	94.57
12	0	-1	-1	93.76	93.90
13	0	0	0	96.61	96.61
14	1	0	-1	95.56	95.45
15	1	0	1	94.56	94.75
16	0	0	0	96.61	96.61
17	0	-1	1	94.97	94.81

The regression analysis was performed to estimate the response function as a second order polynomial

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

where Y is the estimated response, β_0, β_i, β_{ii} and β_{ij} are the regression coefficients for the intercept, linearity, square, and interaction; and X_i and X_j are the independent coded variables. The equations were validated by the statistical tests called the analysis of variance (ANOVA). 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 removal of phenol. The optimal values of the test variables were first obtained in coded units and then converted to the uncoded units.

2.2 Experiments

300 ppm of Phenol solution and 0.1 M NaOH solution was prepared by dissolving them in distilled water. For ELM preparation, Span 80 was used as a surfactant due to the popularity as an emulsifier for liquid. Xylene was used as a diluent for the membrane. An emulsion of volume 12mL was prepared by mixing the surfactant and diluent in a ratio of 3:97 together with 0.1M NaOH solution as an internal stripping agent (internal phase) in a ratio of 1:1 by volume. The mixture of W/O was then emulsified using a high-speed homogenizer Ultra Turrax IKA-T25, operating at a rotational speed of 8000 rpm for 6 min to obtain a white color liquid membrane. The parameters such as Surfactant concentration, M/I ratio and E/E ratio was varied to observe their effects on the percentage removal of phenol. Calibration curve for absorbance of phenol concentration was prepared for checking the absorbance of phenol solution using different known concentration samples. The ELM prepared to be dispersed into phenol synthetic solution (external phase) in a beaker in a ratio of 1:2 by volume and stirred by an IKA RW 20 overhead stirrer with a speed of 400 rpm for 4 min. A 4mL of extracted phenol sample was taken and analyzed using UV- Vis Spectrophotometer Shimadzu-UV-2450 for phenol concentration. Detection of phenol observed at an absorbance value of 270 nm. The concentration of phenol was estimated from the absorbance-phenol calibration curves. The response of the experiments measured in terms of percentage removal of phenol, which defined by equation (2).

$$\text{Removal of Phenol (\%)} = \left[\frac{(c_0 - c_1)}{c_0}\right] \times 100 \qquad (2)$$

Where c_0 is the initial and c_1 is the final phenol concentration in the external phase.

3. RESULTS AND DISCUSSION

The effect of process variables like Surfactant concentration, M/I ratio and E/E ratio on the removal of phenol was investigated using response surface methodology according to Box–Behnken Design. The batch runs were conducted in Box–Behnken designed experiments to visualize the effects of independent factors on responses. The coded values of the test variables and the experimental results of percentage removal of phenol using Xylene are presented in Table 2. Multiple regression analysis of the experimental data yielded the following regression equation for the percentage removal of phenol.

$$Y = 96.61 + 0.80 \times X_1 - 0.18 \times X_2 - 0.51 \times X_3 + 0.25 \times X_1 \times X_2 + 0.16 \times X_1 \times X_3 - 0.96 \times X_2 \times X_3 - 1.32 X_1^2 - 1.44 X_2^2 - 0.99 X_3^2 \qquad (3)$$

Where Y is the percentage removal of phenol using xylene, X_1 is the surfactant concentration, X_2 is the M/I ratio and X_3 is the E/E ratio. The value of regression coefficient (R^2 = 0.9942) is closer to one indicates that the correlation is best suited in predicting the values for the removal system and the predicted values are found to be closer to the experimental results shown in Chart 1.

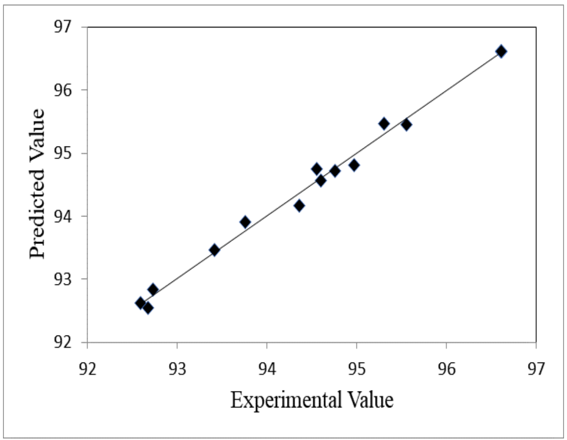

Chart – 1: Predicted Versus Experimental values for phenol removal

Table 3 shows the ANOVA model for the percentage removal of phenol using xylene. 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 fisher's 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 (134.47) and a very low probability value (P = <0.0001). The Predicted R^2 of 0.9080 is in reasonable agreement with the Adjusted R^2 of 0.9869. "Adequate Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Here the ratio of 31.698 indicates an adequate signal. The P values are used as tools to check the significance of each of the coefficients, which in turn, may indicate the patterns of the interaction among the variables. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case X_1, X_2, X_3, X_1X_2, X_2X_3, X_{12}, X_{22}, X_{32} are significant model terms. Values greater than 0.10 indicate the model terms are not significant. This implies that the linear effects of Surfactant concentration (P = < 0.0001), M/I ratio (P = 0.0206) and E/E ratio (P = < 0.0001) are more significant. Table 3 also indicate that the square effects of Surfactant concentration, M/I ratio and E/E ratio (P = <0.0001) and interactive effects of Surfactant concentration and M/I ratio (P = 0.0213) and M/I ratio and E/E ratio (P = < 0.0001) had very significant influence on the removal of phenol using emulsion liquid membrane. From Table 3 it was also observed that the linear effect of X_2 and X_3, interactive effect of X_2X_3 and square effect of X_1, X_2 and X_3 shown negative effects.

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.

Table - 3 Analysis of Variance for the selected quadratic model

Source	*Sum of Squares*	*Degrees of freedom*	*Mean Squares*	*F Value*	*p-value Prob>F*
Model	*33.96*	*9*	*3.77*	*134.47*	*< 0.0001*
X_1-Span 80	*5.09*	*1*	*5.09*	*181.32*	*< 0.0001*
X_2-M/I	*0.25*	*1*	*0.25*	*8.86*	*0.0206*
X_3-E/E	*2.05*	*1*	*2.05*	*73.07*	*< 0.0001*
X_1X_2	*0.25*	*1*	*0.25*	*8.73*	*0.0213*
X_1X_3	*0.10*	*1*	*0.10*	*3.54*	*0.1021*
X_2X_3	*3.69*	*1*	*3.69*	*131.37*	*< 0.0001*
X_1^2	*7.36*	*1*	*7.36*	*262.44*	*< 0.0001*
X_2^2	*8.79*	*1*	*8.79*	*313.31*	*< 0.0001*
X_3^2	*4.09*	*1*	*4.09*	*145.58*	*< 0.0001*
Residual	*0.20*	*7*	*0.03*		
Lack of Fit	*0.20*	*3*	*0.07*		
Pure Error	*0.00*	*4*	*0.00*		
Cor Total	34.16	16			

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 removal of phenol by ELM using xylene is shown in Fig. 1-3. Each 3D plot represents the number of combinations of the two-test variable. The maximum percentage removal of phenol 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. Fig. 1 shows the interaction effect of the Surfactant concentration and M/I ratio on phenol removal. As expected, the interactive effect of the Surfactant concentration and M/I ratio on phenol removal depicts a bell-shaped response surface, and there is a local maximum in the phenol removal with respect to the initial Surfactant concentration and M/I ratio. The interaction effect of the Surfactant concentration and M/I ratio on phenol removal is shown in Fig. 2. An increase in the Surfactant concentration with E/E ratio up to the optimum point increased the percentage removal of phenol to a maximum level, and with a further increase in the Surfactant concentration with E/E ratio, the trend is reversed. The interaction effect of the E/E ratio and M/I ratio on phenol removal is shown in Fig. 3. An increase in the E/E ratio with M/I ratio increased the percentage removal of phenol gradually, but at an E/E ratio and M/I ratio, the trend is reversed.

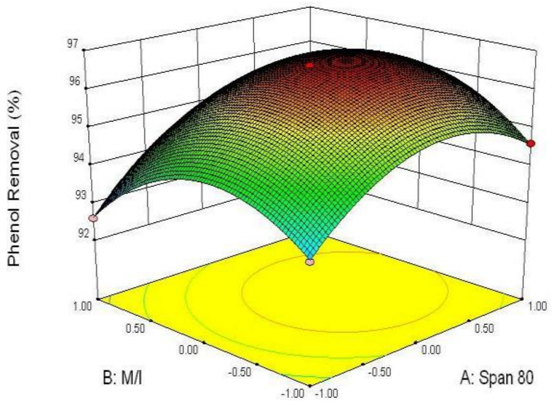

Fig. 1: 3D surface plot of interaction between Span 80 and E/E for phenol removal

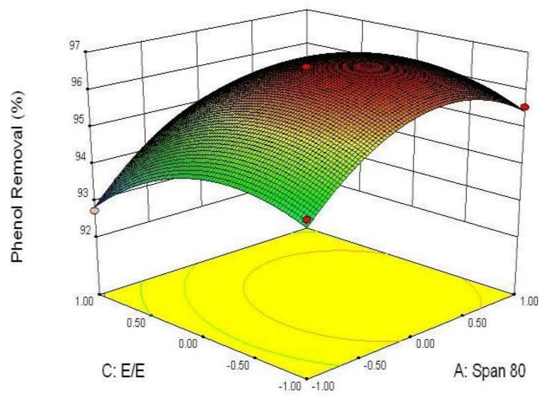

Fig. 2: 3D surface plot of interaction between Span 80 and M/I for phenol removal

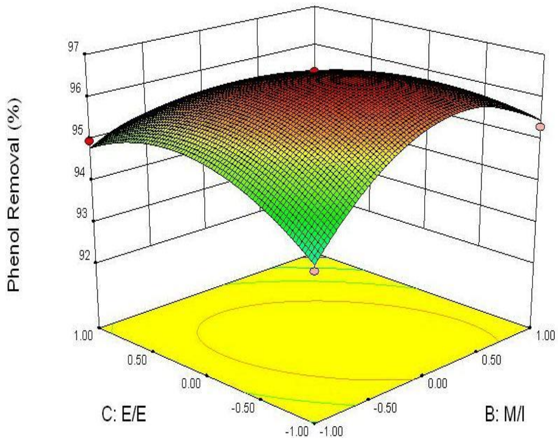

Fig. 3: 3D Surface plot of interaction between E/E and M/I for phenol removal

The sequential quadratic programming in MATLAB 7 is used to solve the second-degree polynomial regression equations (3). The optimum values of test variables in coded units are X_1 = 0.2901, X_2 = 0.0500, and X_3 = -0.2602. They are converted into uncoded units for the actual values and the optimum conditions for the maximum percentage removal of phenol values were: surfactant concentration (3.29 %), M/I ratio (1.05, v/v), and E/E ratio (0.474, v/v). Under optimal conditions, the model predicted a maximum predicted efficiency was 96.79%.

4. CONCLUSIONS

The response surface methodology based on a Box-Behnken design was successfully employed to optimize the phenol removal from synthetic wastewater. The second-order polynomial model gave a satisfactory description of the experimental data. The optimized conditions for the removal of phenol were determined as follows: surfactant concentration (3.29 %), M/I ratio (1.05, v/v), and E/E ratio (0.474, v/v). Under the optimal condition, the predicted maximum percentage removal of phenol was 96.79%. Good agreement was found between the experimental and predicted results. ANOVA showed a high R^2 value of regressions model equation (R^2 = 0.9942) which shows that the model is accurately predicts the experimental data. Thus, the quadratic model equation could explain the performance of ELM for phenol removal process with high level of significance.

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