Extraction of reactive dye via synergistic Aliquat 336/D2EHPA using emulsion liquid membrane system

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Abstract−Facilitated transport of Orange 3R was performed by means of emulsion liquid membrane (ELM) technique containing double extractants of Aliquat 336 and D2EHPA as extractant and synergist extractant, respectively. Cooking palm oil, sorbitan monooleate (Span 80), and sodium hydroxide were used as diluent, surfactant and stripping agent, respectively. Several parameters influencing the extraction of Orange 3R via ELM, namely effect of extraction time, agitator speed, Span 80 concentration and treatment ratio, were experimentally investigated and optimized using response surface methodology (RSM). Results demonstrated that about 91% of Orange 3R was successfully extracted under optimum conditions of 12 minutes of extraction time, 413 rpm of agitator speed, 3.2% (w/v) of sorbitan monooleate, and 1 : 9.8 of treatment ratio. Additionally, the aforementioned optimum conditions were found to be more suitable to treat low concentration of Orange 3R (less than 100 ppm) from simulated textile wastewater. The findings reveal that reactive Orange 3R dye is able to be selectively extracted using double extractants via sustainable ELM process as well as providing high potential application in the dye removal from industrial textile wastewater.

Keywords: Dye, Extraction, Response Surface Methodology, Emulsion Liquid Membrane

INTRODUCTION

Dyes are useful in various types of applications, especially textile, dyeing, paper and pulp as well as in the paint industry [1]. Among these, the textile industry uses the highest proportion of dyes (54%) followed by dyeing (21%), paper and pulp (10%) and paint (8%) industries [2]. Almost 10,000 tons of dyes have been used and 100 tons of dye effluents are produced annually from the textile industry [3]. Frequently, once dyes have served their purpose, mostly they are released without further precaution into environmental water bodies. Unfortunately, the released dyes adversely affect the surroundings and living things. As an example, they are able to damage the productivity of soil, deteriorate the quality of water and induce human health issues such as irritation, eye burns and so on [4,5]. Normally, the dye wastewater is composed of high biological oxygen demand (BOD), chemical oxygen demand (COD), colours, and suspended solid [6,7]. The international standard discharge of dye wastewater containing BOD, COD, colors and suspended solid is below 30, 50, 1, and 20 ppm, respectively [8].

Indeed, various methods have been applied for dye removal, including biological, chemical, and physical techniques. Through biological treatment, the aerobic and anaerobic processes are combined to treat the dye before being released into the environment

[9]. This kind of method is very economical and can be achieved easily. However, it is unable to completely remove the dye from wastewater and only reduces the chemical oxygen demand in the dye wastewater. Additionally, this treatment deals with living thing and is limited by the growth rate which sometimes is unstable [5]. Meanwhile, electrochemical [10], oxidation [11], photochemical [12] and ozonation [13] processes are among the chemical treatments used for dye removal. These techniques are expensive, high production of byproduct, pH dependent and so forth. Subsequently, physical methods are used for dye treatment including adsorption [14], coagulation and flocculation [15], ion exchange [16], nanofiltration [17], membrane filtration [18] and reverse osmosis [19]. Adsorption normally suffers of high cost of adsorbent. Coagulation and flocculation generate high amount of concentrated sludges. Besides, ion exchange is only suitable for a few types of dyes, whereas nanofiltration, membrane filtration and reverse osmosis involve high cost of operation.

Emulsion liquid membrane (ELM) technology has become one of the alternative methods for the separation of various organic and heavy metals from wastewater. This method is known to be simple, low cost, energy saving, high separation factor, low chemical usage and so forth [20-23]. Essentially, the ELM system involves three phases: external feed, liquid membrane and stripping (internal) phases. Dye wastewater represents a feed phase to be treated. Meanwhile, liquid membrane phase is composed of water-in-oil (W/O) emulsion, which consists of aqueous stripping phase (stripping agent solution) entrapped in the organic phase (extractant, solvent, and

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surfactant). The solvent plays a role to dilute the extractant and the surfactant increases the interfacial tension among both feed and membrane phases. During extraction, the dye complex in the feed phase binds with the extractant at the interfaces of feed and liquid membrane phase. The dye-extractant complex diffuses across the liquid membrane phase before reacting with stripping agent in the stripping phase [24]. The stable ELM is comprised of a high quantity of finer W/O emulsion droplets. However, up to a certain limit, these droplets become bigger, which induces instability problem [25]. An extractant is of great importance in the ELM formulation as it facilitates the transport of solute across the membrane phase. Bahloul et al. [26] extracted about 98.98% of dye using Aliquat 336 as an extractant. Also, Muthuraman and Teng [27] extracted methyl red using xylene as an extractant. However, the use of single extractants sometimes results in high consumption of chemicals, third phase formation and slow kinetic reaction [28]. Recently, the use of a mixture of extractants was able to overcome the inefficiency of utilizing the single extractant. The binary mixture of extractants can synergistically improve the kinetic reaction among the solute and extractant. It can be performed using various combinations of extractants such as acidic-acidic, acidic-basic, basic-basic, basic-neutral, acidic-neutral and so forth [29]. Sustainability of ELM can be achieved via incorporation of an environmentally friendly solvent such as vegetable palm oils (VPO). VPO provides high number of advantages over petroleum based solvents including renewable, nonvolatile, nonflammable, biodegradable and nontoxic [30-32]. Response surface methodology (RSM) is one of the established statistical approaches for optimization of process parameters. This statistical method reduces the research workload, design of the experiments, optimization, and determining the significant parameters affecting the extraction efficiency [33].

Dyes are categorized into three major groups, including anionic (direct acid and reactive dyes), cationic (basic dyes) and nonionic (dispersed dyes) [34]. Azo, dye is one of the anionic reactive dyes which has become the largest group of colorants used for nearly 75% of all products of textile dyes. This is due to their high stability, excellent colorfastness, bright color as well as simple application in various industries involving cellulosic, fibres, wool and polyamide [35,36]. Also, it is designed to be chemically and photolytically stable, which is highly resistant to microbial degradation. The presence of very small amounts of azo dyes in aqueous solution (less than 1 ppm) is highly visible and aesthetically unpleasant [37,38]. Thus, the release of azo reactive dyes into the environment, even at smaller amounts, is undesirable. Previously, ELM was widely used for the removal of cationic dyes such as methylene blue and crystal violet [39-43]. As for anionic dye, ELM has been used for the removal of Golden Yellow [44], Congo Red [34], Acid Yellow 99 [45], MB R 12 red [46] and Red 3BS [47]. Orange 3R is one of the highly used azo dyes in the textile industry. To date, only solvent extraction of Orange 3R has been reported [48]. To the best of our knowledge, there is no work reported yet regarding the extraction of Orange 3R reactive dye using ELM. Meanwhile, the basic extractant was used for anionic Orange 3R dyes extraction since it should react with positively charged ions from basic extractant during anion exchange mechanism. However, Rahman et al. [48] reported that the synergistic solvent extraction of Orange 3R involving the mixtures of the basic extractants provided low extraction of Orange 3R extraction. Hence, in a current work, a new approach was carried out by mixing the acidic extractant (D2EHPA) and basic extractant (Aliquat 336) for the ELM extraction of Orange 3R. This is the first work reporting the synergistic green ELM extraction of Orange 3R using binary mixture of Aliquat 336/D2EHPA in cooking palm oil. The parameters involved for optimization via RSM method include extraction time, agitator speed, Span 80 concentration, and treatment ratio. Besides, the stability of water-in-oil-in-water (W/O/W) emulsion in response to different variables namely extraction time, Span 80 concentration and agitator speed were observed as well.

EXPERIMENTAL

1. Materials

Orange 3R as a targeted solute in the external feed phase was attained from Batik company in Terengganu. The simulated Orange 3R solution was prepared by diluting the known concentration of the reactive dye in the deionized water. N-Methyl-N, N, N-trioctylammonium chloride (Aliquat 336) (95% assay) and Bis-(2-ethylhexyl) phosphate (D2EHPA) (95% assay) as extractants were obtained from Merck. An emulsifier or surfactant, sorbitan monooleate (Span 80) (99% assay) was procured from Merck. Sodium hydroxide (NaOH) (98% assay) as a stripping agent was purchased from J.T. Baker. Palm oil (BURUH brand) was from Lam Soon Edible Oil Sdn Bhd. All chemicals were used without further purification as received from the suppliers. The chemical structures of Orange 3R, Aliquat 336, D2EHPA are depicted in Fig. 1.

2. Analytical Instruments

The equipment used in this experiment included homogenizer for emulsion preparation, Metler Toledo pH meter for pH reading,
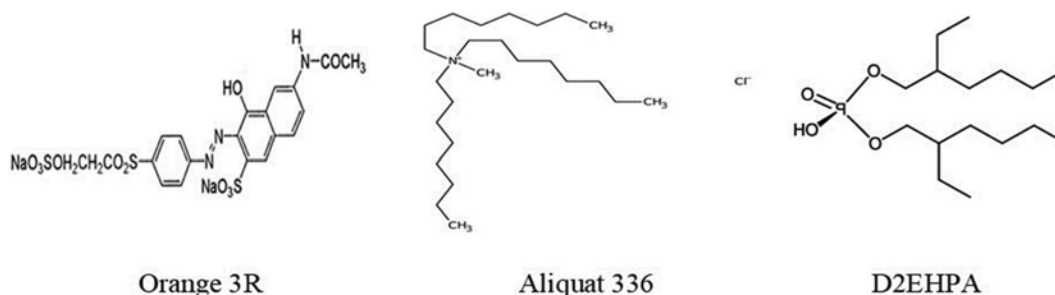

Fig. 1. Structures of Orange 3R, Aliquat 336 and D2EHPA.

UV-visible spectrophotometer (Jenway 7305) for analysis of Orange 3R concentrations (wavelength of 494 nm) and a microscope (Olympus CX31) for the observation of ELM droplet structure.

3. W/O Emulsion Liquid Membrane (ELM) Preparation

W/O ELM contains four main: extractant, diluent, surfactant and stripping agent. It was prepared by emulsifying the aqueous stripping agent (NaOH solution) and organic phase (Aliquat 336, D2EHPA and Span 80 in palm oil) in volume ratio of 1 : 3 by means of a homogenizer (12,000 rpm) for about five minutes. The W/O ELM was freshly prepared before extraction.

4. Extraction Procedure

The prepared W/O emulsion was dispersed into an agitator vessel containing simulated Orange 3R wastewater solution at an extraction speed of 150 rpm and treatment ratio of 1 : 6.5 for 15 minutes. This mixture was left in a separation funnel for about 30 minutes for phase separation. A small drop of W/O/W emulsion was tested under microscope using magnification of 400X to observe the structure of ELM droplet with regard to the different surfactant concentrations as well as time and speed of extractions. ELM droplet was analyzed under a microscope wherein the droplet size was measured using Sauter mean diameter (d_{32}) as represented in Eq. (1). The ELM swelling was evaluated through measurement of the emulsion volume before and after the extraction process, while the dye concentration in the treated feed phase was analyzed by means of a UV-Vis spectrophotometer. The experiment was conducted at room temperature ($25\pm1\,^{\circ}C$) in triplicate. A schematic diagram of the ELM process for Orange 3R extraction is depicted in Fig. 2.

$$d_{32}=\Sigma \ (n_i \cdot d_i^3)/\Sigma \ (n_i \cdot d_i^2) \tag{1}$$

where n and d represent the number and diameter of droplets, respectively.

5. Analysis of Data

In the ELM system, the performance of Orange 3R extraction was determined using Eq. (2):

Table 1. Range and levels of variables

Parameters	Symbol	Range and levels		
		−1	0	+1
Extraction time, min	X_1	1	8	15
Agitator speed, rpm	X_2	150	300	450
Span 80 concentration, w/v %	X_3	1	4	7
Treatment ratio	X_4	1 : 1	1 : 6.5	1 : 10

$$\text{Extraction (\%)}=\frac{C_i-C_f}{C_i}\times 100 \tag{2}$$

$$\text{Recovery (\%)}=\frac{C_{int}}{4TRC_i}\times 100 \tag{3}$$

where C_i and represent initial dye content in the simulated Orange 3R wastewater (ppm) as a feed phase, C_f signifies the dye concentration in the external feed phase after extraction; C_{int} signifies the concentration of Orange 3R in the stripping (internal) phase and TR is treatment ratio.

6. Experimental Design

The experiment was designed using Box-Behnken design (BBD) to predict the optimum conditions for the parameters affecting the extraction of Orange 3R. Four parameters were investigated, such as extraction time, agitator speed, sorbitan monooleate (Span 80) concentration, and treatment ratio. The range and levels of these parameters were ranked at three different levels, which are low, medium and high and coded as −1, 0 and +1, respectively as depicted in Table 1. The references of low, medium and high levels of each parameter were based on the ranges of parameters studied by the previous works [39,47]. Using the experimental design, about 27 experiments with triplicate runs were performed at a central point to determine the errors as tabulated in Table 2.

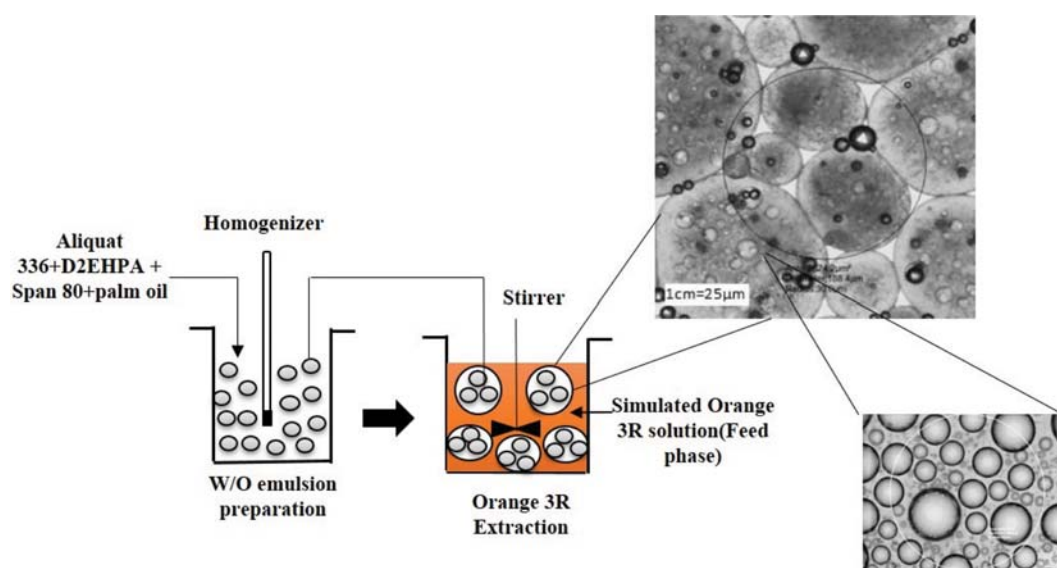The empirical model was fitted using a second-order polynomial as per Eq. (4):

Fig. 2. Schematic diagram of ELM extraction of Orange 3R [49].

Table 2. Design of experiment under different conditions of variables studied

Run no.	Parameters				Extraction (%)	
	X_1	X_2	X_3	X_4	Experimental	Predicted
1	1	150	4	6.5	11	13
2	15	150	4	6.5	53	39
3	1	450	4	6.5	34	33
4	15	450	4	6.5	71	80
5	8	300	1	1	97	94
6	8	300	7	1	97	95
7	8	300	1	10	73	58
8	8	300	7	10	57	49
9	8	300	4	6.5	92	83
10	1	300	4	1	66	69
11	15	300	4	1	100	99
12	1	300	4	10	8	12
13	15	300	4	10	76	75
14	8	150	1	6.5	10	16
15	8	450	1	6.5	88	79
16	8	150	7	6.5	19	31
17	8	450	7	6.5	58	55
18	8	300	4	6.5	91	83
19	1	300	1	6.5	8	23
20	15	300	1	6.5	51	60
21	1	300	7	6.5	3	6
22	15	300	7	6.5	70	68
23	8	150	4	1	78	83
24	8	450	4	1	98	98
25	8	150	4	10	5	19
26	8	450	4	10	75	80
27	8	300	4	6.5	65	83

$$\hat{Y} = \beta_o + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3$$
$$+ \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 \tag{4}$$

where $\hat{Y}$ is the predicted response (response function), β_o 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. The mathematical model equation was verified by analysis of variance (ANOVA) analysis using F-value and coefficient of determination (R^2) [33,34,50]. Probability value (p-value) was useful to evaluate the significant variables towards the response [37]. Then, the response surface plots depicted the influence of the variables towards extraction efficiency of Orange 3R.

RESULTS AND DISCUSSION

1. Extraction Mechanism of Orange 3R using Double Extractants in ELM System

The dye extraction was carried out using two extractants, Aliquat 336 and D2EHPA. Fig. 3 illustrates the transport mechanism of Orange 3R extraction through ELM system. As mentioned in our previous work, Aliquat 336 functions as a main extractant which can selectively bind with Orange 3R complex at the feed/membrane interface through anion exchange mechanism. Meanwhile, D2EHPA is categorized as an acidic carrier which extracts compound via cation exchange mechanism, hence unable to extract Orange 3R. In the membrane phase, it plays a role as a synergist extractant [37]. D2EHPA molecules have oxygen atoms which possesses higher electronegativity compared to nitrogen atoms in Aliquat 336 molecules. As a result, it has a high affinity to form hydrogen bond with the triglyceride compounds, TG in palm oil molecules as liberated in Eq. (5). During the extraction, D2EHPA acts as a shield which prevents the interaction occurs among Aliquat and TG, thus improving the extraction efficiency of dye.

$$2(RH)_2(org) + 2TG(org) \rightarrow 2(RH \cdots TG \cdots RH)(org) \tag{5}$$
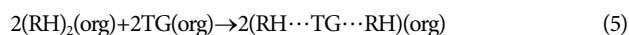
At the feed-membrane interface, Aliquat 336 ($NR_4^+Cl^-$) reacts with Orange 3R dye through cation exchange mechanism, releasing chloride ion into the feed phase as Eq. (6):

$$Dye^-(aq) + NR_4^+Cl^-(org) \rightarrow NR_4^+Dye^-(org) + Cl^-(aq) \tag{6}$$
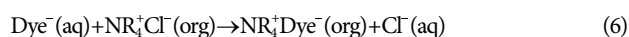
Then, the extractant-dye complex, $NR_4^+Dye^-$(org) diffuses across the membrane phase before being stripped by NaOH at the interface of the membrane and stripping phases as shown in Eq. (7). The extractant that has low solubility in stripping phase was regenerated back into the liquid membrane phase for the reaction with
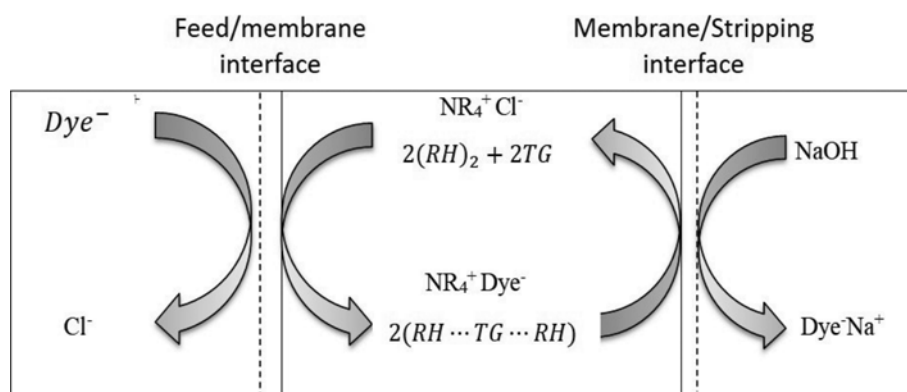
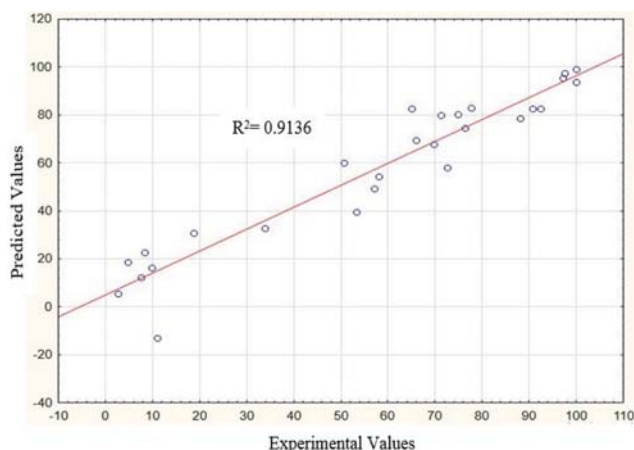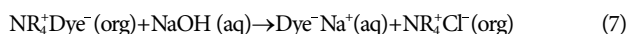**Fig. 3. Transport mechanism of Orange 3R extraction through ELM system.**

Fig. 4. Experimental and predicted result of Orange 3R extraction.

the incoming dyes complex [51].

$$NR_4^+Dye^-(org)+NaOH\ (aq)\rightarrow Dye^-Na^+(aq)+NR_4^+Cl^-(org) \qquad (7)$$

2. Analysis of Model

The predicted model was established to show the relationship among the response (extraction percentage) and the parameters studied. The reliable model obtained can predict the response at various combinations of the process parameters. The quadratic model of Orange 3R extraction was obtained using the least square method. The least square method minimizes the sum of squared errors, thus fitting the model. The predicted mathematical model of Orange 3R extraction is given in Eq. (8):

$$\begin{aligned}
Y=&46.5324+23.1072X_1+18.9483X_2-1.8063X_3-20.4575X_4 \\
&+13.4901X_1^2+10.4730X_2^2+8.3617X_3^2-1.7873X_4^2 \\
&-1.2716X_1X_2+6.19X_1X_3+8.134X_1X_4 \\
&-9.7169X_2X_3+11.7523X_2X_4-2.5447X_3X_4
\end{aligned} \qquad (8)$$

The fit quality of the model was checked by means of coefficient of determination (R^2). R^2 value determines the proportion of the response variation that can be elucidated by the estimated model. Usually, an R^2 value closer to one indicates that the estimated model perfectly clarifies all the response variability. According to Rajasimman et al. [52], the reasonable R^2 values of 0.75 and above explain most of the variability response in the model. The predicted and experimental response data are given in Fig. 4. The predicted results were obtained using Eq. (8). Meanwhile, the R^2 value obtained from the graph was 0.91 signifying that 91% of the response data was accountable by the model while, only 9% of the total variation is unexplained by model. This implies that the predicted values obtained from Eq. (8) are closer to the experimental values. Obviously, the quadratic model was well fitted and satisfied a good pre-
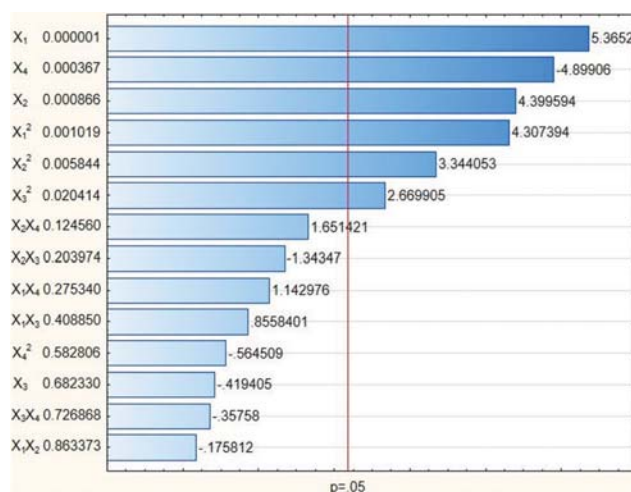

Fig. 5. Pareto analysis of regression coefficient for Orange 3R extraction.

diction of the response within the parameters condition ranges.

Henceforth, the reliability of the aforementioned mathematical model was also validated using ANOVA. Through ANOVA, the tabulated F-value ought to be less than the calculated F-value so that the model can provide a better estimation with the experimental data [33,53]. Table 3 shows the ANOVA analysis for the Orange 3R extraction at 95% of confidence level. Note that the calculated F-value (9.06) is higher compared with the tabulated one (2.64), demonstrating the fact that the model turns out to be significant as well as rejecting the null hypothesis (H_o). H_o recalls that all coefficients are zero and all variables studied insignificantly influence the dye extraction. It can be inferred that the model has a good prediction of response at 95% confidence level. Hence, the variables studied are also considered to have significant effect on the Orange 3R extraction.

In terms of the evaluation of the significant variables, ρ-values are used to check the significance of each coefficient. Fig. 5 depicts a Pareto chart together with ρ-values of the coefficients. Meanwhile, Table 4 illustrates the significance of the parameters in the model. A coefficient with p-value less than or equal to 0.01 implies that H_o can be rejected at a 0.01 significance level, whereas the coefficient with p-value higher than 0.01 but less than or equal to 0.05 ($0.01<p$-value≤0.05), the H_o can be rejected at 0.05 significance level [54]. It is demonstrated that the linear term of the model such as extraction time, X_1 ($p=0.000001$), treat ratio, X_4 ($p=0.000367$), agitator speed, X_2 ($p=0.000866$) as well as quadratic model term of X_1^2 ($p=0.001019$) and X_2^2 ($p=0.005844$) were convincing at 99% confidence level, thus decreasing the H_o at 0.01 significance level. In the meantime, X_3^2 ($p=0.020414$) was convincing at 95% confi-

Table 3. Analysis of variance (ANOVA) for quadratic model of Orange 3R extraction

Source	Sum of square (SS)	Degree of freedom (DF)	Mean square	F-value (calculated)	F-value (tabulated) ($\alpha=0.05$)
Regression	26554.55	14	1896.75	9.06	2.64
Residual	2510.96	12	209.25		
Total SS	29065.51	26			

Table 4. The significance of the parameters in the model

| Source	Coefficient	DF	Mean square	F-value	P-value Prob>F	Comment
Regression	46.5324	14				
X_1	23.1072	1	6023.35	28.78585	0.000001	Significant
X_1^2	13.4901	1	3882.29	18.55364	0.001019	Significant
X_2	18.9483	1	4050.27	19.35643	0.000866	Significant
X_2^2	10.4730	1	2339.94	11.18269	0.005844	Significant
X_3	−1.8063	1	36.81	0.17590	0.682330	
X_3^2	8.3617	1	1491.59	7.12839	0.020414	Significant
X_4	−20.4575	1	5022.09	24.00080	0.000367	Significant
X_4^2	−1.7873	1	66.68	0.31867	0.582806	
X_1X_2	−1.2716	1	6.47	0.03091	0.863373	
X_1X_3	6.1900	1	153.27	0.73246	0.408850	
X_1X_4	8.1340	1	273.36	1.30639	0.275340	
X_2X_3	−9.7169	1	377.67	1.80491	0.203974	
X_2X_4	11.7523	1	570.66	2.72719	0.124560	
X_3X_4	−2.5447	1	26.76	0.12786	0.726868	
Residual		12	209.247			
Total SS		26				

R-squared=0.9136; Adjusted R-squared=0.9046
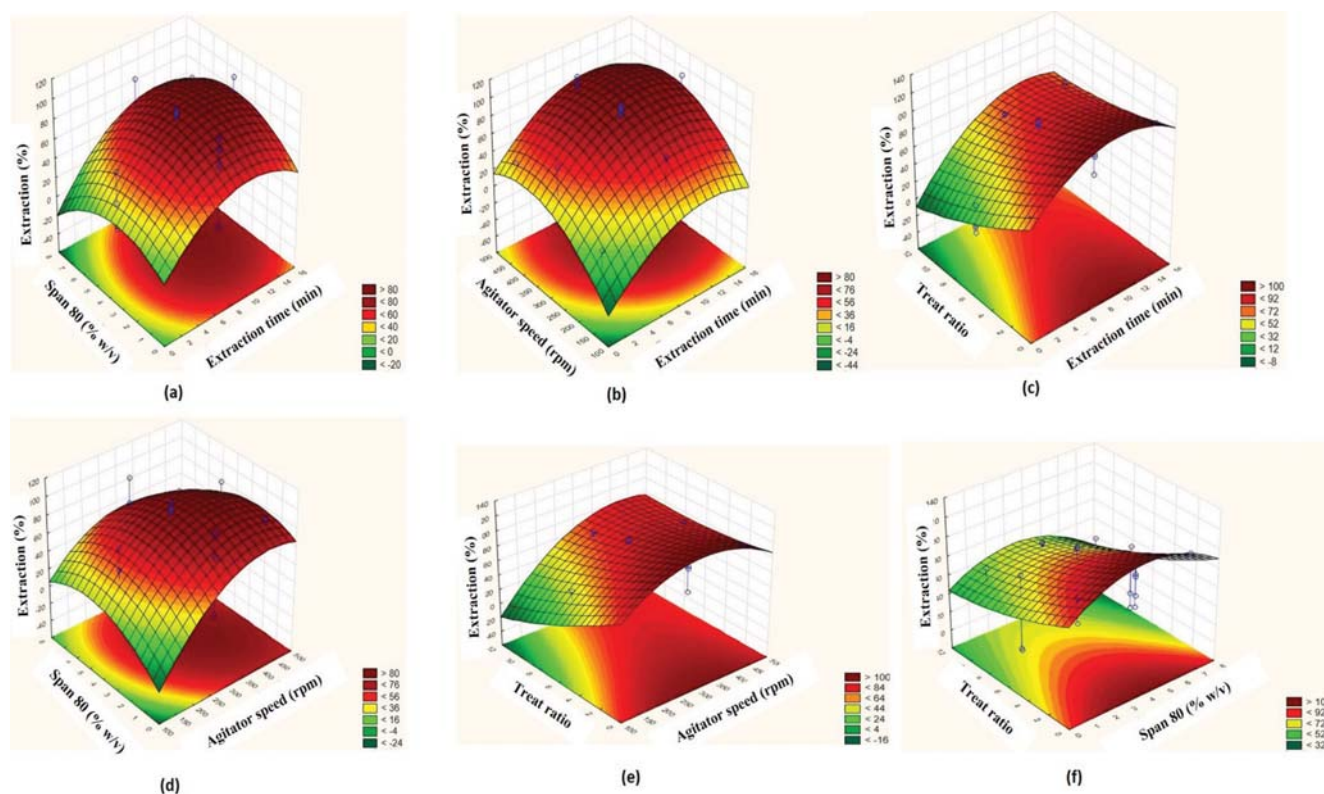
Fig. 6. 3D response surface plot as a function of different variables affecting the Orange 3R extraction.

dence level and rejects the H_o at 0.05 significance level. The rest of the terms were considered insignificant at 95% confidence level since their probability value was higher than 0.05. Hence, the important variables affecting the extraction efficiency of Orange 3R are arranged in the following order: extraction time>treat ratio> agitator speed>Span 80 concentration.

3. Effect of Parameters on Orange 3R Extraction

Fig. 6 shows several 3D response surface plots representing the relationship between the extraction time, agitator speed, Span 80 concentration and treat ratio towards Orange 3R extraction. Based

on the Pareto analysis, there is no interaction effect observed among the variables, demonstrating that they work independently towards the response. Figs. 6(a) to (c) exhibit the effect of extraction time towards the extraction efficacy of Orange 3R. Extraction time was found to be the most significant effect as mentioned in the previous Pareto analysis. It is defined as the duration contact between the emulsion and aqueous feed phases in a three phase dispersion of W/O/W emulsion system [24]. Obviously, 1 min of extraction time insignificantly affects the dye extraction performance. It can be explained by the fact that too short a contact time is actually insufficient for the production of stable emulsion liquid membrane. At this stage, the emulsion droplets predominantly exist at a large size (37.74 µm) with low surface area for mass transfer of dye as depicted in Fig. 7(a). Such a phenomenon causes low complexation to occur among the dye ions and extractant molecules at the interface of feed and membrane phases. Also, Chiha et al. [55] re-

ported that a short contact time causes too rapid a reaction between the targeted solute and extractant. Also, swelling involves the transport of water molecules from the feed to internal phases, hence decreasing the solute concentration. A small amount of swelling (3%) is observed showing that the extractant and surfactant have the ability to attract the water molecules from the feed to the internal phases (Table 5). Evidently, a rise in the extraction time up to 15 min gradually increases the extraction efficiency of Orange 3R. Obviously, the emulsion liquid membrane seems to be more stable as a result of production of high number of smaller emulsion droplets (27.60 µm) when longer contact time occurs between both emulsion and feed phases as illustrated in Fig. 7(c). Similarly, Seifollahi and Rahbar-Kelishami [56] reported that an increment in the extraction time offers adequate time available for the solute ions to form a complex with the carrier at the feed-membrane interface. Kumar et al. [33] also revealed that an increment in the extraction
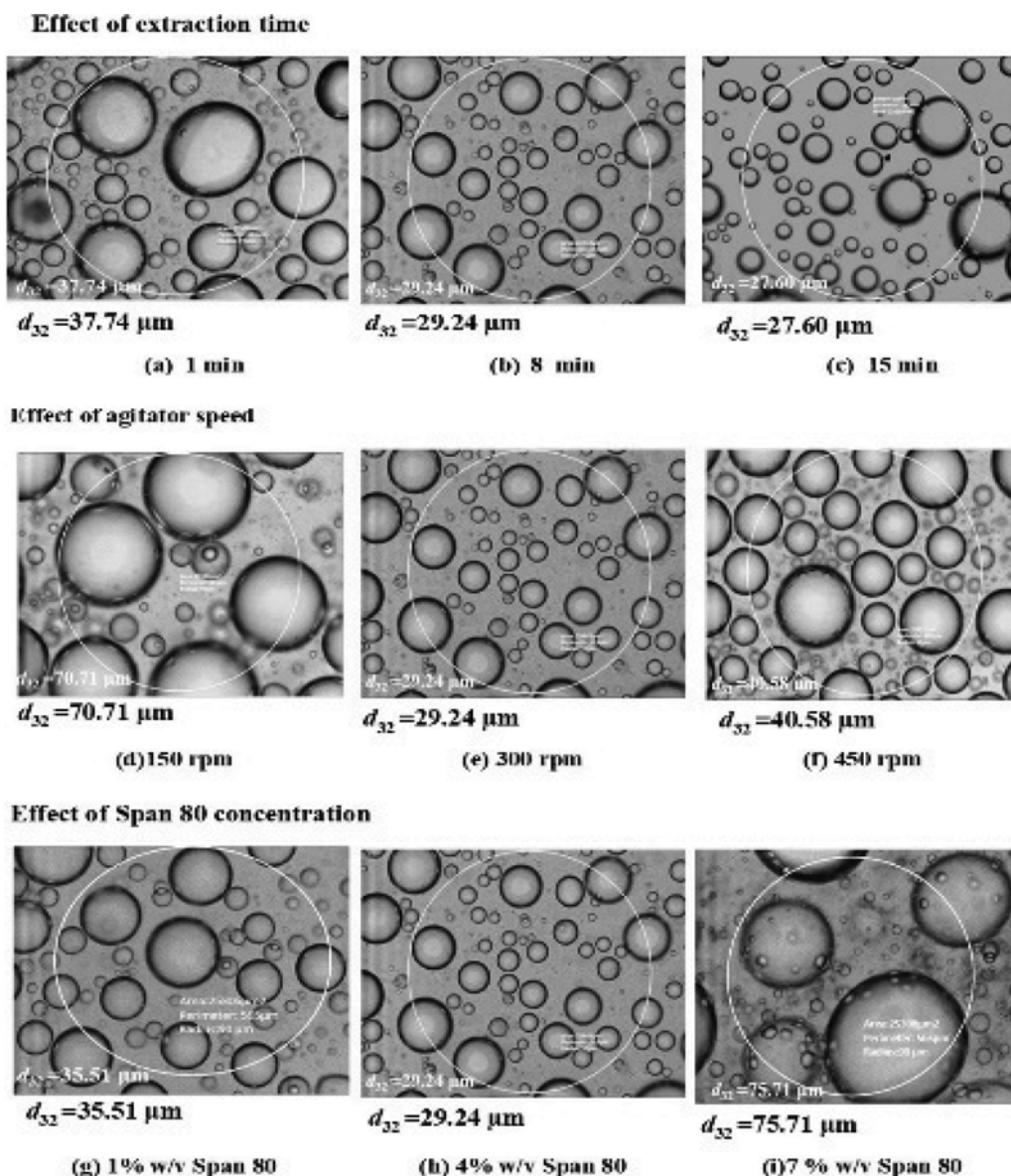

Fig. 7. Image of W/O/W emulsion under microscope with respect to the different parameters.

Table 5. Swelling percentage at various parameters studied

Parameters	Ranges	Swelling (%)
Extraction time (min)	1	3
	8	2
	15	5
[Span 80] (% w/v)	1	2
	4	1
	7	43
Agitator speed (rpm)	150	2
	300	0
	450	1

time generates smaller internal droplets, which subsequently provides large interfacial mass transfer for the extraction of dye from external feed phase. Nevertheless, the emulsion swelling kept increasing up to 5% upon extending the extraction time up to 15 min. This means that a longer extraction time provides longer contact between feed and emulsion phases, which subsequently provides high contact between the extractant and water molecules, hence inducing the high swelling.

The influence of treatment ratio towards extraction efficacy of Orange 3R is presented in Figs. 6(c), (e) and (f). Treatment ratio (emulsion to feed phase ratio) appears as the second significant factor influencing the orange 3R extraction. In fact, treatment ratio controls the interfacial mass transfer area and determines the efficiency of ELM process. Initially, ELM was able to treat the feed phase containing Orange 3R below treatment ratio of 1 : 6.5. However, the Orange 3R extraction efficiency decreased as the treatment ratio was augmented from 1 : 6.5 to 1 : 10. The plausible reason is due to the high volume of feed phase, which minimizes the dispersion of emulsion, thus reducing the interfacial mass transfer area for dye extraction into the membrane phase. Likewise, Jiao et al. [54] revealed that a high treat ratio provides insufficient emulsion phase for the treatment of solute ion in the feed phase. Balasubramanian and Venkatesan [21] revealed that an increase in the treatment ratio reduces the area of emulsion per total external phase volume in the ELM system, hence promoting leakage problem.

Meanwhile, agitator speed is also another crucial factor influencing solute ion extraction in ELM. Figs. 6(b), (d) and (e) demonstrate the effect of agitator speed towards extraction efficiency of Orange 3R. As can be seen, the effect of agitator speed showed a similar trend with the extraction time. Enhancing the agitator speed from 150 to 450 rpm significantly increased the extraction performance of Orange 3R. This implies that the emulsion was in a stable state owing to the presence of high quantity of finer internal droplets, which provided a high surface area for mass transfer of solute ion during extraction. This is strongly supported by the size

of emulsion droplets, which decreased from 70.71 to 29.24 μm (Fig. 7(d) and (e)) as increasing the agitator speed from 150 to 300 rpm, respectively. Such result is strongly supported by Raji et al. [25], who found that enhancing the energy dissipation rate or agitation speed leads to the reduction of the emulsion globule size. Likewise, Davoodi-Nasab et al. [57] reported that an increase of intensity of agitation speed enhances the available interfacial area for the solute ion transfer. Nevertheless, beyond 300 rpm, the size of emulsion droplets increased up to 40.58 μm (Fig. 7(f)). It seems possible the emulsion globules tend to coalesce among each other, hence forming bigger globules which can lead to the leakage problem. This is in agreement with Kumar et al. [33] indicating that an increase in the stirring speed beyond maximum limit reduces the emulsion stability. Emulsion swelling also showed a very small difference as increasing the agitator speed up to the maximum level (Table 5). Small amount of swelling indicated that the emulsion was stable enough to withstand the stability of ELM system.

On the other hand, Span 80 concentration turns out to be the lowest significant factor influencing the Orange 3R extraction. The effect of Span 80 concentration in response to the extraction efficiency of Orange 3R is depicted in Figs. 6(a), (d) and (f). As can be noted, the Orange 3R extraction increased upon enhancing Span 80 concentration from 1 to 4% w/v. At this stage, finer emulsion droplets also were produced (35.51 to 29.24 μm). Likewise, the emulsion swelling also decreased to 1%, signifying that 4% w/v of Span 80 was considered sufficient to preserve the emulsion stability for Orange 3R extraction. It can be inferred that the emulsion becomes stable as the interfacial tension between feed and emulsion phases is highly reduced. This is in agreement with the previous work who claimed that the presence of emulsifier or surfactant enables to reduce the interfacial tension among water and oil at the liquid-liquid interface, thus preserving the emulsion stability and solute ion transfer at the interface of feed and membrane phases [58]. Though, the extraction efficiency of Orange 3R was adversely affected when increasing Span 80 concentration up to the maximum level of 7% w/v.

As can be seen, the emulsion droplets seem to be bigger (75.71 μm) as a consequence of too high coalescence occurring among them. At this point, the swelling percentage also drastically increased to 43%. It is obvious that a high volume of water was transferred into the internal phase. Such trend is in accordance with Ahmad et al. [59] who indicated that Span 80 provides low hydrophilic-lipophilic (HLB) value and is considered a strong hydrophilic. The high concentration of Span 80 encourages the hydrophilic side of Span 80 transfer more water into the internal stripping phase, thus causing a severe emulsion swelling.

4. Optimization of Orange 3R Extraction

Table 6 illustrates the predicted optimum conditions of each parameter studied on the Orange 3R extraction. These consist of

Table 6. Validation of optimum conditions for Orange 3R extraction

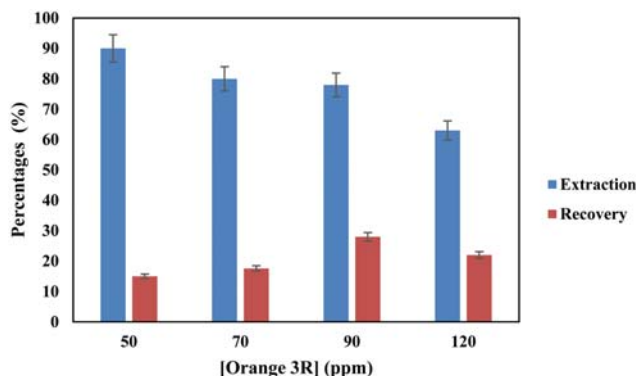| Extraction time (min)	Treat ratio	Agitator speed (rpm)	[Span 80] (% w/v)	Orange 3R extraction (%)		
				Predicted (%)	Experimental (%)	Error (%)
12	1 : 9.8	413	3.2	91	90	1

Fig. 8. Effect of initial dye concentration on extraction and recovery performance.

3.2% (w/v) of sorbitan monooleate concentration, 1 : 9.8 of treatment ratio, 413 rpm of agitator speed and 12 minutes of extraction time. Using these conditions, an experiment was run to validate the prediction result. As a result, the difference of the extraction result between the predicted and experimental provides only 1% error, which is acceptable. Hence, this model is capable of predicting any response within the range of parameters studied.

5. Effect of Initial Orange 3R Concentration at Feed Phase

Fig. 8 demonstrates the influence of initial dye concentration on the extraction and recovery of Orange 3R under optimum conditions. The extraction efficiency of Orange 3R decreased from 90 to 63% as the initial concentration of Orange 3R was increased from 50 to 120 ppm, respectively. Basically, high initial feed concentrations induce the saturation effect with dye-carrier complex in the membrane phases, thus decreasing the extraction performance of dye. Similar observation was reported by Mokhtari and Pourabdollah [60], who indicated that the mass transfer resistance in the emulsion globule becomes important at higher concentration of solute complex, thus decreasing the rate of extraction yield. Subsequently, the recovery of Orange 3R increased with the initial feed phase concentration wherein up to 28% of Orange 3R was recovered upon enhancing the Orange 3R concentration up to 90 ppm. Thereafter, slight decrement was observed at 120 ppm of dye (22%). Low recovery was observed due to the highly stable dye-carrier complex which is quite difficult to strip out into the stripping phase and might need longer time. Additionally, the decrement in the recovery may be due to the insufficient extractant to form a complex with dye solute. Hence, in this work, the ELM formulation is more suitable for the treatment of 50 ppm of Orange 3R.

6. Comparison on Extraction Performance of Orange 3R

Table 7 presents a comparison of extraction performance of

Table 7. Comparison on extraction performance of Orange 3R using several different methods

Method	Extraction (%)	References
Adsorption	67	[37]
Advanced oxidation	41	[38]
Solvent extraction	70	[48]
Emulsion liquid membrane	91	Present work

Orange 3R with respect to various methods including adsorption, advanced oxidation, solvent extraction, and emulsion liquid membrane. As reported by Ahmad and Rahman [37], about 67% of Orange 3R was removed via adsorption process using coffee husk based activated carbon (CHAC) prepared through physicochemical activation. The innovation of alternative activated carbon precursors mainly from agricultural wastes is highly encouraged. However, adsorption only leads to the removal of Orange 3R dyes without degrading them, hence producing large amounts of sludge as well as creating a waste disposal problem. As for the degradation of Orange 3R dye, Chen et al. [38] studied an advanced oxidation process involving photocatalytic decolorization of Orange 3R dye using titanium (IV) oxide as a photocatalyst, since this compound requires low cost and has remarkable photoactivity and photochemical stability. However, only around 41% of Orange 3R color was reduced using this advanced oxidation technique. Henceforth, Rahman et al. [48] reported the Orange 3R dye extraction using solvent extraction process. It turns out that only 70% of Orange 3R was successfully extracted using a mixture of basic extractants containing tridodecylamine (TDA) and trioctylamine (TOA). On the other hand, the present work shows that synergistic emulsion liquid membrane extraction of Orange 3R dye using binary mixture of the acidic (D2EHPA) and basic extractant (Aliquat 336) was capable of extracting the Orange 3R dye up to 91%.

CONCLUSIONS

Synergistic green extraction of Orange 3R was successfully performed using ELM process containing a binary mixture of Aliquat 336 and D2EHPA in palm oil. Around 91% of Orange 3R was extracted under optimum conditions of 12 minutes of extraction time, 413 rpm of agitator speed, 3.2% (w/v) of sorbitan monooleate as well as 1 : 9.8 of treatment ratio. Both Aliquat 336 and D2EHPA behaved as extractant and synergist extractant, respectively. Through transport mechanism of Orange 3R extraction in ELM process, Aliquat 336 selectively binds with Orange 3R complex at the feed/membrane interface through anion exchange mechanism. Meanwhile, D2EHPA acts as a shield that inhibits the interaction among Aliquat 336 and TG in palm oil, thus improving the extraction efficiency of dye. Moreover, it was found that the optimized conditions are capable of treating lower concentration of Orange 3R wastewater (below 100 ppm). Compared to the other extraction methods, the synergism in ELM process is capable of improving the extraction efficiency of Orange 3R dye from textile wastewater.

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