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Selection of design parameters and optimization of operating parameters of soybean oil-based bulk liquid membrane for Cu(II) removal and recovery from aqueous solutions

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ABSTRACT

The objectives of this work were to select suitable design parameters and optimize the operating parameters of a soybean oil-based bulk liquid membrane (BLM) for Cu(II) removal and recovery from aqueous solutions. The soybean oil-based BLM consists of an aqueous feed phase (Cu(II) source), an organic membrane phase (soybean oil (diluent), di-2-ethylhexylphosphoric acid (D2EHPA) (carrier) and tributylphosphate (phase modifier)) and an aqueous stripping phase (sulfuric acid solution (H_2SO_4)). Effects of design parameters (stirring condition and stripping/membrane to feed/membrane interface area ratio) of soybean oil-based BLM on the Cu(II) removal and recovery from aqueous solutions were investigated and the suitable parameters were selected for further studies. Optimization of the operating parameters (D2EHPA concentration, H_2SO_4 concentration, stirring speed, temperature and operating time) of soybean oil-based BLM for maximum percentage (%) recovery of Cu(II) was then conducted using Response Surface Methodology and the optimum parameters were determined. A regression model for % recovery was developed and its adequacy was evaluated. The experimental % recovery obtained under the optimum operating conditions was compared with the predicted one and they were found to agree satisfactorily with each other.

1. Introduction

Excessive discharge of Cu(II) into waterways by various industrial activities (electrical, construction, transport, etc.) is endangering the environment due to its toxicity at low concentrations, bioaccumulation tendency and persistency in nature [1]. Over the years, numerous techniques have been used to remove Cu(II) from aqueous solutions which include chemical precipitation [2], membrane filtration [3], ion-exchange [4], solvent extraction [5], electrolysis [6] and biosorption [7]. However, these techniques have their own inherent limitations such as less efficiency, sensitive operating conditions, production of secondary sludge, high capital and operating costs, and further the disposal is a costly affair [8]. Hence, more efficient and cost-effective treatment techniques are sought after to overcome these difficulties.

Of late, a technique that combines both the extraction and stripping processes of solvent extraction in a single unit, called liquid membrane, has been given considerable attention by a host of researchers in the removal and recovery of Cu(II) from aqueous solutions [9–11]. This is attributed to its outstanding characteristics such as simultaneous removal and recovery of Cu(II) in a single unit, non-equilibrium mass transfer, high selectivity, high recovery, high fluxes and low energy consumption [12]. Among all types of liquid membrane, bulk liquid membrane (BLM) is the simplest type of non-dispersive liquid membrane used by numerous researchers to remove and recover Cu(II) from aqueous solutions. However, most of the BLM used apply petroleum-based organic solvents as their membrane phases, for instance kerosene- [13] and chloroform-based [9] ones, which are usually toxic and non-biodegradable. Recently, greener solvents such as vegetable oil-based organic solvents were found to remove Cu(II) effectively from aqueous solutions [14]. In fact, vegetable oil-based organic solvents, such as coconut oil-based ones, have been applied in the supported liquid membrane, another type of non-dispersive liquid membrane, to remove and recover Cu(II) from aqueous solutions [15]. However, to our knowledge, there has not been any research work on the application of vegetable oil-based organic solvents in BLM.

BLM can be designed with a wide variety of configurations which, in most cases, consist of two parts: a common part containing the membrane (M) phase and a separate part where the feed (F)

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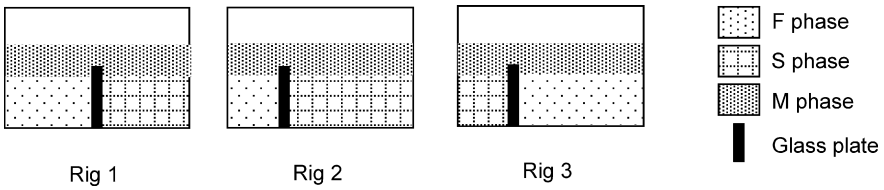

Fig. 1. Experimental rigs of soybean oil-based BLM.

and stripping (S) phases are divided by a solid impermeable barrier. The latter provides a dispersion-free contact between the two miscible F and S phases. In the present study, two design parameters of a soybean oil-based BLM, namely stirring condition and S/M to F/M interface area (S:F) ratio, were investigated into their effects on the removal and recovery of Cu(II) from aqueous solutions. Various operating parameters (carrier and stripping agent concentrations, stirring speed, temperature and operating time) of soybean oil-based BLM in the selected design were then optimized for the maximum recovery of Cu(II) using Response Surface Methodology (RSM).

2. Materials and methods

2.1. Materials

Refined soybean oil was supplied by Soon Soon Oil Mill Sdn. Bhd., Malaysia and was used without further purification. Copper sulfate pentahydrate ($CuSO_4$•$5H_2O$) (R and M Chemicals, ≥99.6% purity), di-2-ethylhexylphosphoric acid (D2EHPA) (Acros Organics, ≥99% purity), tributylphosphate (TBP) (Merck, ≥99% purity), sulfuric acid (H_2SO_4) (Merck, ≥98% purity), acetic acid (CH_3COOH) (System® ChemAR™, ≥99.5% purity), sodium acetate (CH_3COONa) (System® ChemAR™, ≥99% purity), sodium hydroxide (NaOH) (Merck, ≥99% purity) and sodium sulfate (Na_2SO_4) (Merck, ≥99% purity) were used as received.

2.2. Experimental setup

Fig. 1 shows the experimental rigs (Rigs 1–3) of soybean oil-based BLM used in this work. They are cubical glass containers (160 mm length × 90 mm width × 100 mm height) divided into two compartments by a 40 mm-height glass plate of thickness 2 mm. One compartment is filled with an aqueous F phase while another one with an aqueous S phase. These aqueous phases are layered with an organic M phase. The plate is placed at specific positions so that it gives S:F ratios of 1:1, 2.5:1 and 1:2.5 to Rigs 1–3, respectively. Accordingly, the volumes (200 mL) of F, M and S phases were set equally for Rig 1, while those for Rigs 2 and 3 were set differently at 100, 200, 290 mL and 290, 200, 100 mL, respectively. The F phase contained an initial concentration of Cu(II) of 500 mg/L and 250 mM Na_2SO_4 (inert salt) [16] which was prepared by dissolving appropriate amounts of $CuSO_4$•$5H_2O$ and Na_2SO_4 in 0.1 M acetate buffer solution of pH 4.46 [16], whereas the S phase was H_2SO_4 [17] at various concentrations (1.5–3.0 M). The buffer solution was prepared by mixing suitable quantities of 0.1 M CH_3COOH and 0.1 M CH_3COONa. The M phase, on the other hand, was prepared by mixing soybean oil (diluent) with different concentrations (77.5–107.5 mM) of D2EHPA (carrier) and 60 mM TBP (phase modifier) [14,16]. During the experiments, some, or all, of these phases were stirred at different speeds (70–150 rpm) by overhead mechanical stirrers (IKA, RW 20), with the soybean oil-based BLM being placed in a water bath of which the temperature (35–52 °C) was controlled by a thermostated hot-plate (Cole-Parmer, StableTemp). A thermometer was used to monitor the temperature of water bath from time to time. Fig. 2 shows an example of the experimental setup of soybean oil-based BLM for Rig 2 with four stirrings for all phases.

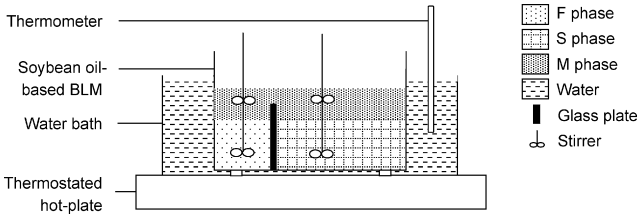

Fig. 2. Experimental setup of soybean oil-based BLM for Rig 2.

2.3. Selection of design parameters

Effects of two design parameters of soybean oil-based BLM, namely stirring condition and S:F ratio, on the removal and recovery of Cu(II) were investigated. Initially, effect of different stirring conditions was carried out using Rig 1 by stirring some or all its phases (Fig. 3). A blank test where no stirring was applied to any phases was also conducted. The best stirring condition was then used to investigate the effect of S:F ratio on Cu(II) removal and recovery using Rigs 1–3 (Fig. 1). All experiments were carried out

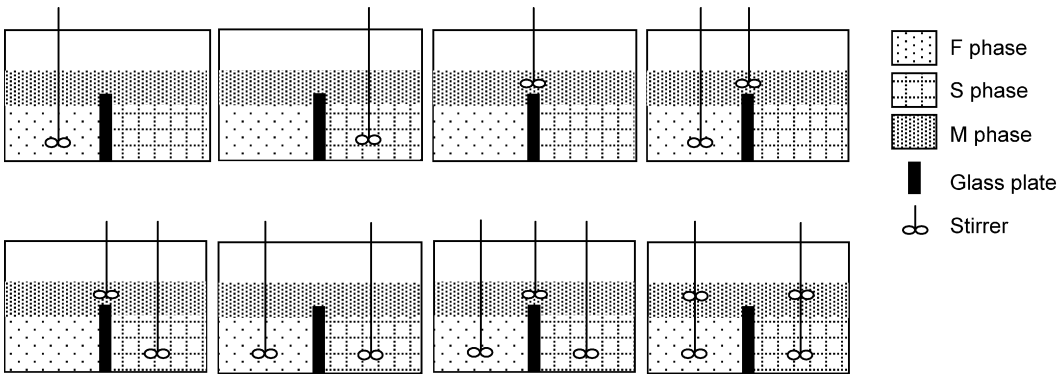

Fig. 3. Different stirring conditions studied using Rig 1.

Table 1
Parameters and levels applied in 2^{5-1} fractional factorial design.

Parameters	Symbols	Units	Levels	
			−1	+1
[D2EHPA]	A	mM	85	100
[H_2SO_4]	B	M	1.5	3
Stirring speed	C	rpm	100	130
Temperature	D	°C	25	35
Operating time	E	h	20	24

for 5 h at room temperature (25 °C [14,16,17]), with stirring speed of 100 rpm ([14,16,17]), [D2EHPA] of 85 mM [16] in the M phase and 1.5 M H_2SO_4 [17] in the S phase. At the end of each experiment, samples (5 mL) of F and S phases were collected and analyzed for Cu(II) concentration by a flame atomic absorption spectrophotometer (Perkin Elmer, AA-400) at a wavelength of 324.75 nm after appropriate filtration and dilution. The percentage (%) removal of Cu(II) was then calculated according to:

$$\%\ \text{removal} = \frac{[\text{Cu}]_{\text{o,F}} - [\text{Cu}]_{\text{f,F}}}{[\text{Cu}]_{\text{o,F}}} \times 100 \quad (1)$$

where $[\text{Cu}]_{\text{o,F}}$ and $[\text{Cu}]_{\text{f,F}}$ are the initial and final Cu(II) concentrations in the F phase, respectively. The % recovery of Cu(II), on the other hand, was given by:

$$\%\ \text{recovery} = \frac{[\text{Cu}]_{\text{f,S}}}{[\text{Cu}]_{\text{o,F}} - [\text{Cu}]_{\text{f,F}}} \times 100 \quad (2)$$

where $[\text{Cu}]_{\text{f,S}}$ is the final Cu(II) concentration in the S phase. During the analysis, the initial concentrations of Cu(II) in both the M and S phases were assumed zero. All experiments were carried out in duplicate or triplicate and the relative standard deviation between replicate samples within an experiment range was less than 2%.

2.4. Optimization of operating parameters

Various operating parameters of soybean oil-based BLM, namely [D2EHPA], [H_2SO_4], stirring speed, temperature and operating time, were optimized for the maximum % recovery of Cu(II) using RSM. It started with screening experiments to determine which of the various operating parameters were likely to be important in the response surface study. Next, an experimental design was selected to evaluate the relations existing between the important parameters and the % recovery of Cu(II) (response). Experiments were then conducted according to the selected experimental design, followed by data analysis which includes regression analysis, model adequacy checking and determination of optimum conditions [18]. All experiments were carried out in duplicate or triplicate and the relative standard deviation between replicate samples within an experiment range was less than 2%. The data analysis involved in RSM, on the other hand, was performed with the Minitab software (Release 14, Minitab Inc., State College, PA).

2.4.1. Screening experiments

Screening of various operating parameters affecting Cu(II) recovery through soybean oil-based BLM was conducted using a two-level fractional factorial design. Table 1 shows the parameters and levels applied in the 2^{5-1} fractional factorial design, where the experimental domain of each parameter was determined from the preliminary experiments. The low and high levels of these parameters are coded as −1 and +1, respectively. Other parameters such as $[\text{Cu}]_{\text{o,F}}$ (500 mg/L (7.88 mM)), initial pH of F phase (4.46), Na_2SO_4 (250 mM) and TBP (60 mM) concentrations were fixed at specific values as obtained from our previous work [16]. The sample collection and analysis of each experiment were as described in Section 2.3, except for the analysis of % removal and recovery of Cu(II) where only the latter was performed. The statistical significance of each parameter and their combinations were then evaluated with the Minitab software at 5% significance level.

2.4.2. Optimization experiments

Optimization of the significant parameters affecting Cu(II) recovery through soybean oil-based BLM obtained from the screening experiments (Section 2.4.1) was carried out using the central composite design (CCD). Table 2 summarizes the parameters studied in five levels ($-\alpha$, −1, 0, 1, α) in CCD, where levels −1 and +1 represent the low and high values, $-\alpha$ and α indicate the low and high extreme values, and 0 is the center value of each parameter. Since [H_2SO_4] was found not to influence the % recovery of Cu(II) significantly, it was fixed at 1.5 M [17] throughout the optimization experiments. Other parameters such as $[\text{Cu}]_{\text{o,F}}$, initial pH of F phase, Na_2SO_4 and TBP concentrations, as well as the procedures of sample collection and analysis for each experiment, were as described in Section 2.4.1.

2.4.3. Regression analysis

A multiple regression analysis was performed on a regression model which corresponds to the following second-order response function:

$$y = \beta_{\text{o}} + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum \sum_{j<i} \beta_{ij} x_i x_j + \varepsilon \quad (3)$$

where β_{o}, β_i, β_{ii} and β_{ij} are the coefficients of intercept, linear, quadratic and interaction variables, respectively, y is the dependent variable or the response, x_i and x_j are the independent variables in coded unit, and ε is the error term that accounts for the effects of excluded parameters. The equation used for coding is:

$$x = \frac{X - (X_{high} + X_{low})/2}{(X_{high} - X_{low})/2} \quad (4)$$

where x is the coded variable, X is the natural variable, while X_{high} and X_{low} are the high and low values of the natural variables, respectively. During the analysis, coefficients that caused the model (Eq. (3)) to best fit a set of collected response variable data obtained from the optimization experiments (Section 2.4.2) were determined by the least squares method [18] with the aid of the Minitab software.

2.4.4. Determination of optimum operating parameters

To determine the optimum operating parameters of soybean oil-based BLM, the numerical optimization feature of the Minitab software was used. The software searched for a combination of parameters that simultaneously satisfied the ultimate goals and limits placed on the response and each of the parameters. In consideration of the increasingly stringent effluent discharge limits, coupled with the great value of Cu(II) in various engineering applications [1], the optimization criterion was maximized for the % recovery of Cu(II) (response) while the values of other parameters were set in the ranges studied. The optimum values of parameters obtained were then assessed by the composite desirability, which carries a value from 0 to 1, to determine the degree of satisfaction of the optimum values for the ultimate goal of response [19].

3. Results and discussion

3.1. Effect of stirring condition

Fig. 4 shows the % removal and recovery of Cu(II) obtained at different stirring conditions using Rig 1. For cases with no stirring ({1}) and one stirring for the S phase ({3}), the % removal achieved is about 30% only. For the rest of the cases ({2}, {4}, {5}, {6}, {7}, {8} and {9}) studied, % removal of more than 80% are recorded.

Table 2
Parameters and levels applied in CCD.

Parameters	Symbol	Unit	Levels				
			$-\alpha$	−1	0	1	α
[D2EHPA]	A	mM	77.50	85	92.50	100	107.50
Stirring speed	C	rpm	70.00	90	110.00	130	150.00
Temperature	D	°C	40.00	43	46.00	49	52.00
Operating time	E	h	24.00	26	28.00	30	32.00

$\alpha = \pm 2$.

This implies that stirring of either the F, M, or all phases inclined to improve the transport of Cu(II) from F into M phases by minimizing the boundary layers in the aqueous and organic phases [20]. The corresponding % recovery achieved in these cases are, however, much lower, which are about 10% only or lower. Nevertheless, it should be noted that stirring of M phase increases the % recovery appreciably. If the M phase is stirred ({4}, {5}, {6}, {8} and {9}), a substantial amount of Cu(II) is stripped, with % recovery of about 10%. These findings could be explained by the viscous M phase, which was soybean oil-based organic solvent, used in this work. Apparently, stirring of M phase increased its fluidity and, thus, enhanced the transport of Cu(II) from M into S phases. The best stirring condition, i.e. four stirrings for all phases ({9}), which achieved Cu(II) removal and recovery of >90% and >10%, respectively, was selected for further studies.

3.2. Effect of S:F ratio

Fig. 5 shows the % removal and recovery of Cu(II) obtained at different S:F ratios using Rig 1 (S:F ratio of 1:1), Rig 2 (S:F ratio of 2.5:1) and Rig 3 (S:F ratio of 1:2.5) with four stirrings for all phases. It is found that Cu(II) removal of more than 90% is achieved by S:F ratios of 1:1 and 2.5:1, while less than 80% is achieved by S:F ratio of 1:2.5. This implies that the bigger S:F ratio (2.5:1) did not affect the % removal much but inclined to reduce it when the smaller S:F ratio (1:2.5) was used. The smaller S:F ratio means a greater Cu(II) mass in the F phase and, hence, results in a lower % removal achieved within the same operating time. On the other hand, the highest % recovery (~18%) is accomplished at S:F ratio of 2.5:1 while the lowest one (<10%) is obtained at S:F ratio of 1:2.5. This could be explained by the larger S/M interfacial area available for the transport of Cu(II) from M into S phases with increasing S:F ratio. Since the S:F ratio of 2.5:1 achieved the highest % removal (>90%) and recovery (~18%) of Cu(II), it was selected for further studies.

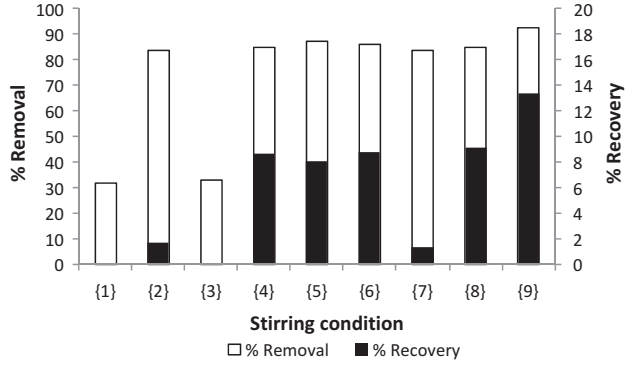

Fig. 4. % Removal and recovery of Cu(II) obtained at different stirring conditions using Rig 1 ({1}: no stirring; {2}: one stirring for F phase; {3}: one stirring for S phase; {4}: one stirring for M phase; {5}: two stirrings for F and M phases; {6}: two stirrings for S and M phases; {7}: two stirrings for F and S phases; {8}: three stirrings for all phases; {9}: four stirrings for all phases).

3.3. Screening of operating parameters

The design matrix and results of 2^{5-1} fractional factorial design (16 runs) with five parameters ([D2EHPA], [H_2SO_4], stirring speed, temperature and operating time) and one response (% recovery) are given in Table 3. The experimental sequence (Std Order) was randomized in order to minimize the unexpected variability in the observed response. All experiments were conducted under homogeneous conditions in one block of measurements. The average % recovery measured from replicate samples was found to range from 17.39 to 68.87%, and the significant effect of each parameter on % recovery was evaluated by a normal probability plot of standardized effects (Fig. 6) at 5% significance level using the Minitab software. Fig. 6 suggests that the main effects of stirring speed (C) and temperature (D), as well as the interaction effect of ([D2EHPA] × operating time) (AE) are the influential parameters to % recovery and, thus, were selected for further studies.

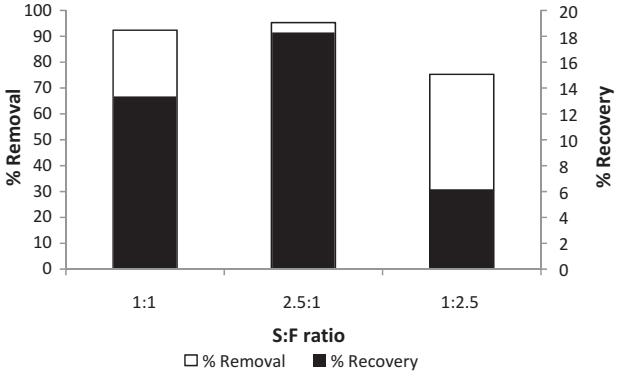

Fig. 5. % Removal and recovery of Cu(II) obtained at different S:F ratios using Rig 1 (S:F ratio = 1:1), Rig 2 (S:F ratio = 2.5:1) and Rig 3 (S:F ratio = 1:2.5).

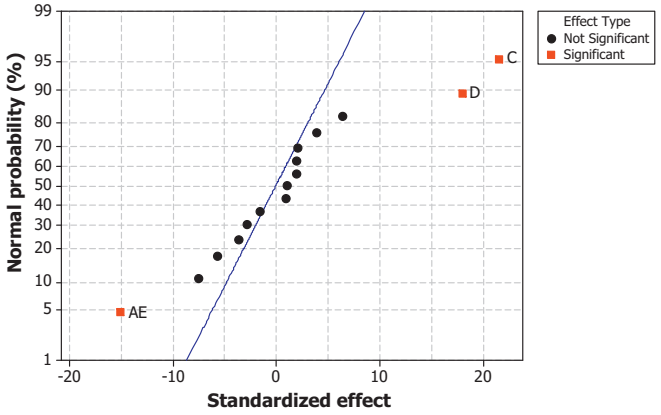

Fig. 6. Normal probability plot of standardized effects.

Table 3
Design matrix of 2^{5-1} fractional factorial design and average % recovery measured.

Std order	Run order	Blocks	Parameters[a]					% recovery (avg)
			A	B	C	D	E	
4	1	1	100	3	100	25	24	29.72
14	2	1	100	1.5	130	35	20	68.87
11	3	1	85	3	100	35	24	41.64
7	4	1	85	3	130	25	24	47.00
6	5	1	100	1.5	130	25	24	30.53
15	6	1	85	3	130	35	20	52.01
2	7	1	100	1.5	100	25	20	35.44
8	8	1	100	3	130	25	20	52.58
16	9	1	100	3	130	35	24	50.52
12	10	1	100	3	100	35	20	34.88
13	11	1	85	1.5	130	35	24	67.79
10	12	1	100	1.5	100	35	24	40.83
1	13	1	85	1.5	100	25	24	34.85
3	14	1	85	3	100	25	20	17.39
9	15	1	85	1.5	100	35	20	35.65
5	16	1	85	1.5	130	25	20	33.84

[a] A: [D2EHPA] (mM); B: [H_2SO_4] (M); C: stirring speed (rpm); D: temperature (°C); E: operating time (h); std: standard; avg: average; all variables are in uncoded units.

Table 4
Design matrix of CCD and average % recovery measured.

Std order	Run order	Blocks	Parameters[a]				% recovery (avg)
			A	C	D	E	
21	1	1	92.5	110	40	28	59.99
20	2	1	92.5	150	46	28	79.04
19	3	1	92.5	70	46	28	42.95
16	4	1	100	130	49	30	97.56
3	5	1	85	130	43	26	73.90
29	6	1	92.5	110	46	28	59.43
12	7	1	100	130	43	30	71.64
10	8	1	100	90	43	30	53.77
7	9	1	85	130	49	26	90.21
13	10	1	85	90	49	30	71.48
8	11	1	100	130	49	26	86.15
27	12	1	92.5	110	46	28	59.93
2	13	1	100	90	43	26	46.70
14	14	1	100	90	49	30	79.61
15	15	1	85	130	49	30	90.89
28	16	1	92.5	110	46	28	59.42
9	17	1	85	90	43	30	55.61
6	18	1	100	90	49	26	66.06
22	19	1	92.5	110	52	28	94.95
5	20	1	85	90	49	26	63.96
1	21	1	85	90	43	26	52.13
17	22	1	77.5	110	46	28	70.30
11	23	1	85	130	43	30	74.69
18	24	1	107.5	110	46	28	63.13
26	25	1	92.5	110	46	28	57.82
24	26	1	92.5	110	46	32	86.05
4	27	1	100	130	43	26	59.74
23	28	1	92.5	110	46	24	68.02
25	29	1	92.5	110	46	28	57.78

[a] A: [D2EHPA] (mM); C: stirring speed (rpm); D: temperature (°C); E: operating time (h)

3.4. Optimization of operating parameters

The design matrix and results of CCD with four parameters ([D2EHPA], stirring speed, temperature and operating time) and one response (% recovery) are given in Table 4. There are altogether 29 experimental points which are composed of 16 factorial points (Std Order 1–16), 8 star points (Std Order 17–24) and 5 replicates of the center point (Std Order 25–29). Similar to the screening experiments (Section 3.3), all optimization experiments were conducted randomly in one block of measurements. The average % recovery measured from replicate samples was found to range from 42.95 to 97.56%, and the variation in reproducibility between experiments based on the five replicate samples of the center point was computed to be 1.70%.

3.5. Regression model

Table 5 shows the estimated coefficients (Coef) of each variable term in a regression model for % recovery (Eq. (5)), along with the corresponding standard deviation (SD_{coef}), *t*-statistics (*t*-stat) and probability (*P*) values determined at 5% significance level. Variable terms with $P < 0.05$, i.e. A, C, D, E, A^2, D^2, E^2, AC, AD and AE, are considered statistically significant. Therefore, a second-order polynomial model in coded unit that correlates % recovery with all the

Table 5
Estimated coefficients of the regression model for % recovery (Eq. (5)).

Term[a]	Coef	SD_{coef}	*t*-Stat	*P*
Constant	58.876	0.7856	74.944	0.000
A	−1.083	0.3586	−3.019	0.009
C	9.485	0.3586	26.452	0.000
D	9.486	0.3586	26.454	0.000
E	3.853	0.3586	10.744	0.000
A × A	2.014	0.3449	5.841	0.000
C × C	0.584	0.3449	1.694	0.112
D × D	4.703	0.3449	13.637	0.000
E × E	4.594	0.3449	13.322	0.000
A × C	−1.098	0.4392	−2.499	0.026
A × D	2.333	0.4392	5.311	0.000
A × E	1.966	0.4392	4.477	0.001
C × D	0.746	0.4392	1.699	0.111
C × E	−0.428	0.4392	−0.973	0.347
D × E	0.620	0.4392	1.412	0.180

[a] A: [D2EHPA]; C: stirring speed; D: temperature; E: operating time; all variables are in coded units.

Table 6
ANOVA of the regression model for % recovery (Eq. (5)).

Source	DF	Seq SS	*F*	*P*
Regression	14	5866.68	135.80	0.000
Linear	4	4703.04	381.02	0.000
Square	4	977.48	79.19	0.000
Interaction	6	186.16	10.05	0.000
Residual error	14	43.20		
Lack-of-fit	10	39.17	3.89	0.101
Pure error	4	4.03		
Total	28	5909.88		

SD_{reg} = 1.757; R^2 = 0.993; R^2(adj) = 0.985; SD_{reg} = standard deviation of regression; DF = degrees of freedom; seq SS = sequential sum of squares; *F* = *F* values from Fisher's statistical test.

significant variable terms is expressed as:

$$\%\ \text{recovery} = 58.876 - 1.083A + 9.485C + 9.486D + 3.853E + 2.014A^2 + 4.703D^2 + 4.594E^2 - 1.098\text{AC} + 2.333\text{AD} + 1.966\text{AE} \quad (5)$$

The positive coefficients of variable terms in Eq. (5) indicate their synergistic effects on % recovery, while the negative coefficients show their antagonistic effects. Accordingly, the order of decreasing significance of each variable term with respect to its effects on % recovery is $D \approx C > D^2 \approx E^2 > E > AD > A^2 \approx AE > AC \approx A$. This denotes that the main effects C (stirring speed) and D (temperature) are the primary operating parameters that influence % recovery relative to the other parameters. Two of these parameters are associated to the fluidity or viscosity [20] of the soybean oil-based M phase which is generally more viscous than the classical petroleum-based M phase [21]. This implies that the viscosity of M phase is the most important factor that governs the Cu(II) transport through soybean oil-based BLM and this is consistent with the previous findings [22].

3.6. Model adequacy checking

Table 6 shows the analysis of variance (ANOVA) of the regression model for % recovery (Eq. (5)) obtained at 5% significance level. The regression model and each variable term (linear, square and interaction) in the model show *P* values of less than 0.05 and, thus, are statistically significant. The high *P* value ($P > 0.05$) of lack-of-fit indicates that the model is adequate for predicting the % recovery of Cu(II) through soybean oil-based BLM within the experimental domain studied. To test the global fit of the model, the coefficient of determination (R^2) and the adjusted R^2 (R^2(adj)) [18] were evaluated. The value of R^2, i.e. 0.993 (Table 6), denotes that the sample

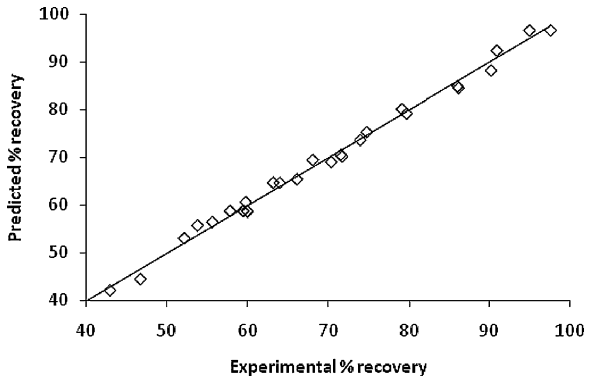

Fig. 7. Comparison of predicted and experimental % recovery.

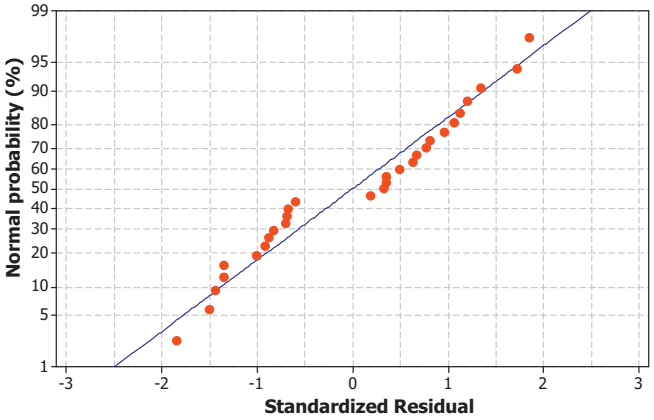

Fig. 8. Normal probability plot of standardized residuals.

variation of 99.3% for % recovery is attributed to the regressors in the model and only 0.7% of the total variability is not explained by the model. The value of R^2(adj), i.e. 0.985 (Table 6), which deviates 0.8% from the value of R^2, indicates that the model is highly significant and there is small chance for the inclusion of any insignificant terms in the model [18]. Fig. 7 shows the predicted % recovery at 95% confidence level plotted against the experimental % recovery. All data points locate around a linear line (Fig. 7), indicating the good fit of model to the experimental data. The adequacy of model was also examined from the normal probability plot of standardized residuals (Fig. 8). As shown in Fig. 8, all points cluster along a straight line and the standardized residuals for all fitted values are within small magnitudes of ±2. These indicate that A, C, D, E, A^2, D^2, E^2, AC, AD and AE are the only significant effects and that the underlying regression assumptions [23] are satisfied. Therefore, the model (Eq. (5)) can be used as a predictive tool to estimate the % recovery of Cu(II) through soybean oil-based BLM over the entire uncertainty range of parameters studied.

3.7. Response contour and determination of optimum operating parameters

Fig. 9 shows the two-dimensional response contour plots of % recovery of Cu(II) versus two of the operating parameters studied when the other two parameters are held at high values (+1). It is found that % recovery increases with stirring speed (Fig. 9a) and temperature (Fig. 9b) at different [D2EHPA] studied. This may be attributed to the reduction in the thickness of boundary layers of aqueous and organic phases in soybean oil-based BLM with increasing stirring speed [20], as well as the viscosity drop of these phases and enhancement in the complexation and decomplexa-

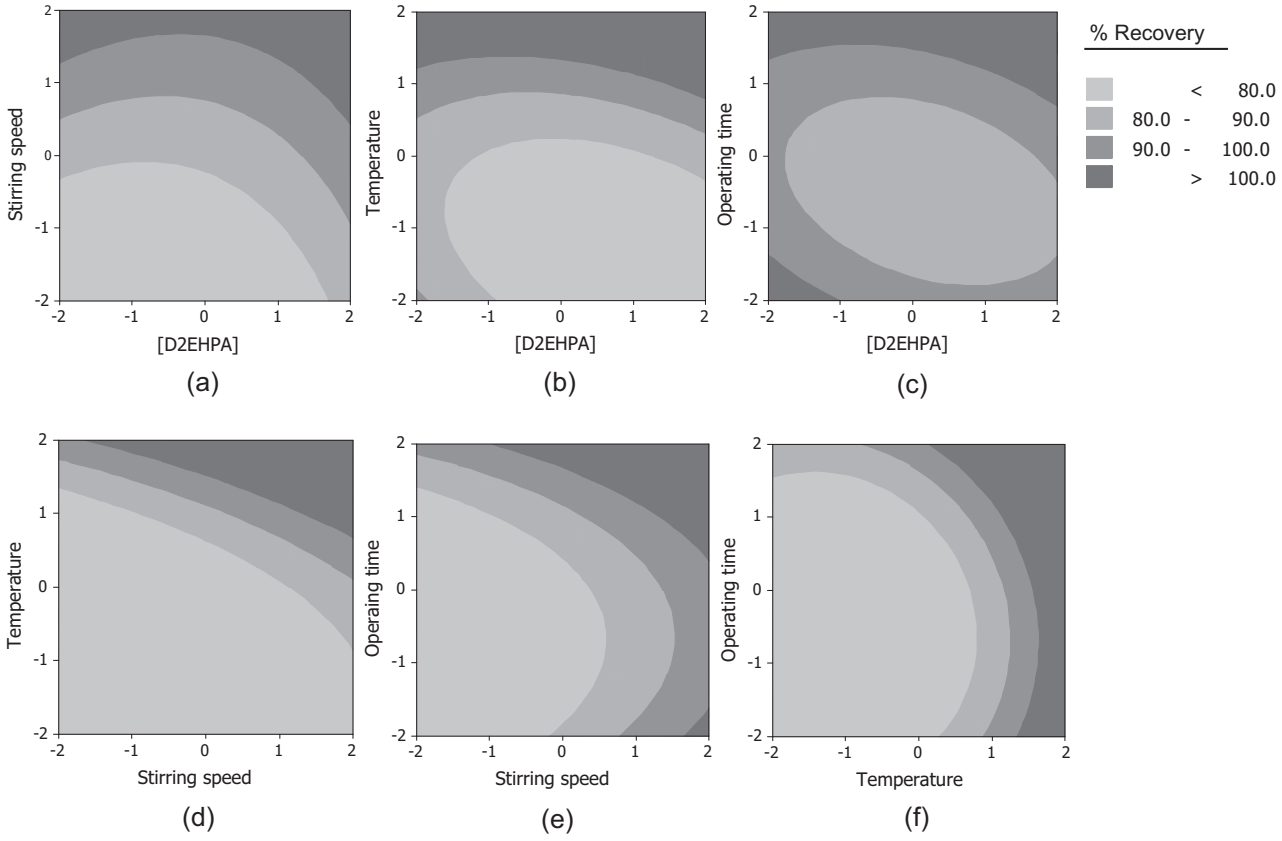

Fig. 9. Two-dimensional response contour plots.

Table 7
Optimum conditions and model validation.

Composite desirability	Parameters[a]				Predicted % recovery	Experimental % recovery	% deviation
	A	C	D	E			
1.00	87.88	150	40	24	99.99	98.56	1.44

[a] A: [D2EHPA] (mM); C: stirring speed (rpm); D: temperature (°C); E: operating time (h); all parameters are in uncoded units.

tion reactions of Cu(II) at F/M and S/M interfaces with increasing temperature [20,22]. Reduction in the thickness of boundary layers and viscosity of phases improved the hydrodynamic condition in soybean oil-based BLM and, thus, accelerated the transport of Cu(II) by diffusion from F to M and M to S phases. Enhancement in the interfacial complexation and decomplexation reactions of Cu(II), on the other hand, improved the Cu(II) removal and recovery processes at F/M and S/M interfaces. However, % recovery is found to decrease with operating time at lower range (levels −2 to 0), but increase with operating time at higher range (levels 0–2) throughout [D2EHPA] range studied (Fig. 9c). The former could be deduced from the saturation of metal complexes in the M phase which hindered the carrier-facilitated transport of Cu(II) by diffusion, while the latter was due to the possible 'jumping' transport of Cu(II) from one carrier molecule to another in the M phase at the point of saturation which is more effective than the common carrier facilitated transport [24–26]. At different stirring speeds, however, % recovery is not affected much by [D2EHPA] (Fig. 9a), but increases with temperature (Fig. 9d) and operating time (Fig. 9e). This implies that the antagonistic effect of high viscosity in the M phase due to high [D2EHPA] could be offset by high temperature and operating time. At lower temperature range (levels −2 to 0), % recovery decreases with [D2EHPA] (Fig. 9b) while remains essentially unchanged at a low value of 80% with increasing stirring speed (Fig. 9d) and operating time (Fig. 9f). This is expected since high [D2EHPA] induced high viscosity in the M phase and, thus, encumbered the Cu(II) transport through soybean oil-based BLM [22]. At higher temperature range (levels 1–2), however, % recovery remains nearly constant at a high value of >90% throughout [D2EHPA] range studied (Fig. 9b) while increases with stirring speed (Fig. 9d) and operating time (Fig. 9f). This is attributed to the ability of high temperature to offset the negative effect of high viscosity in the M phase as explained earlier. On the other hand, reduction of % recovery with increasing [D2EHPA] at lower range of operating time (levels −2 to 0) (Fig. 9c) may be explained by the increasing viscosity of the M phase and the insufficient time available for Cu(II) transport across soybean oil-based BLM. At higher range of operating time (levels 0–2), however, [D2EHPA] becomes not influential to % recovery (Fig. 9c). This may be due to the extended time available for Cu(II) transport across soybean oil-based BLM which suppresses the effect of increasing viscosity of M phase caused by high [D2EHPA]. Meanwhile, the increment of % recovery with stirring speed (Fig. 9e) is due to the enhancement in the hydrodynamic condition in soybean oil-based BLM, whereas that with increasing temperature (Fig. 9f) is caused by the improved medium viscosity and interfacial complexation–decomplexation reaction of Cu(II) as described earlier.

Table 7 presents the optimum operating parameters in uncoded units ([D2EHPA] = 87.88 mM, stirring speed = 150 rpm, temperature = 40 °C and operating time = 24 h) obtained from the Minitab software which give the highest composite desirability (1.00). The small deviation (1.44%) between the experimental (98.56%) and predicted (99.99%) values of % recovery indicates that the model (Eq. (5)) is sufficient to predict the % recovery in the range of parameters studied. To evaluate the reproducibility of the experimental results, experiments under the optimum operating conditions were repeated three times and the relative standard deviation between the replicate samples was found to be less than 1%.

4. Conclusion

Investigation of the effects of design parameters (stirring condition and stripping/membrane to feed/membrane interface area ratio) of soybean oil-based BLM revealed that they affected Cu(II) removal and recovery from aqueous solutions. The removal process was improved greatly by stirring either the feed, membrane, or all phases, but was only enhanced slightly with a higher stripping/membrane to feed/membrane interface area ratio. The recovery process was improved considerably by stirring the membrane phase and applying a higher stripping/membrane to feed/membrane interface area ratio. The suitable design parameters of soybean oil-based BLM for Cu(II) removal and recovery from aqueous solutions were selected as follows: stirring condition of four stirrings for all phases and stripping/membrane to feed/membrane interface area ratio of 2.5:1. Screening of various operating parameters ([D2EHPA], $[H_2SO_4]$, stirring speed, temperature and operating time) of soybean oil-based BLM using the 2^{5-1} fractional factorial design revealed that all parameters, except $[H_2SO_4]$, affected % recovery of Cu(II) significantly and, thus, were optimized for the maximum % recovery of Cu(II) with the central composite design. A quadratic model for % recovery as a function of the significant parameters was developed and its R^2 (0.993) and R^2(adj) (0.985) values were determined. The high R^2 values indicate that the model is highly significant and provides a good estimate of the response within the experimental domain studied. The optimum operating parameters for predicting the targeted % recovery were determined as follows: [D2EHPA] of 87.88 mM, $[H_2SO_4]$ of 1.5 M, stirring speed of 150 rpm, temperature of 40 °C and operating time of 24 h. The experimental % recovery (98.56%) obtained under the optimum operating conditions agrees well with the predicted one (99.99%).

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References

[1] M. Csuros, C. Csuros, Environmental Sampling and Analysis for Metals, CRC Press LLC, The United States of America, 2002.
[2] F.M. Pang, S.P. Teng, T.T. Teng, A.K. Mohd Omar, Heavy metals removal by hydroxide precipitation and coagulation–flocculation methods from aqueous solutions, Water Qual. Res. J. Can. 44 (2009) 174–182.
[3] H. Bessbousse, T. Rhlalou, J.-F. Verchère, L. Lebrun, Removal of heavy metal ions from aqueous solutions by filtration with a novel complexing membrane containining poly(ethyleneimine) in a poly(vinyl alcohol) matrix, J. Membr. Sci. 307 (2008) 249–259.
[4] A. Chen, G. Qui, Z. Zhao, P. Sun, R. Yu, Removal of copper from nickel anode electrolyte through ion exchange, Trans. Nonferrous Met. Soc. China 19 (2009) 253–258.
[5] F. Xie, D. Dreisinger, Studies on solvent extraction of copper and cyanide from waste cyanide solution, J. Hazard. Mater. 169 (2009) 333–338.
[6] B. Yang, C. Wang, D. Li, F. Yin, Y. Chen, N. Wang, Selective separation of copper and cadmium from zinc solutions by low current density electrolysis, Trans. Nonferrous Met. Soc. China 20 (2010) 533–536.
[7] Y.A. Yahaya, M.M. Don, S. Bhatia, Biosorption of copper(II) onto immobilized cells of Pycnoporus sanguineus from aqueous solutions: equilibrium and kinetic studies, J. Hazard. Mater. 161 (2009) 189–195.
[8] T.A. Kurniawan, G.Y.S. Chan, W.H. Lo, S. Babel, Physico-chemical treatment techniques for wastewater laden with heavy metals, Chem. Eng. J. 118 (2006) 83–98.
[9] T.R. Reddy, J. Ramkumar, S. Chandramouleeswaran, A.V.R. Reddy, Selective transport of copper across a bulk liquid membrane using 8-hydroxy quinoline as carrier, J. Membr. Sci. 351 (2010) 11–15.
[10] M. Chiha, O. Hamdaoui, F. Ahmedchekkat, C. Pétrier, Study on ultrasonically assisted emulsification and recovery of copper(II) from wastewater using an emulsion liquid membrane process, Ultrason. Sonochem. 17 (2010) 318–325.
[11] W. Zhang, C. Cui, Z. Ren, Y. Dai, H. Meng, Simultaneous removal and recovery of copper(II) from acidic wastewater by hollow fiber renewal liquid membrane with LIX984N as carrier, Chem. Eng. J. 157 (2010) 230–237.
[12] Z.Q. Ren, W. Zhang, Y. Dai, Y. Yang, Z. Hao, Modeling of effect of pH on mass transfer of copper(II) extraction by hollow fiber renewal liquid membrane, Ind. Eng. Chem. Res. 47 (2008) 4256–4262.
[13] G. León, M.A. Guzmán, Facilitated transport of copper through bulk liquid membranes containing different carriers: compared kinetic study, Desalination 223 (2008) 330–336.
[14] S.H. Chang, T.T. Teng, N. Ismail, Extraction of Cu(II) from aqueous solutions by vegetable oil-based organic solvents, J. Hazard. Mater. 181 (2010) 868–872.
[15] P. Venkateswaran, A.N. Gopalakrishnan, K. Palanivelu, Di(2-ehtylhexyl)phosphoric acid-coconut oil supported liquid membrane for the separation of copper ions from copper plating wastewater, J. Environ. Sci. 19 (2007) 1446–1453.
[16] S.H. Chang, T.T. Teng, N. Ismail, Optimization of Cu(II) extraction from aqueous solutions by soybean oil-based organic solvent using Response Surface Methodology, Water, Air, Soil Pollut. (2010), doi:10.1007/s11270-010-0610-y.
[17] S.H. Chang, T.T. Teng, N. Ismail, Efficiency, stoichiometry and structural studies of Cu(II) removal from aqueous solutions using di-2-ethylhexylphosphoric acid and tributylphosphate diluted in soybean oil, Chem. Eng. J. 166 (2011) 249–255.
[18] R.H. Myers, D.C. Montgomery, Response Surface Methodology: Process and Product Optimization Using Designed Experiments, second ed., John Wiley & Sons Inc., The United State of America, 2002.
[19] S Armenta, S. Garrigues, M. de la Guardia, Optimization of transmission near infrared spectrometry procedures for quality control of pesticide formulations, Anal. Chim. Acta 571 (2006) 288–297.
[20] G. Muthuraman, T.T. Teng, C.P. Leh, I. Norli, Use of bulk liquid membrane for the removal of chromium(VI) from aqueous acidic solution with tri-n-butyl phosphate as a carrier, Desalination 249 (2009) 884–890.
[21] P. Venkateswaran, K. Palanivelu, Vegetable oil as greener liquid membrane, in: P.B. Warey (Ed.), New Research on Hazardous Materials, Nova Science Publishers Inc., The United States of America, 2007, pp. 347–369.
[22] S. Shailesh, P.N. Pathak, P.K. Mohapatra, V.K. Manchanda, Transport studies of uranium across a supported liquid membrane containing N,N-di(2-ethylhexyl) isobutyramide (D2EHIBA) as the carrier, J. Membr. Sci. 272 (2006) 143–151.
[23] W.D. Berry, Understanding Regression Assumptions, Sage Publication Inc., The United States of America, 1993.
[24] E.L. Cussler, R. Aris, A. Brown, On the limits of facilitated diffusion, J. Membr. Sci. 43 (1989) 149–164.
[25] A.A. Kalachev, L.M. Kardivarenko, N.A. Plate, V.V. Bagreev, Facilitated diffusion in immobilized liquid membranes: experimental verification of the "jumping" mechanism and percolation threshold in membrane transport, J. Membr. Sci. 75 (1992) 1–5.
[26] R. Gawroński, P. Religa, Transport mechanism of chromium(III) through the unmixed bulk liquid membrane containing dinonylnaphthalenesulfonic acid as a carrier, J. Membr. Sci. 289 (2007) 187–190.