

# Efficient Dye Removal from Aqueous Solutions Using Rhamnolipid Biosurfactants by Foam Flotation

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**ABSTRACT:** Methylene blue was efficiently removed from aqueous solution by foam flotation using a rhamnolipid biosurfactant as a dye collector. The effects of four parameters, namely, pH (1.5–11.5), frother concentration (5–65 ppm), aeration rate (2–6 L/min) and rhamnolipid to methylene blue weight ratio (0.5–6.5), on dye removal were studied and optimized using response surface methodology. Results showed that dye removal increases by increasing of all parameters; however, the nonlinear trend was observed for the effects of frother concentration and rhamnolipid to methylene blue ratio. Optimum removal conditions, resulting in about 93% dye removal, was achieved at pH value of 11.5, methyl isobutyl carbinol (MIBC) concentration of 35 ppm, air flowrate of 4 L/min, and rhamnolipid to methylene blue ratio of 3.5, after only 10 min flotation. Investigations also showed that the presence of electrolyte can significantly decrease the removal efficiency. Kinetics study revealed that the process follows the first order model with a rate constant of about 0.288 sec<sup>-1</sup>. This study demonstrates that rhamnolipid could be considered as a potentially efficient and environment friendly collector for the treatment of dye contaminated wastewater.

**KEYWORDS:** Methylene blue; Rhamnolipid biosurfactant; Foam flotation; Experimental design; Water recovery.

## INTRODUCTION

Dyes are of most important pollutants produced by a large variety of industries, such as textile, paper, leather, cosmetics, printing, plastic, pharmaceuticals and food industries. Discharging of colored effluents into waters causes environmental problems due to the toxicity and recalcitrance of dyestuffs. The complex molecular structure of such materials makes them fairly stable against light and heat and therefore, natural biodegradation. In addition, the presence of dyes in water sources hinders the penetration of sunlight into the deep zones and endangers

the aquatic life [1, 2]. Hence, dyes contaminated waters have become a challenging environmental problem of great concern worldwide. In this regard, many efforts have been undertaken and a variety of methods are developed for the treatment of colored effluents. These methods include photodegradation, ion exchange, precipitation, electrochemical treatment, adsorption, flotation, etc. [3-5].

Among the available methods, adsorption has been investigated more because of its lower cost, simple operating process and high availability of adsorbents.

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Various adsorbents such as agricultural wastes [5–8], polymers [3, 9–11], charcoal [12, 13], activated carbon [14–17], minerals [18–23], etc. have been effectively used for the dye removal from aqueous solutions. However, problems such as low efficiency, difficult regeneration, and secondary pollution have challenged the applicability of these low cost adsorbents [1]. Recently, some researchers have efficiently applied nanomaterials such as nanocomposites [4, 25–27], nanoparticles [28–32], nanofibers [33] and nanorods [2, 34], as dye adsorbent to the treatment of dye polluted water. Although nanomaterials are more effective than conventional adsorbents but still relatively difficult synthesis and regeneration, production costs and potential environmental impacts challenge their industrial application.

Today, it is well known that some microorganisms are able to produce surface-active compounds that can vary in their chemical structure and size. Since the last decade of the past century, the concern about environmental protection has led to an increased interest in the production and properties of these natural products. The main advantages of biosurfactants over their chemical counterparts are their lower toxicity, better environmental compatibility, biodegradability, and effectiveness in a wide range of temperatures and pH. Last, but not least, their production by renewable resources provides further impetus for serious consideration of biological surfactants as possible alternatives of the commonly used industrial chemicals [35, 36]. Although there is rather a large body of literature on the use of synthetic, modified or mineral adsorbents in the removal of dyes from aqueous solutions, few scientific researches which apply bioproducts have been found. For example, *Farah et al.* [37] used dried biomass of Baker's yeast to remove astrozone blue basic dye from an aqueous solution. *Su et al.* [38] assessed *Imperata cylindrical* strain as an adsorbent for methylene blue removal. They reported that *Imperata cylindrical* can be used as an efficient adsorbent for dye removal after process optimization. *Cheng et al.* [39] also used a combined method to remove methylene blue from synthetic dye polluted water by using rice straw and *Phanerochaete chrysosporium* strains. Recently, *Afroze et al.* [40] successfully used *Eucalyptus sheathiana* bark biomass as a dye adsorbent for the treatment of colored aqueous solution.

Rhamnolipid biosurfactant derived from *Pseudomonas aeruginosa* bacteria is a well-known bioproduct efficiently

used in the remediation of heavy metal contaminated soils [41–44] due to the high binding capacity with metal cations and treatment of wastewater [45–49] due to the high surface activity and foamability. The present study focuses on the potential application of rhamnolipid biosurfactant in foam flotation to remove methylene blue from aqueous solution. The main and interaction effects of parameters influencing the removal efficiency, including pH, frother concentration, aeration rate, rhamnolipid to methylene blue ratio, contact time, and electrolyte type and concentration were investigated using a systematic experimental design. The flotation modelling, optimization, and kinetics were also evaluated.

## EXPERIMENTAL SECTION

### Reagents

Rhamnolipid (RL), which is a biologically produced surface-active glycolipid, was examined as an alternative collector to common chemical surfactants. This biosurfactant was prepared at the National Institute of Genetic Engineering and Biotechnology (Tehran, Iran). The structure and surface activity of biosurfactants were characterized in detail [50, 51], presenting an anionic character (CMC ~ 10 ppm). The following chemicals were also used: Methylene Blue (MB) as the dye material; hydrochloric acid (HCl) and sodium hydroxide (NaOH) as solution pH-regulators; and sodium chloride (NaCl) and calcium chloride (CaCl<sub>2</sub>) as the electrolyte sources, and methyl isobutyl carbinol (MIBC) as the process frother. Chemical structures of the used reagents are shown in Fig. 1.

### Flotation column

The foam flotation tests were carried out in a 60 cm in height acrylic column cell with an internal diameter of 5.7 cm. Bubbles were generated carefully by sparging air through a sintered glass frit (10–15 μm, porosity 4), installed at the base of the column, at a controlled pressure of 1.00±0.05 atm. The air compressor was supported with an in-line air filter (0.2–0.4 μm) to avoid sparger blockage and a manometer (Dwyer model RMA-12-SSV, USA) to control the airflow at required rates. A port 5 cm above the sparger was used for sampling.

### Foam flotation tests

The foam flotation experiments were conducted based on a Central Composite Experimental Design (CCD) to evaluate

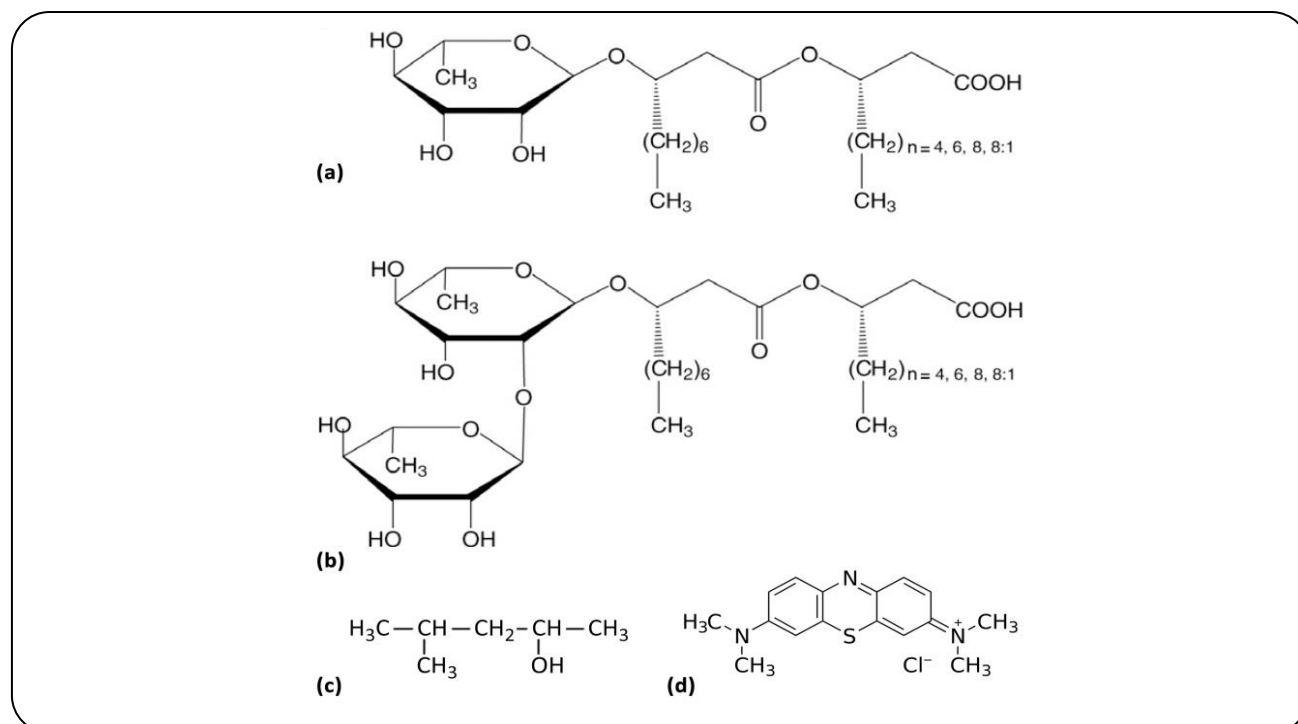


Fig. 1: Chemical structures of surfactants used in foam flotation experiments: mono-RL (a), di-RL (b), MIBC (c), and MB (d).

the effects of the initial solution pH, the Rhamnolipid to Methylene Blue (RL/MB) weight ratio, the frother concentration (MIBC) and aeration rate (Q). Using the central composite design, both main effects, either linear or non-linear, and interaction effects can be recognized. In addition, CCDs are very powerful designs for process optimization and identification of optimal conditions under which maximum process efficiency can be obtained. The methylene blue removal was treated as a process response. Since the flotation performance is directly affected by foam properties, water recovery was also considered as process response. The stability of foam can be described in terms of thin liquid film between bubbles in the foam phase; therefore, water recovery can be used as a foam stability measure. The levels of variables studied are given in Table 1. The final experimental design used for flotation tests is shown in Table 2.

For each test, 1000 mL of an initial solution containing 20 ppm MB and requisite amounts of rhamnolipid and MIBC was prepared in double distilled water. After pH adjustment, the solution was stirred with a magnetic stirrer for 30 min to ensure consistent mixing of all reagents. Bubble generation was begun just after the solution was introduced into the column, filling it with bubbles. The movement of the bubbles upward was turbulent.

Immediately, a foam layer formed at the top of the solution, creating a distinct interface. The flotation process was permitted to run for 10 min. Afterwards, the remained solution was sampled and analysed. The MB content of the samples was measured by the Shimadzu UV-Vis/NIR spectrophotometer in the range of 200–800 nm. The aqueous solutions of methylene blue showed a clear absorbance band near 664 nm. Effect of salt addition on separation efficiency was also studied after the optimum conditions for maximum MB removal were determined. The process kinetics was investigated by a periodical sampling of the solution during the optimum test. Before each sampling, about 3 mL of solution was drained from the sampling port to withdraw an actual sample. To minimize the entrainment of the air bubble, samples were withdrawn very slowly. All experiments were conducted at room temperature, about 25–27°C. The MB removal was calculated using the equation below:

$$R_{\text{MB}}(\%) = \frac{C_0 - C_i}{C_0} \times 100 \quad (1)$$

Where  $C_0$  is the initial MB concentration and  $C_i$  is the MB concentration after 10 min of flotation. In order to measure the water recovery, the water discharged out

**Table 1: Level of variables for CCD foam flotation studies.**

Flotation variables	Lower Ex. Level	Low level	Mid-level	High level	Higher Ex. Level
A: pH	1.5	4	6.5	9	11.5
B: MIBC, ppm	5	20	35	50	65
C: Q, l/min	2	3	4	5	6
D: RL/MB ratio	0.5	2	3.5	5	6.5

**Table 2: Design consisted of experiments for the study of operating parameters with experimental results.**

Run	A: pH	B: MIBC (ppm)	C: Q (l/min)	D: RL/MB Ratio	MB Removal (%)	Water Recovery (%)
1	4	20	5	5	2.56	16.16
2	4	50	3	2	5.25	25.48
3	6.5	35	4	3.5	78.32	67.57
4	6.5	35	4	3.5	59.64	58.08
5	6.5	5	4	3.5	17.68	17.81
6	9	50	3	2	38.74	13.92
7	9	20	3	2	49.11	5.51
8	6.5	35	4	3.5	61.12	62.26
9	9	20	5	5	67.5	21.43
10	4	20	3	5	5.30	23.57
11	1.5	35	4	3.5	39.46	62.50
12	4	50	5	2	69.55	68.61
13	4	20	5	2	9.16	36.64
14	6.5	65	4	3.5	61.54	56.77
15	6.5	35	4	6.5	32.83	19.57
16	4	20	3	2	16.71	43.93
17	6.5	35	2	3.5	25.03	36.87
18	9	20	3	5	66.26	20.21
19	4	50	5	5	18.92	45.22
20	9	50	3	5	69.27	19.79
21	11.5	35	4	3.5	92.21	49.45
22	6.5	35	4	0.5	46.28	56.46
23	6.5	35	4	3.5	80.04	67.57
24	4	50	3	5	7.03	30.23
25	6.5	35	4	3.5	56.73	62.26
26	9	20	5	2	83.33	61.96
27	9	50	5	2	81.34	60.26
28	6.5	35	4	3.5	61.20	57.45
29	6.5	35	6	3.5	79.06	65.58
30	9	50	5	5	71.44	41.11

of the flotation column as the foam was weighed and substitute in the following equation:

$$R_w(\%) = \frac{W_d}{W_0} \times 100 \quad (2)$$

Where  $W_0$  is the initial weight (~ volume) of water within the flotation column and  $W_d$  is the total weight of water discharged out of the column after 10 min of flotation.

## RESULTS AND DISCUSSION

### Statistical analysis of experimental design

Generally, central composite design applies a nonlinear multi-variable regression equation to model the relation between process response and operating variables, as below:

$$y = b_0 + \sum b_i x_i + \sum b_{ij} x_i x_j + \varepsilon \quad (3)$$

where  $y$  is the predicted response,  $b_0$  the constant coefficient,  $b_i$  the linear coefficients,  $b_{ij}$  the nonlinear coefficients,  $x_i$  and  $x_j$  are coded values of the independent process variables, and  $\varepsilon$  is the residual error. The values of the coefficients are calculated by using Design Expert v.7 (DX7) software. The best fitted model equations were obtained for MB removal and water recovery as follows:

$$\begin{aligned} \text{Methylene blue removal}(\%) = & 64.57 + \quad (4) \\ & 13.19A + 10.97B + 13.51C - 2.99D - 4.53AB \\ & 5.55AD + 5.99BC - 7.56CD - 7.76B^2 - 4.65C^2 - \\ & 7.77D^2 - 4.82ABC + 3.13ABD - 4.04BCD - \\ & 7.11A^2B - 4.37A^2C + 11.34AB^2 \end{aligned}$$

$$\begin{aligned} \text{Water recovery}(\%) = & 62.53 - 2.99A + \quad (5) \\ & 6.67B + 9.42C - 7.18D + 5.12AC + 5.18BC - \\ & 6.78CD - 3.61A^2 - 8.71B^2 - 4.80C^2 - 8.10D^2 \end{aligned}$$

Where factors are in coded form.

Model Eqs. (4) and (5) were used to evaluate the influence of the process variables on MB removal and water recovery. The significance of the models is evaluated by Analysis of Variance (ANOVA). Tables 3 and 4 show the ANOVA results. A confidence interval of 95% was chosen for the determination of the significance of main and interaction effects. As shown in Table 3, the suggested regression model is significant due to the value of Fisher's  $F$ -test ( $F$  model = 13.48) with a very low

probability value ( $p$  model < 0.0001). The low probability value for the water recovery model also indicates that it is significant. Table 3 also indicates that the effects of pH, MIBC concentration and aeration rate are significant ( $p$  values less than 0.05). The interaction effects between pH and rhamnolipid to MB ratio (AD), MIBC concentration and aeration rate (BC), and aeration rate and rhamnolipid to MB ratio (CD) are also significant. Although the effects of rhamnolipid to MB ratio and interaction of pH and MIBC concentration are not significant they had a sharp effect on the model accuracy. In the case of water recovery (Table 4), significant variables are MIBC concentration, aeration rate and rhamnolipid to MB ratio.

Normal probability plot of the residuals is another useful tool for the evaluation of the significance of the process prediction model [52]. The normal probability of the residuals for MB removal is shown in Fig. 2 indicating that almost no serious violation of the assumptions underlying the analyses, which confirmed normality assumptions and independence of the residuals. In addition, a closely high value of the adjusted correlation coefficient ( $\text{Adj } R^2 = 87.98\%$ ) also showed the high significance of the model. This fact was also confirmed from the predicted versus observed values plot for MB removal in Fig. 3. The  $\text{Pred } R^2$  was 95.02%, implying that it could explain variability in predicting new observations. This was in reasonable agreement with the  $\text{Adj } R^2$  of 87.98%. Adeq precision shows the signal to noise ratio; a ratio of greater than 4 is a desirable value [53]. In this investigation, the ratio was 11.98, which indicated an adequate signal. Thus, the model could be used to navigate the design space. The water recovery model is of lower, but acceptable accuracy with  $\text{Pred } R^2$  and  $\text{Adj } R^2$  of 82.62% and 71.38%, respectively. Adeq precision was 8.64 and thus, desirable (> 4).

### Effect of solution pH

Fig. 4 shows the main effect plot for solution pH. As seen in Fig. 4, removal efficiency increases as the solution pH is increased. pH values of 1.5 and 11.5 were also considered in experimental design (Table 2) as extrapolation levels. MB removals for pH values of 1.5 and 11.5 were found to be 39.46% and 92.21%, respectively. The solution pH can directly influence the surface activity of rhamnolipid molecules. Foam formation is a dynamic phenomenon and caused

**Table 3: Analysis of variance results for methylene blue removal.**

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	21578.45	17	1269.321	13.48164	< 0.0001	significant
pH (A)	1391.281	1	1391.281	14.777	0.0023	
MIBC Conc. (B)	961.8498	1	961.8498	10.21594	0.0077	
Air flowrate (C)	1459.62	1	1459.62	15.50284	0.0020	
RL/MB ratio (D)	214.8615	1	214.8615	2.282075	0.1568	
AB	327.8816	1	327.8816	3.482477	0.0866	
AD	492.951	1	492.951	5.235703	0.0411	
BC	573.4828	1	573.4828	6.091042	0.0296	
CD	915.2138	1	915.2138	9.720615	0.0089	
Residual	1129.822	12	94.15183			
Lack of Fit	607.8648	7	86.83783			

**Table 4: Analysis of variance results for water recovery.**

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	9069.382	11	824.4892	7.347706	0.0002	significant
pH (A)	214.5026	1	214.5026	1.91161	0.1847	
MIBC Conc. (B)	762.6287	1	762.6287	6.796416	0.0184	
Air flowrate (C)	2131.37	1	2131.37	18.9944	0.0004	
RL/MB ratio (D)	1237.976	1	1237.976	11.03263	0.0040	
AC	419.328	1	419.328	3.736979	0.0701	
BC	428.5935	1	428.5935	3.819551	0.0673	
CD	735.9013	1	735.9013	6.558225	0.0203	
Residual	1907.577	17	112.2104			
Lack of Fit	1811.019	12	150.9183			

by monomer surfactant molecules. Therefore, the thin liquid film characteristics of rhamnolipids molecules adsorbed at the bubble surface determine the foamability of the rhamnolipid adsorption layer. The elasticity must be adequately low to allow expansion of the interface during foam formation, and it should be high enough to maintain the rigidity which is vital for the stabilization of the foam. Özdemir *et al.* [54] showed that rhamnolipid molecules at acidic environment are more surface active due to the increase of electrostatic repulsion forces on rhamnolipid head groups. Therefore, RL molecules at more acidic conditions can form a more compact monolayer at bubble surfaces. The higher compaction on the surface film

increases the rigidity of foam film and thus, decreases the mobility of the foam phase. Therefore, the decreased discharge rate of MB loaded foam out of the flotation column decreases the removal efficiency. The major effect of alkaline pH can be attributed to the increase of Na<sup>+</sup> ions which can compete with MB cations to adsorb on the surface of bubbles loaded by RL anions.

#### **Effect of MIBC concentration**

Effect of MIBC concentration on MB removal is shown in Fig. 5. As seen, removal efficiency increases by MIBC concentration up to about 40 ppm and then, follows a linear trend. At lower frother concentration,

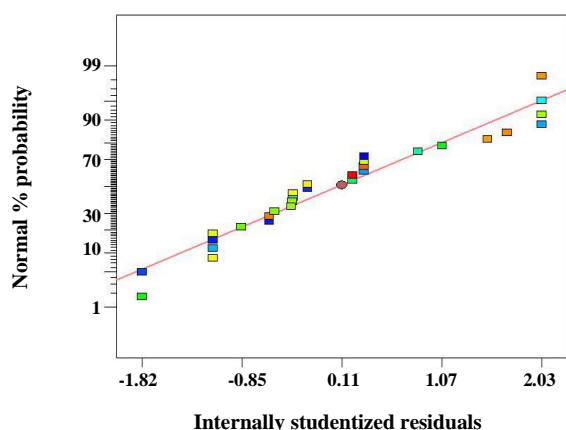


Fig. 2: Normal plot of the residuals for the methylene blue removal model.

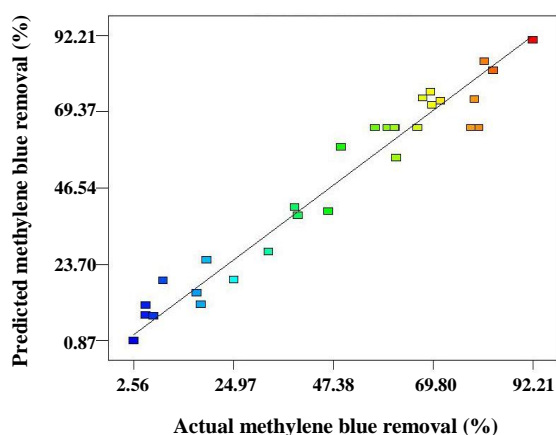


Fig. 3: Relation between observed and predicted methylene blue removal values.

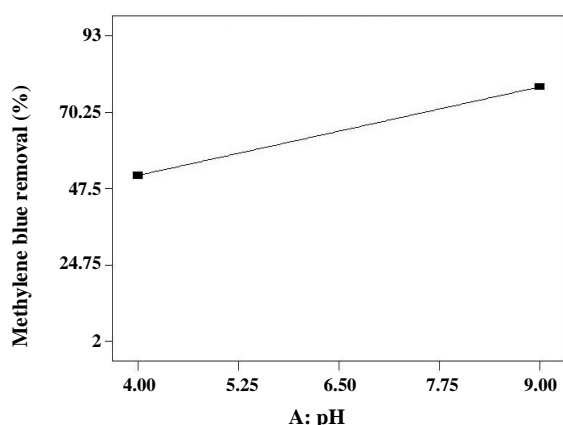


Fig. 4: Effect of solution pH on methylene blue removal.

the foam is continuously bursting due to low stability and releases its load. The foam stability increases by increasing the frother concentration. At a given rhamnolipid concentration, as MIBC concentration increases the adsorption rate of MIBC molecules at bubble surfaces decreases because of the lack of adoption places formerly occupied by RL molecules. However, it should be considered that as the frother concentration approaches to critical micelle concentration ( $CMC_{MIBC} \approx 75$  ppm), the foam formation may be collapsed (Fig. 6) and significantly decreases the MB removal.

#### Effect of aeration rate

The effect of aeration rate on MB removal is shown in Fig. 7. The removal efficiency is improved by increasing the air flow rate since the effective carrying capacity of bubbles increases due to the increase of bubble density (number of bubbles per unit volume of solution). As shown in Fig. 8, the water recovery and thus, the discharge rate of water out of the flotation column increase by increasing the aeration rate. Therefore, it could be expected that the flotation rate increases by aeration flowrate.

#### Effect of rhamnolipid concentration

Fig. 9 shows a non-linear trend in removal efficiency by rhamnolipid concentration with a maximum value at about mid-level. In the present study, rhamnolipid biosurfactant acts as a collector for collecting methylene blue from the solution. Thus, as the collector concentration increases, more MB molecules will attach to rising bubbles loaded by rhamnolipid molecules. In addition, as shown in Fig. 10, water recovery and thus foam stability increase by rhamnolipid concentration due to the increase in liquid film elasticity of bubbles [51]. Higher foam stability lower coalescence of bubble and consequently, lower drop-back of MB molecules to the solution. The removal efficiency decreased at a high level of rhamnolipid concentration. As rhamnolipid concentration increases, the potential for micelle formation also increases; therefore, the formation of micelle in the solution prevents individual rhamnolipid anions to adsorb at bubble surfaces which this, in turn, decreases MB removal using bubbles. In addition, micelle formation has a sharp effect on foam stability (Fig. 10). Disturbing foam stability can increase the drop-back of MB molecules to the solution.

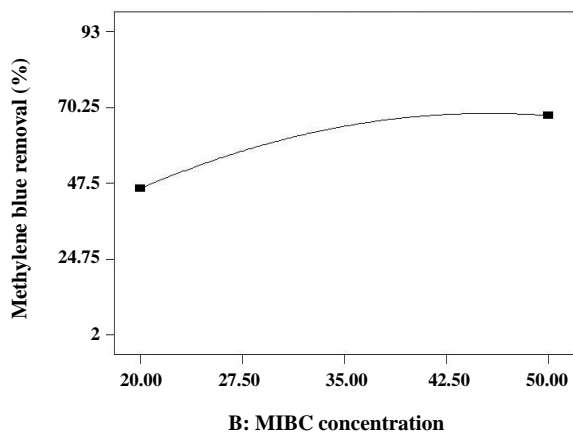


Fig. 5: Effect of MIBC concentration on methylene blue removal.

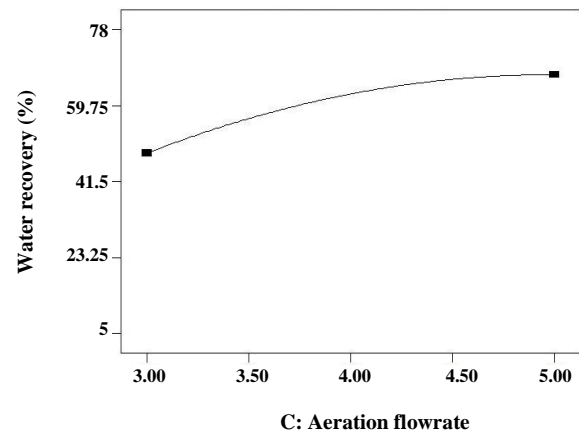


Fig. 8: Effect of aeration rate on water recovery.

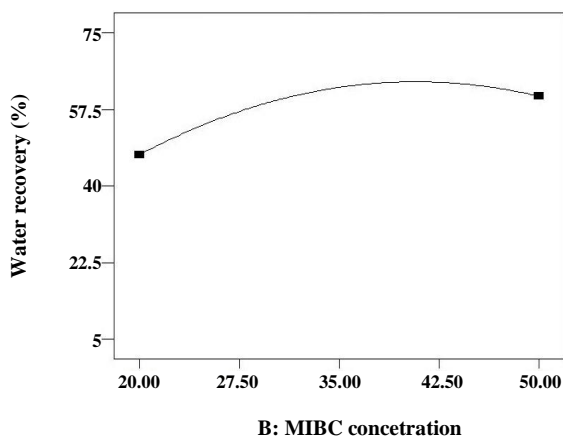


Fig. 6: Effect of MIBC concentration on water recovery.

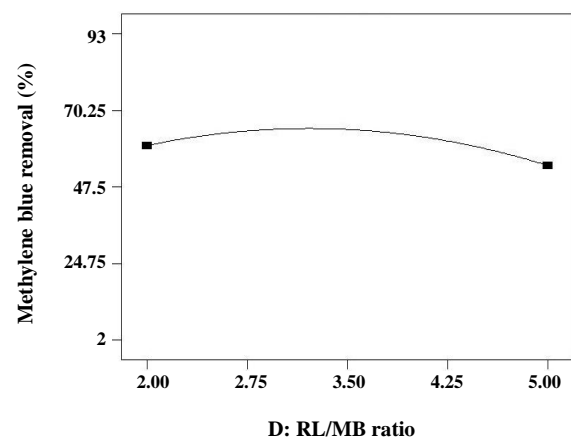


Fig. 9: Effect of rhamnolipid to methylene blue ratio on methylene blue removal.

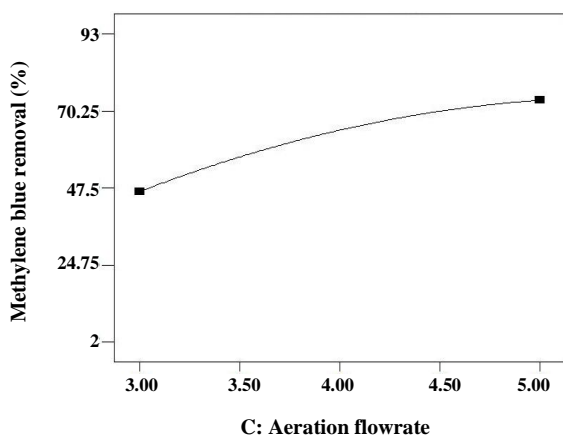


Fig. 7: Effect of aeration rate on methylene blue removal.

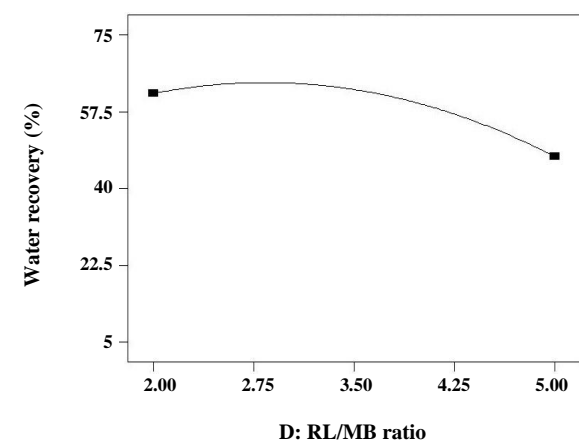


Fig. 10: Effect of rhamnolipid to methylene blue ratio on water recovery.



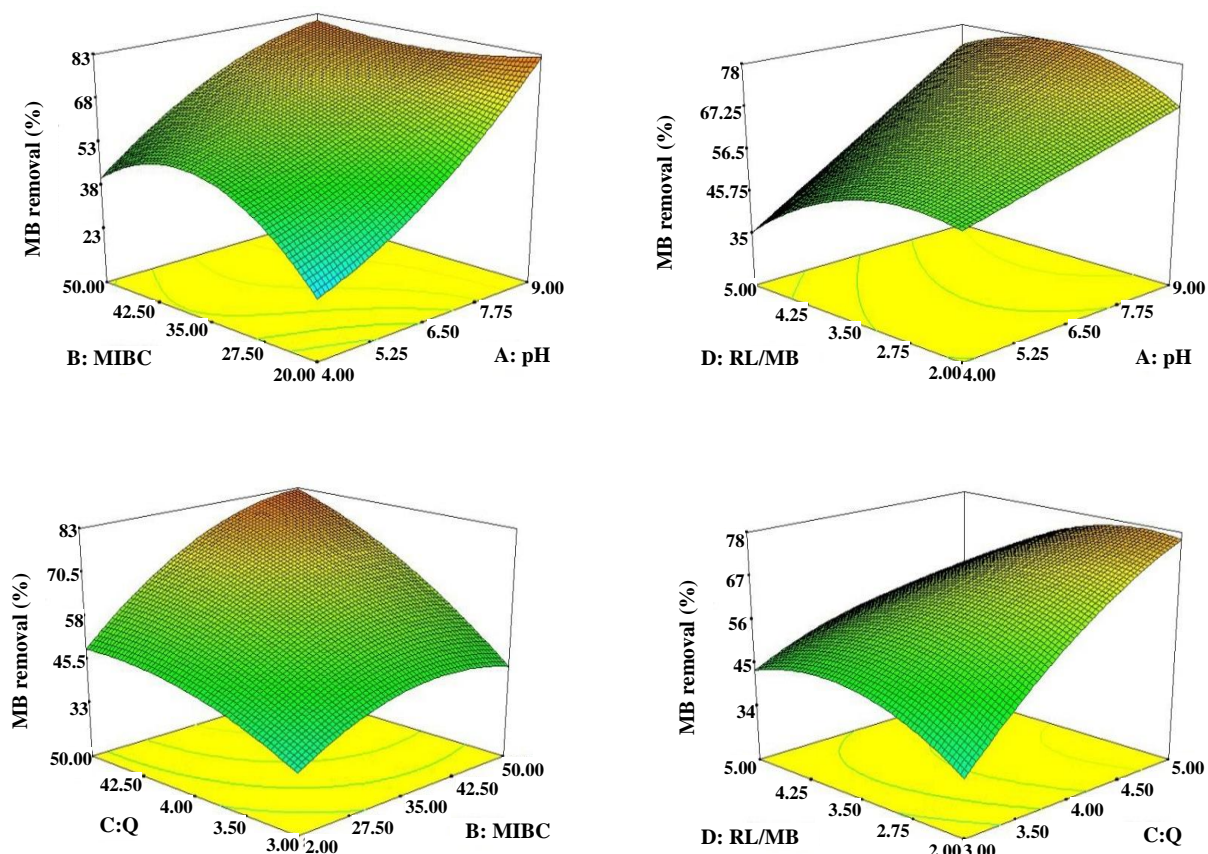


Fig. 11: The response plots showing the interaction effects of operating variables on methylene blue removal.

#### Analysis of interaction effects

The three-dimensional (3D) plots of the model response vs. two independent variables varying within their experimental levels while maintaining other variables at their mid-levels can give useful information on their relationships [55]. Therefore, in order to gain a better understanding of individual effects of the studied operating variables and their corresponding interaction effects on the other variables, 3D response plots for the MB removal was constructed based on the nonlinear model proposed by DX7 software. Since the model in this study had four independent variables, two variables were held constant at their mid-level for each plot. As seen in Table 3, the significant interactions are effects between pH and rhamnolipid to MB ratio (AD), MIBC concentration and aeration rate (BC), and aeration rate and rhamnolipid to MB ratio (CD). The interaction of pH and MIBC concentration (AB) was also considerable

in developing the MB removal model. The corresponding 3D surface plots are visualized in Fig. 11. As seen in Fig. 11, all interactions show non-linear effects on response. These plots are actually a combined effect of MIBC concentration (factor B) and RL/MB ratio (factor D), i.e. those parameters with non-linear effect (see Figs. 5 and 9). Fig. 11 reveals that maximum MB removal can be obtained for pH and aeration rate at high levels and for MIBC concentration and rhamnolipid to methylene blue at about mid-levels.

#### Process optimization

Design Expert is a powerful tool for the prediction of optimal conditions under which maximum response value would be obtained. The software uses the prediction model developed on the basis of statistical analysis and then, presents a list of optimal conditions with their corresponding response values. After setting the value

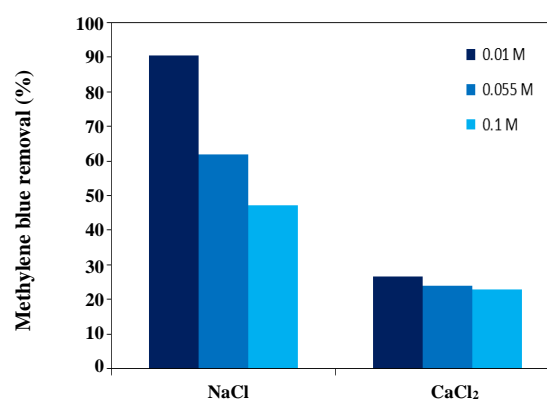
**Table 5: Optimal conditions suggested by DX7 to achieve maximum methylene blue removal.**

Set no.	pH	MIBC Conc.	Air Flowrate	RL/MB Ratio	Predicted Removal (%)	Experimental Removal (%)	
						Replicate 1	Replicate 2
1	10	42.6	5	3.5	95	87.28	88.14
2	12	35	4	3.5	95	87.33	90.61
3	11.5	35	4	3.5	95	93.50	93.16

limits for all model parameters, DX7 presented three optimal conditions sets with maximum MB removal of about 95%. Then, new experiments were conducted under these conditions. Table 5 lists the predicted conditions with experimental results. As seen, maximum MB removal of  $93.33 \pm 0.24\%$  is obtained at pH value of 11.5, MIBC concentration of 35 ppm, air flowrate of 4 l/min, and rhamnolipid to methylene blue ratio of 3.5. These conditions are those used in run 21 in Table 2. In addition, the potential levels were also predicted using 3D response plots.

#### Effect of salt addition

Effect of electrolyte on methylene blue removal was also investigated by adding various concentrations of NaCl and CaCl<sub>2</sub> under optimal conditions. Fig. 12 shows the effects of type and concentration of salts on MB removal. As seen in Fig. 12, the removal efficiency decreases in the presence of all types of salt added. The anionic character of the rhamnolipid molecule is from its carboxyl group. The majority of the carboxyl groups of RL are dissociated to form negatively charged carboxylate groups in the absence of an electrolyte. With the addition of an electrolyte, the ionic strength of the solution increases and the carboxylate groups are shielded by a diffuse layer of counterions. Therefore, the addition of electrolytes neutralizes the head groups by reducing head repulsion and causes more compact foam films (i.e. surfactant molecules come in the vicinity of each other) [56]. Compaction of RL molecular monolayer at bubble surface means a less elastic film which disrupts more readily as it expands under air flow. The structure of the foam will be then with larger bubbles causing less foam volume and less surface area for interaction with MB ions. Besides the interaction of RL on the foam film with cations reduces the interaction with MB ions remarkably. At constant electrolyte concentration, Ca<sup>2+</sup> cations are able to reduce MB removal more effectively compared

**Fig. 12: Effect of salt addition on methylene blue removal.**

to Na<sup>+</sup> ions. In other words, an equal number of double charged Ca<sup>2+</sup> ions can neutralize higher numbers of carboxylate groups which consequently causes more rigid foam films. As seen in Fig. 12, the MB removal also decreases by salt concentration. As salt concentration increases, the elasticity of rhamnolipids decreases and therefore, the shielding effect of higher salt concentrations in the electrical double layer cause the formation of less rigid monolayers than that at lower concentrations. This enhanced elasticity significantly decreases the fluidity of foam and consequently, the MB removal.

#### Kinetic study

Flotation kinetic studies the variation of floated concentration according to flotation time. Studies of flotation kinetics are useful in the elucidation of the mechanism of the process, and serve as predictive tools in the implementation of flotation technology. Chemical kinetics principles are used in the modelling of flotation processes, particularly in the formulation of the basic rate equation [57, 58]:

$$\frac{dC}{dt} = -kC_t^n \quad (6)$$

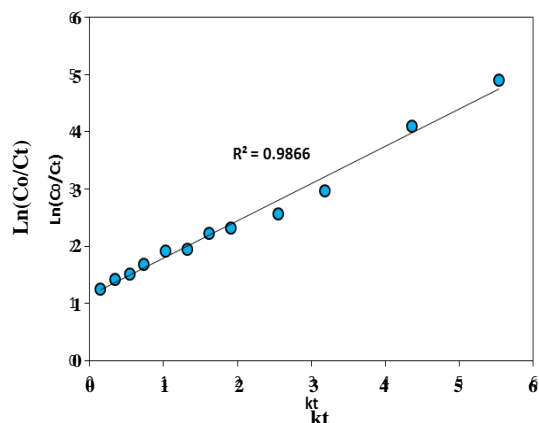


Fig. 13: Fitting plot illustrating the first order kinetics model of MB removal by foam flotation.

Where  $C_t$  is the residual concentration of methylene blue at time  $t$ ,  $t$  is the flotation time,  $n$  is the order of the flotation process and  $k$  is the flotation rate constant. Calculations showed that the best fitting result for the test conducted under optimal conditions was obtained using Eq. (6) for  $n = 1$ , i.e. the first order process, with a correlation coefficient  $R^2$  equal to 98.66% (Fig. 13). The kinetic flotation constant was found to be  $0.288 \text{ sec}^{-1}$ .

## CONCLUSIONS

In summary, the present study reveals that rhamnolipid biosurfactant is effective in methylene blue removal from aqueous solution. Compared to conventional adsorption method with usually very long contact time (usually over 100 min), maximum removal was achieved at a very short time (about 10 min). The process is pH-dependent, and removal increased with an increase in the initial solution pH. The percentage of MB removal increases with an increase in rhamnolipid to MB ratio up to an optimum value and then decreases. The presence of electrolyte in the initial solution decreases the MB removal due to competitive adsorption to rhamnolipid anions. Flotation kinetics was also investigated and was found to be of first-order nature. To our knowledge, this is the first report on the application of rhamnolipid as a collector in the flotation of dye material from aqueous solutions. Hence, more studies are required to generalize the process to practical and industrial application such as frother type optimization to decrease the water recovery, the separation of RL and

MB after the flotation to reuse RL, real involved mechanism and chemical interactions between the used surfactants etc.

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