

An approach on a sustainable and stable continuous emulsion liquid membrane (CELM) for phenol recovery

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Abstract. Throughout this work, continuous emulsion liquid membrane (CELM) was employed for the recovery of phenol using a primary water in oil (W/O) emulsion containing a mixture of kerosene and palm oil as diluent, Span 80 as a surfactant, and sodium hydroxide as a strippant. Several factors influencing the recovery of phenol namely rotational speed, treat ratio and retention time were examined and optimized using response surface methodology (RSM). Results revealed that about 29% of phenol was recovered with 7 times enrichment (2100 ppm) was concentrated in the internal phase under best conditions of 527 rpm of rotational speed, 1:4 of treat ratio and 2.6 min of retention time. Besides, an interaction effect of rotational speed and retention time was found to be significant towards phenol recovery in CELM. Thus, CELM has the ability to recover and concentrate the phenol for other applications.

1. Introduction

The presence of untreated phenol in the water body can be a major threat as they are difficult to degrade biologically since they are toxic for microorganisms. Hence, the treatment of wastewater containing phenol has become one of major concern among the researchers in order to protect the environment. Numerous techniques have been used for phenol removal namely adsorption [1], solvent extraction (SX) [2], membrane separation technologies [3], and so forth. Unfortunately, adsorption provides low efficiency and less possibility in the regeneration of adsorbent [1]. SX has the ability to treat the high concentration of phenol but involves high consumption of extractant [2]. Membrane technologies normally suffer of membrane fouling and instability problem [3]. ELM is one of the effective techniques for phenol removal as it offers some advantages including energy efficient, low cost, high mass transfer interfacial area, high separation factor as well as extraction and recovery process in a single process [4-6]. It is prepared by developing a stable water in oil (W/O) emulsion containing two immiscible phases (organic and aqueous phases) and afterwards the formed emulsion is dispersed into the third phase (wastewater to be treated) by agitation for the removal of desired solute [7]. The main components in the W/O emulsion are carrier/extractant, surfactant, diluent/solvent and strippant. Diluent or solvent dominates the highest proportion of ELM. Petroleum based solvents are usually used in ELM including dichloroethane, heptane, and kerosene but they are toxic, expensive, high volatility, flammable, and



unsustainable for the global green technology [4-7]. New invention has been made in the ELM process via introduction of green diluent of vegetable oils in the ELM process. This approach is helpful in order to promote a more cost effective and environmentally friendly. Contrary to petroleum based diluents, vegetable oils are renewable, non-toxic, inflammable, non-volatile, and biodegradable [7-8].

The stable ELM is highly depending on the stability of W/O emulsion. Essentially, the stable W/O emulsion contains high number of smaller internal droplets consisting of aqueous internal (water) entrapped in the organic phase (oil). However, the droplets can be bigger which thereby encourages the breakage of emulsion droplets in which the internal phase is leaked into the external phase (feed) resulting in low extraction and recovery of desired solute [9]. Meanwhile, performing ELM using batch operation limits the upscaling of ELM process for industrial scale. Development of continuous emulsion liquid membrane (CELM) process is extremely helpful to upgrade this system as well as become reliable for the industry application. Moreover, continuous operation is more suitable for the treatment of large volume of wastewater [10].

In this current work, the recovery of phenol was carried out using continuous emulsion liquid membrane process (CELM). ELM formulation consists of kerosene and palm oil as diluent, Span 80 as a surfactant, and sodium hydroxide NaOH as a strippant. The stability performance of W/O emulsion was evaluated for production of stable emulsion. Meanwhile, variables investigated in the recovery of phenol are rotational speed, treat ratio and retention time which were optimized using response surface methodology (RSM).

2. Methodology

2.1. Reagent and materials

Phenol crystals (99% assay) was supplied by Sigma Aldrich) and used as a source for phenol in the simulated wastewater. Sorbitan Monooleate (Span 80) (99% assay) as a surfactant and kerosene (78% assay) as a diluent were supplied by Merck. Cooking palm oil (BURUH brand) was purchased from Lam Soon Edible Oil Sdn Bhd. Sodium hydroxide (NaOH) (98% assay) as a strippant was acquired from J.T. Baker. All reagents and chemicals were used without further purification as received from the suppliers.

2.2. CELM rig set up

Figure 1 exhibits a CELM rig setup which consists of 1500 mL of extraction tank fitted with a stirrer and four baffles (12cm in diameter and 15cm in height) for better mixing process. Besides, the feed and emulsion tanks were used for feed and emulsion solutions. Two peristaltic pumps and flowmeters were used for pumping and controlling the flowrate of both the feed and emulsion solutions upon transferring into the extraction tank. The sampling tank was used for sample collections.

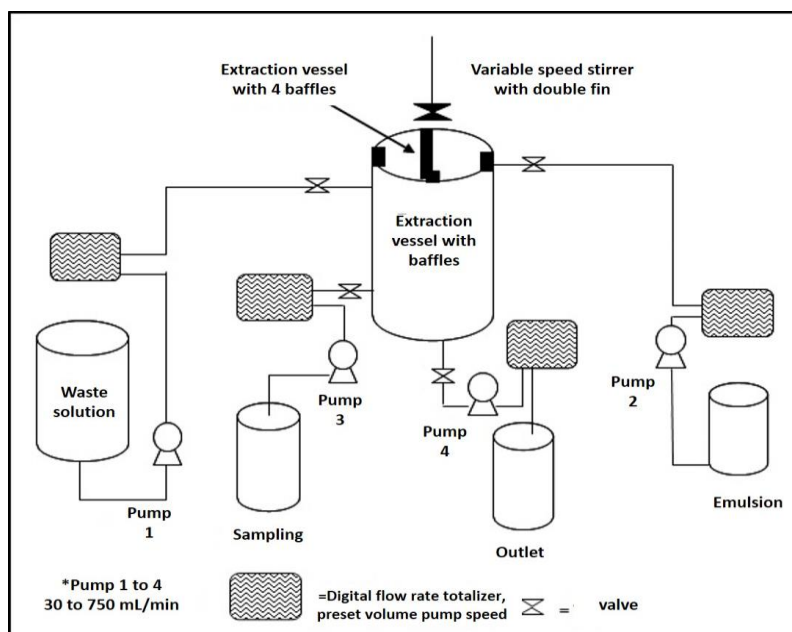


Figure 1. Schematic diagram of SLM process [12].

2.3. Primary water-in-oil (W/O) emulsion preparation

Primary (W/O) emulsion was prepared by blending 75mL of organic phase (Span 80 (3% (w/v)) in the mixture of palm oil and kerosene (70:30)) and internal phase (25mL of NaOH solution) by means of a magnetic stirrer at a speed of 1300 rpm for about 5 min as described in our previous work [11]. The prepared white milky W/O emulsion was freshly prepared each time during the experiment. A small drop of W/O emulsion was tested under microscope (magnification of 400X) to observe the structure behaviour of W/O emulsion droplets.

2.4. ELM extraction of phenol

The simulated phenol wastewater was prepared by diluting the phenol crystal in distilled water at desired concentration. Both primary W/O emulsion and feed phases were mixed in the extraction tank at various treat ratio for about 15 min. The samples were collected from the sampling tank and were moved into a separation funnel to separate the aqueous feed and emulsion phases. The primary emulsion was in the top whereas the feed phase containing the treated phenol solution was at the bottom of the separation funnel. The treated aqueous phenol solution was analyzed using UV-Vis spectrophotometer (Jenway 305). Meanwhile, the remaining emulsion was demulsified using a high voltage coalescer with electric potential of 20 kV at 300 Hz frequency. After demulsification, the organic emulsion phase was separated from the aqueous internal phase. Similarly, the high concentration phenol in the aqueous internal phase was evaluated using UV-Vis spectrophotometer to determine the recovery of phenol as calculated using equations (1) and (2):

$$\text{Recovery (\%)} = \frac{C_{\text{internal}}}{4 \times C_i \times \text{treat ratio}} \times 100 \quad (1)$$

$$\text{Enrichment} = \frac{C_{\text{internal}}}{C_i} \quad (2)$$

where, C_i and represent initial phenol content in the simulated phenol wastewater (ppm), C_{internal} signifies the final phenol concentration in the internal or stripping phase after demulsification (ppm) as well as treat ratio is the ratio of emulsion to the feed phase volume.

2.5 Experimental design

Box-Behnken design (BBD) was used to investigate the interaction of the process parameters and predict the optimum conditions for phenol recovery via response surface methodology (RSM) method using Statistica 8.0. Three variables involve including rotational speed (X_1), treat ratio (X_2), and retention time (X_3). Each variable consists of three different levels from low (-1), medium (0) and high (1). The range and coded level of process variables are listed in table 1. Basically, the ranges of the variables used was chosen based on the study of previous works [11-12]. Total number of experiments was 15 and the complete design matrix of BBD and the experimental result are given in table 2. On the other hand, the mathematical model was fitted using second order polynomial regression model given in equation (3):

$$\hat{Y} = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 \quad (3)$$

where \hat{Y} is the predicted response (response function), β_0 is the intercept coefficient (offset), β_1 , β_2 and β_3 are the linear terms (first order), β_{11} , β_{22} and β_{33} are the quadratic terms (second order), β_{12} , β_{13} and β_{23} are the interaction terms and X_1 , X_2 and X_3 are coded independent variables.

Table 1. Design of experiment for the independent parameters studied.

Parameters	Symbol	Ranges and levels		
		-1	0	+1
Rotational speed, rpm	X_1	400	600	800
Treat ratio	X_2	1:3	1:6.5	1:10
Retention time, min	X_3	2	4	6

Table 2. BBD matrix for phenol recovery using ELM.

Run order	Independent Parameters			Phenol Recovery (%)	
	X_1	X_2	X_3	Observed	Predicted
	Rotational Speed, rpm	Treat Ratio	Retention Time, min		
1	-1	-1	0	30	27
2	1	-1	0	46	39
3	-1	1	0	23	37
4	1	1	0	8	3
5	-1	0	1	30	25
6	1	0	1	32	40
7	-1	0	-1	100	93
8	1	0	-1	25	30
9	0	-1	1	23	28
10	0	1	1	7	0
11	0	-1	-1	28	34
12	0	1	-1	38	35
13	0	0	0	18	22
14	0	0	0	32	22
15	0	0	0	16	22

The abovementioned equation model was verified via analysis of variance (ANOVA) along with coefficient of determination (R^2). ANOVA is able to determine the validity of the predicted model using F-value. Usually, the counted F-value should be bigger in comparison with the F-value obtained from the distribution table to reject the null hypothesis which implies that whole parameters do not give a

significant effect towards recovery yield of phenol. The counted *F-value* is obtained using the calculation from the previous work [13]. Meanwhile the tabulated *F-value* is determined using *F*-distribution table with respect to the degree of freedom (DF) of both regression and residual, respectively at 95% confidence level ($\alpha=0.05$). Meanwhile, the value of R^2 is attained from the parity plot, describing the relationship among the predicted and experimental values. The value of $R^2 \geq 0.75$ is acceptable to give better prediction of response among within the range of the parameters studied [12]. On the other hand, *p*-values was used to identify the important parameters on the phenol recovery. Moreover, the response surface plot has the ability to visualize the individual and interaction effect among these significant variables.

3. Results and discussion

3.1. Facilitated transport mechanism of phenol recovery via ELM system

In the presence of palm oil and kerosene as diluent, the transportation of phenol via ELM system can occur in two ways mechanisms which are simple and facilitated transports. Through simple transport mechanism, phenol dissolves in LM phase and diffuses from feed to the internal phases due to the concentration gradient between these two phases. The reaction of phenol with NaOH in the internal phase produce insoluble compound, sodium phenolate, which cannot diffuse back to the external feed phase [11]. The simple permeation of phenol is liberated through equation (4). Another mechanism is the reaction of triglyceride from palm oil with the phenol compound via hydrogen bonding formation [14-15]. The complex phenol-triglyceride compound diffuses across the LM phase before being stripped out into the internal phase. The extraction mechanism of phenol by triglyceride molecules are shown in figure 2 and the reaction mechanism is depicted in equations (5) and (6).

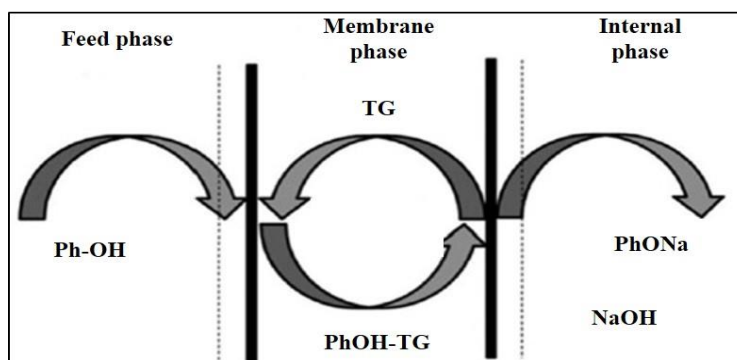
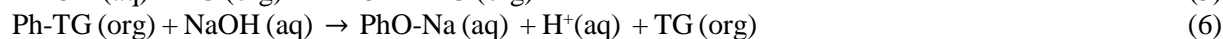
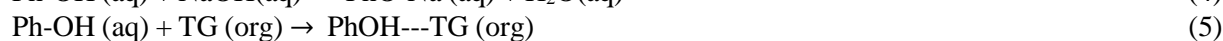
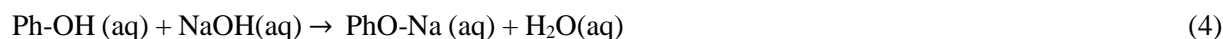


Figure 2. Transport mechanism of phenol using palm oil as diluent [14].

3.2. Stability performance of primary W/O emulsion

Theoretically, the stability of primary W/O emulsion predominantly affects the stability of ELM system. In this work, the stability of W/O emulsion has been investigated using several important variables namely surfactant concentration, emulsification time and emulsification speed. W/O emulsion comprises of a high number of droplets which can change accordingly based on the conditions. In terms of the surfactant concentrations, the size of emulsion droplets significantly decreased from 29.51 to 14.42 μm when enhancing Span 80 concentrations from 1 to 3% (w/v), respectively (Refer figure 3 (a)

to (b)). Nasab et al. [16] indicated that an increment in the surfactant concentration rises the surfactant monolayers adsorbed onto the droplet interface thus reduces the droplet size and stabilizes the emulsion. However, it turns out the emulsion droplets get broader with a further increase Span 80 concentration up to 5% (w/v) (Refer figure 3 (c)). This is in agreement with Jusoh et al. [17] who reported that too high surfactant concentration induces the rapid coalescence among the smaller droplets produced. Such behaviour promotes aggregation to occur and might lead to the breakage problem. Thus, 3% (w/v) Span 80 is preferable to produce a stable W/O emulsion in this present investigation.

On the other hand, low emulsification time of 3 min produces large size of W/O emulsion droplet (35.99 μm) (Refer figure 3(d)). At this moment, the low production of the smaller droplet is observed, indicating that the emulsion seems unstable yet. Salman and Mohammed [18] found that low emulsification time provides insufficient contact between the aqueous internal and organic phase, causing the emulsion being not well emulsified. The size of W/O emulsion droplets decreases to 14.42 μm (Refer figure 3(e)) upon prolonging the emulsification time up to 5 min. At this stage, the W/O emulsion seems to achieve the stability owing to the production of higher number of finer emulsion droplets. Study by Ahmad et al. [19] claimed that a stable emulsion composed of high volume of smaller droplets which provide the high interfacial areas for mass transfer of targeted solute. With increasing the emulsification time up to 7 min increases the size of the emulsion droplets up to 17.78 μm (Refer figure 3(f)). In fact, the longer contact among the internal and organic phase generates high volume of lower size emulsion droplets. Nevertheless, these smaller droplets started to coalesce, forming a bigger droplet which enable to promote the emulsion breakage. Hence 3 min of emulsification time is adequate to form the stable W/O emulsion.

In order to evaluate the effect of emulsification speed towards W/O emulsion stability, the experiments were performed by varying the emulsification speed from 900 to 1500 rpm as shown in figure 3(g) to 3(i). As rising the emulsification speed from 900 to 1300 rpm, the size of W/O emulsion droplets decrease from 21.28 to 14.42 μm , respectively. It means the stability of W/O emulsion is proportional to the high emulsification speed. Similarly, Salman and Mohammed [18] also observed that the emulsion stability increases with increases the homogenizer speed. The size of emulsion droplets continually decreases upon extending the speed up to 1500 rpm (9.43 μm). However, at this stage, the emulsion becomes highly viscous. Likewise, Balasubramanian and Venkatesan [20] also reported beyond maximum speed a mayonnaise-like" emulsion was formed. The, 1300 rpm of emulsification speed is more preferable for generation of stable W/O emulsion.

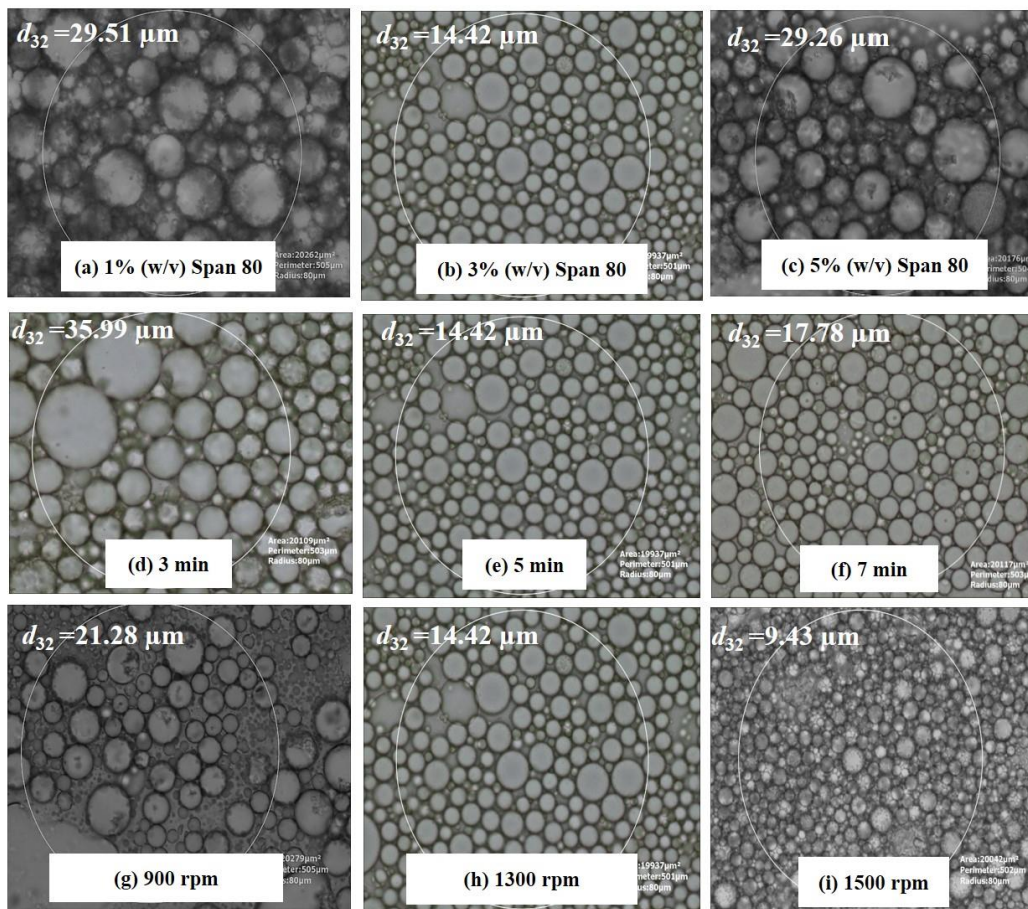


Figure 3. Microscopic image of W/O emulsion droplet with respect to the different variables conditions.

3.3. Statistical analysis for phenol recovery

The regression analysis of the model generates the following regression equation (7) for the percentage recovery of phenol.

$$Y = 40.47 - 0.35X_1 + 492.05X_2 + 18.28X_3 - 1404.95X_2^2 + 2.84X_3^2 + 0.49X_1X_2 - 0.05X_1X_3 - 31.92X_2X_3 \quad (7)$$

The aforementioned equation model was validated by analysis of variance (ANOVA) using *F-value* as tabulated in table 3. Indeed, the counted *F-value* should be higher than the *F-value* from the distribution table to decline the null hypothesis which indicates that all the factors studied insignificantly affect the response [21]. Evidently, the model turns out to be significant as the *F-calculated* (4.824) is higher than the *F-tabulated* (4.774). Subsequently, figure 4 (a) depicts the coefficient of determination, R^2 of 0.8967 which indicates that 89.67% of total variability in response can be explained by the model. Sidik et al. [22] found that the high R^2 value provides a good agreement between the predicted and experimental data. Meanwhile, the significant and interaction effect of the parameters are determined by means of Pareto chart in figure 4 (b). Pareto chart provides the *P-values* (probability of the null hypothesis) which become the point of reference for the significant parameters. Using a 5% significance level, a parameter is considered significant if the *P-value* coefficients is less than 0.05[12]. Based on the Pareto analysis, the interaction effect of rotational speed and retention time (X_1X_3) turns out to be the coefficient with the lowest probability of null hypothesis ($P=0.022138$), hence declining null hypothesis at 98% significant level. The other coefficients only reject the null hypothesis lower than 95%. Hence, the

abovementioned interaction effect appears as the significant parameters influencing the recovery of phenol in this study.

Table 3. ANOVA analysis of model.

Sources	Sum of square (SS)	Degree of Freedom (Df)	Mean Square (MS)	F-calculated	F-tabulated ($\alpha= 0.05$)
Regression	6059.85	9	673.317	4.824	> 4.773
Residual	697.821	5	139.564		
Total	6757.67	14			

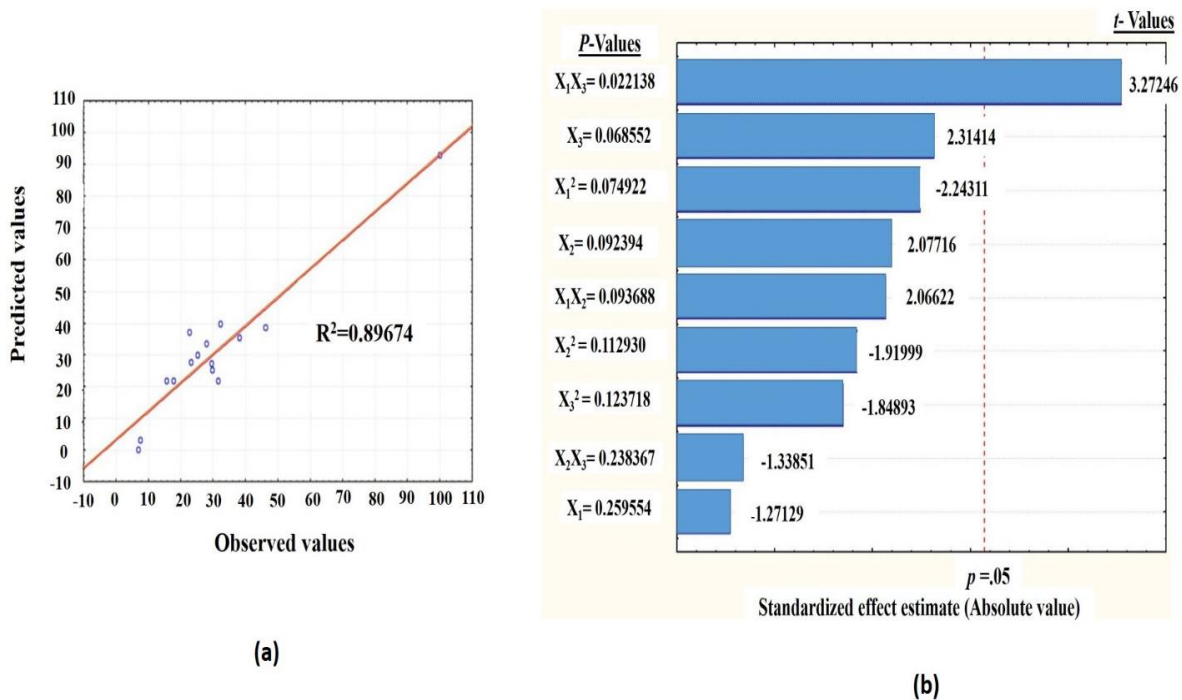


Figure 4. (a) Predicted and observed (experimental) values for model (b) and Pareto chart for model.

3.4. Variables effect on response

Figure 5 exhibits three dimensional (3D) response surface plot describing the effect of the parameters studied towards recovery of phenol. Figure 5(a) and (c) demonstrate the effect of treat ratio on the recovery performance of phenol. Through Pareto analysis, treat ratio seems to provide less significant effect towards the recovery efficiency. At low treat ratio of 0.10 adversely affected the recovery of phenol. This is due to the low dispersion of W/O emulsion on the feed phase, hence reduces the contact time between the feed and emulsion phase. This is in accordance with Ahmad et al. [23] who observed that low emulsion to feed ratio limits the interfacial area for mass transfer due to the difficulties in the emulsion dispersion. Increasing treat ratio up to 0.15 slightly increases the recovery efficacy. Such result is in line with Kumbar [24] who indicated the increment of treat ratio improves the dispersibility of the emulsion system and mass transfer of solute during recovery. Nonetheless, beyond 0.15 of treat ratio

reduces the efficiency of recovery due to the inadequate volume of emulsion to treat the high volume of feed phase results in lower interfacial dispersion area of emulsion towards feed phase. Work by Ng et al. [25] also reported that beyond maximum treat ratio insignificantly affects the permeation of solute into the membrane phase, hence reducing the efficiency performance of extraction.

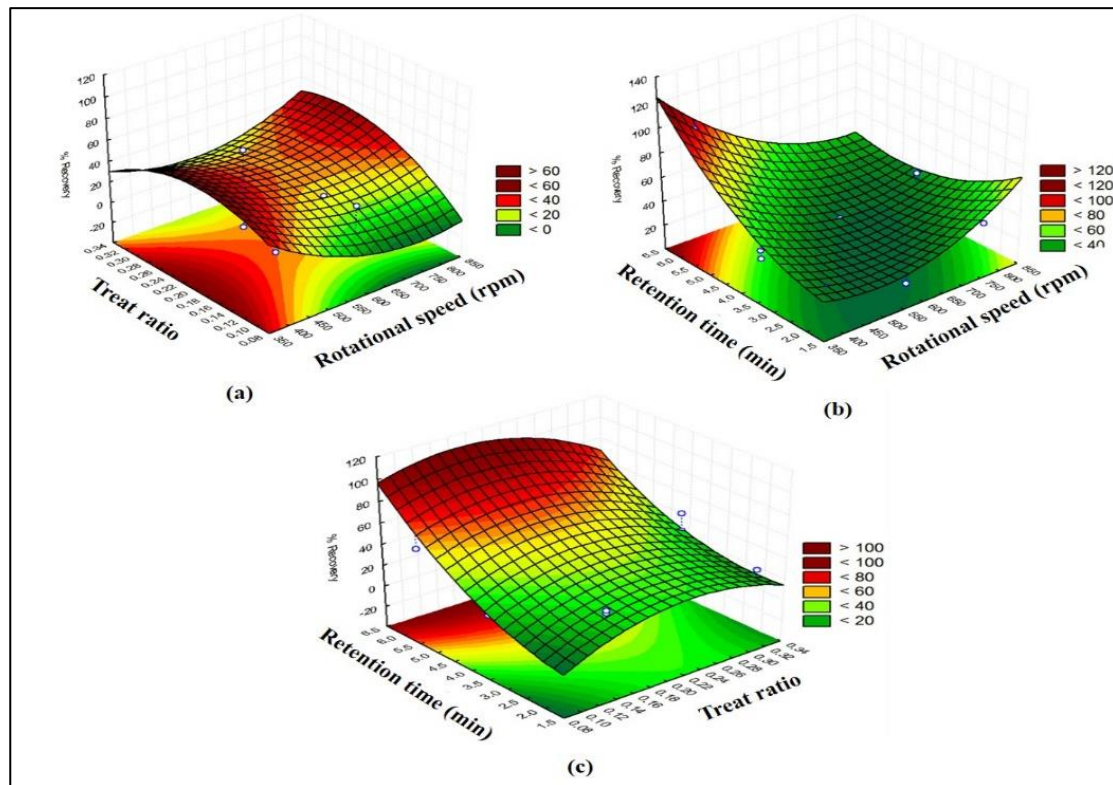


Figure 5. 3D response surface plot of variables effect towards response.

Figure 5(b) and (c) depict the effect of retention time towards recovery efficiency of phenol. Obviously, the recovery efficacy of phenol is proportional with the increment of retention time. Initially the minimum retention time of 2 min is too rapid and provides insufficient contact between the feed and emulsion phase. Upon enhancing up to 6 min significantly increases the recovery performance when reaching almost 100%. Clearly 6 min is adequate for the maximum recovery of phenol. On the other hand, the effect of rotational speed on the recovery efficiency seems quite different as demonstrated in figure 5(a) and (b). From Pareto chart, there is no interaction between treat ratio and rotational speed. Hence these factors work independently towards recovery of phenol. As observed in figure 5(a), the recovery of phenol shows a decrement trend when increasing the rotational speed from 400 to 800 rpm. Basically, increasing the level of rotational speed increases the interfacial area and mass transfer of targeted solute. However, excessive speed tends to break the emulsion droplets, hence reduces the overall enrichment and recovery efficiency. Similar observation was reported by Kulkarni and Mahajani [26] who revealed that at macroscopic image, some droplets are broken due to high shear after reaching the bigger size. Though, as mentioned earlier from Pareto chart, both retention time and rotational speed had an interaction effect among each other. They showed a similar trend wherein the recovery of phenol improved as enhancing both of these effects up to the maximum level. In fact, the well mixed emulsion and feed solution in the extractor tank is highly depends on the impeller strength (rotational speed) and residence time (retention time) [10, 12]. Previous work revealed that the reasonable retention time provides a maximum contact between both emulsion and feed phase, hence resulting in better dispersion [27].

3.5. Prediction on best conditions for phenol recovery

The 3D surface plot obtained are saddle shape which are difficult to find the maximum point [28]. Therefore, Statistica only can give the prediction of the best conditions for phenol recovery. Table 4 shows that about 29% of phenol was recovered under predicted best conditions of 527 rpm of rotational speed, 2.6 min of retention time and 0.23 (1:4) of treat ratio. These prediction was confirmed by the experiments with 0.02% error for phenol recovery. Hence, it is showed that the model is able to predict the response within the range studied. Meanwhile, the enrichment of phenol in the internal phase was obtained about 7 times. Advantageously, CGELM is capable of recovering and concentrating the phenol in the internal phase which can be used for other applications.

Table 4. Prediction on best conditions for phenol recovery.

Rotational speed	Retention Time	Treat ratio	Recovery (%)		Error (%)	Initial phenol (ppm)	phenol stripping phase (ppm)	Enrichment in the internal (times)
			Predicted	Observed				
527 rpm	2.6 min	1:4	29.40	28.95	0.02	300	2100	7

Conclusion

Through this work, the recovery of phenol was carried out using continuous emulsion liquid membrane process. The stable water in oil emulsion was observed at 3% (w/v) of Span 80, 5 min of emulsification time and 1300 rpm of emulsification speed. Meanwhile, about 29% of phenol was recovered with 7 times of enrichment in the internal phase (2100 ppm) under predicted best conditions of 527 rpm of rotational speed, 1:4 of treat ratio and 2.6 min of retention time.

Acknowledgments

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