



Box–Behnken design and analysis for liquid–liquid extraction of methyl red dye from its aqueous solution with benzene

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Abstract

Liquid–liquid extraction has gained huge attention in chemical industries for the removal of valuable products. The aim of this research to optimize the percentage dye removal, distribution coefficient and solvent capacity for liquid–liquid extraction of methyl red dye from its aqueous solution with benzene as an extractant. In this work, effect of parameters such as dye concentration in feed (20–100 ppm), extraction time (10–30 min), and dye solution to solvent ratio (1–3 mL/mL) was examined at constant pH, and temperature of 3, and 27 ± 2 °C. Response surface methodology (RSM)-based Box–Behnken design was used for optimization by considering independent and dependent factors. The optimization results reveal that the percentage dye removal, distribution coefficient and solvent capacity of 81.28%, 4.33 and 21.7 mg/L were achieved at dye concentration in feed, extraction time, and dye solution to solvent ratio of 45 ppm, 27 min, and 1.5 mL/mL, respectively. Thus, benzene could be the potential solvent for liquid–liquid extraction of methyl red dye from its aqueous solution.

Keywords Methyl red · Benzene · Liquid–liquid extraction · Optimization

List of symbols

β_o	Intercept
β_i	Linear coefficient
β_{ii}	Squared coefficient
β_{ij}	Interaction coefficient
Y	Response matrix
X	Input matrix
ε	Random error
A	Concentration of dye in feed
B	Extraction time
C	Dye solution to solvent ratio
Y_1	Dye removal
Y_2	Distribution coefficient
Y_3	Solvent capacity

Introduction

The textile industry is one of the important industries generating a large amount of industrial wastewater (Khan and Malik 2014). The main attraction of any fabric is its colour from synthetic dyes (Husain 2006). Synthetic dyes offer a wide range of bright colours. However, their toxicity has caused great concern to environmental activists (Frick 2003). The use of synthetic dyes has a negative effect on all types of life. Sulphur, naphthalene, vat dyes, nitrates, acetic acid, soaps, enzymes, chromium compounds, copper, arsenic, lead, cadmium, mercury, nickel, cobalt and some by-products make textile waste highly toxic. These organic substances react with many disinfectants, especially chlorine, to generate carcinogenic substances (Kuppusamy et al. 2016). If this wastewater enters the fields, it will clog the soil pores and reduce the productivity of the soil (Abou-Hadid 2003).

According to the United States Geological Survey (USGS), if wastewater is not treated properly, the environment and human health will be adversely affected (Missimer and Maliva 2018). Vulnerabilities include fish and wild-life populations, lack of oxygen, beach closures and other restrictions on recreational water use (Topare et al. 2011). There are two main stages in wastewater treatment: primary and secondary treatment (Udayakumar et al. 2021). In the primary condition, the solids are allowed to settle, and the

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waste is removed from the water. They use biological processes to further purify secondary wastewater (Asthana et al. 2017). Sometimes these conditions are combined, and in some cases, additional treatment such as tertiary treatment and advanced sewage treatment is used (Nascimben Santos et al. 2020). The primary treatment involves screening and sedimentation. Screening removes large floating objects such as rags and sticks that can clog pipes or damage equipment. After the sewage is filtered, it goes to a tank where solids can be removed by sedimentation (Nithya et al. 2021).

Wastewater is treated by conventional methods such as oxidation, adsorption, and membrane processes (Kapoor and Sivamani 2021). In addition, liquid–liquid extraction is one of the methods that are not employed in broad wastewater research due to its high operational cost (Fredij et al. 2015). Liquid–liquid extraction, also known as solvent extraction and separation, is a method of separating compounds or metal complexes into two different unmixed liquids, usually water and an organic solvent. From a liquid, the net transfer of one or more organisms from one liquid state to another, usually happens from water to organic matter (Huddleston et al. 1999). The exchange is driven by chemical energy, i.e., the overall composition of the chemical components that make up the solvents and solvents during the transfer is in a stable structure low free energy (Rosenthal et al. 1996). However, liquid–liquid extraction methods are required when factors such as low volatility, heat-sensitive materials, high operating costs/investments, and complex process sequences are involved (De Castro and Garcia-Ayuso 1998).

Next, it is necessary to consider the solvent recovery features because they will also affect the overall process economics (Degryse et al. 2009). In most cases, the bulk of the capital expenditure is paid in the extraction column. Materials that cannot withstand boiling compounds (azeotropes) or filtration temperatures can often be separated even under vacuum by liquid–liquid extraction (Bidari et al. 2013). In dilute solutions in equilibrium, the ratio of the concentrations of a solution in two phases is called the distribution coefficient or distribution constant. Thus, the distribution coefficient based on the weight fraction of the solution can be given in two stages. The concentration of the solution and the ratio of the solvent in the solution are called the selective or separation factor. Higher values of the distribution coefficient are generally desirable because a given extraction duty will require less solvent. The solvent must be insoluble in the original liquid, and it must be highly soluble to dissolve (Sprakel and Schuur 2019).

From the analysis of literature, methylene blue dye is removed using 0.072 M salicylic acid (Soniya and Muthuraman 2015), and mixture of edible paraffin oil and heptane in the volume ratio of 4:1 (Zereshki et al. 2018), and reported 93 and 95% removal, respectively, through liquid membrane technologies. Similarly, astacryl golden yellow, Rhodamine B, and methyl violet dyes are removed using palm oil (Muthuraman

and Palanivelu 2006), sunflower oil (Muthuraman and Teng 2009a, b), and waste vegetable oil (Shokri et al. 2020), respectively, and reported > 90% removal through liquid membranes (Chang 2020). Hence, in the present work, solvent extraction is attempted for the removal of methyl red dye from its aqueous solution using benzene as a solvent, and optimized using three-factor-three-level Box–Behnken design.

Materials and methods

Chemicals

Methyl red, benzene, and separating funnel were used from the laboratories of University of Technology and Applied Sciences Salalah, Oman. Double distilled water was used unless otherwise specified.

Batch liquid–liquid extraction studies

A stock solution (1000 ppm) of methyl red dye was prepared by dissolving 1 g of dye in 1 L of water. Standard solutions were prepared at the concentration of 20, 60 and 100 ppm. The dye solution of 100 mL was mixed with benzene solvent at a specified time. The mixture was allowed to equilibrium in a separating funnel. After equilibrium, extract (top) and bottom (raffinate) layers form. The dye concentration in raffinate was determined using UV–visible spectrophotometer to calculate percentage dye removal, distribution coefficient, and solvent capacity, as given in Equations (1) to (4) below.

$$\begin{aligned} \text{Percentage dye removal} \\ &= \frac{\text{Concentration of dye in extract}}{\text{Concentration of dye in feed}} \times 10 \end{aligned} \quad (1)$$

$$\text{Distribution coefficient} = \frac{\text{Concentration of dye in extract}}{\text{Concentration of dye in raffinate}} \quad (2)$$

$$\begin{aligned} \text{Solvent capacity} \\ &= \frac{\text{Concentration of dye in extract} \times \text{Volume of dye solution}}{\text{Volume of solvent}} \end{aligned} \quad (3)$$

$$\begin{aligned} \text{Concentration of dye in extract} \\ &= \text{Concentration of dye in feed} \\ &- \text{Concentration of dye in raffinate} \end{aligned} \quad (4)$$

Statistical optimization of liquid–liquid extraction by Box–Behnken design

Response surface methodology develops second-order polynomial equation with minimum trials and error. Also, it is used to study the interaction between

independent factors (Sivamani et al. 2020). It has two designs: Box–Wilson or central composite design and Box–Behnken design. According to their principle, number of experiments performed for Box–Wilson design is $2^f + 2^*f + m$ and $2^*f*(f-1) + m$ for Box–Behnken design, where f is number of independent factors and m is number of centre points (Sivamani and Baskar 2018; Joaquin et al. 2021). Normally, Box–Behnken design provides more accurate results with a lesser number of experiments.

An original version of Design-Expert 13, from Stat-Ease, Inc. USA, was used to perform the response surface design and analysis. Box–Behnken design is used in this research to maximize percentage dye removal, distribution coefficient and solvent capacity at optimum values of dye concentration in feed (20–100 ppm), extraction time (10–30 min), and dye solution to solvent ratio (1–3 mL/mL). In total, 15 experiments were performed for three independent factors with three centre points. All the experiments were performed as per the Box–Behnken design matrix, and the experimental data were tested to fit linear, 2FI (two-factor interactive), quadratic and cubic models for their significance. Then, the data were fitted to the significant quadratic equation to investigate the effect of independent factors on the response as represented in Eq. (4) and model coefficients evaluated using Eq. (5). After evaluation, the coefficients were substituted in Eq. (4) for checking the deviation between experimental and predicted values. The significance of the model was tested using analysis of variance (ANOVA) based on high F -value and low p -value with 95% confidence level (Sivamani et al. 2020). Also, regression coefficient R^2 , difference between adjusted and predicted R^2 , and predicted residual error sum of squares (PRESS) values were also assessed to find the goodness-of-fit between experimental and predicted values (Vijayanand et al. 2021).

$$Y = \beta_0 + \sum_{i=1}^n \beta_i X_i + \sum_{i=1}^n \beta_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n \beta_{ij} X_i X_j + \epsilon \quad (5)$$

$$\beta = (X^T X)^{-1} (X^T Y) \quad (6)$$

where β_0 is an intercept; β_i , β_{ii} , β_{ij} are linear, squared and interaction coefficients, respectively, Y is the response; X_i and X_j are independent factors; and ϵ is a random error.

Results and discussion

Statistical optimization of liquid–liquid extraction by Box–Behnken design

Table 1 shows the independent factors and levels selected for liquid–liquid extraction of methyl red dye from its aqueous solution with benzene as an extractant. The number of experiments performed in Box–Behnken design is $2^*f*(f-1) + m = 2 \times 3 \times 2 + 3 = 15$ according to the principle.

Table 2 shows the Box–Behnken matrix of 15 experiments for liquid–liquid extraction of methyl red dye from its aqueous solution with benzene as an extractant. The various models, viz., linear, 2FI, quadratic and cubic models were tested for liquid–liquid extraction of methyl red dye from its aqueous solution with benzene as an extractant.

The values of F , p , R^2 , difference between adjusted and predicted R^2 and PRESS were used to check the significance of model. A sufficient F -value, low p -value of < 0.05 , $R^2 > 0.8$, difference between adjusted and predicted $R^2 < 0.2$ and a least value of PRESS for quadratic model implied that it is significant and suitable for the liquid–liquid extraction of methyl red dye from its aqueous solution with benzene as an extractant.

The experimental data were fitted to the quadratic model, as represented in Eqs. (6), (7) and (8) for percentage dye removal, distribution coefficient and solvent capacity, respectively. All the intercept, linear, interactive and quadratic coefficients were alternative at negative and positive signs, respectively. The responses, percentage dye removal, distribution coefficient and solvent capacity tend to increase with increase in independent factors, dye concentration in feed, extraction time, and dye solution to solvent ratio in the studied range. According to the principle of maxima and minima, negative coefficients in linear terms and positive coefficients in quadratic terms tend to decrease the response and vice versa. Similarly, a decline in positive coefficient terms tends to diminish the dependent factor and vice versa (Chandrasekaran and Sivamani 2018). In Eqs. (6)–(7), positive values of coefficients in linear terms and negative values of coefficients in quadratic terms tend to maximize the responses. Also, all the data points lie within $\pm 10\%$ of predicted and experimental values, which is in agreement with the statistical inference (Table 3).

Table 1 Independent factors and levels used for liquid–liquid extraction of methyl red dye using benzene

Independent factor	Symbol	Unit	Levels		
			Low (–1)	Centre (0)	High (+1)
Concentration of dye in feed	A	ppm	20	60	100
Extraction time	B	min	10	20	30
Dye solution to solvent ratio	C	mL/mL	1	2	3

Table 2 Box–Behnken design matrix for liquid–liquid extraction of methyl red dye using benzene

Run	Concentration of dye in feed A (ppm)	Extraction time B (min)	Dye solution to solvent ratio C (mL/mL)	Dye removal Y_1 (%)	Distribution coefficient Y_2	Solvent capacity Y_3 (mg/L)
1	20	20	1	69.42	4.28	13.88
2	60	20	2	68.57	4.23	20.57
3	60	10	3	58.28	3.59	11.65
4	60	20	2	67.71	4.17	20.31
5	60	20	2	66.85	4.12	20.05
6	20	20	3	81.42	5.02	5.42
7	60	10	1	45.42	2.8	27.25
8	20	10	2	46.28	2.85	4.62
9	100	30	2	57.42	3.54	28.71
10	100	20	1	47.14	2.9	47.14
11	20	30	2	80.57	4.97	8.05
12	60	30	1	56.57	3.49	33.94
13	100	20	3	55.71	3.43	18.57
14	60	30	3	66	4.07	13.2
15	100	10	2	48	2.96	24

Table 3 Analysis of variance (ANOVA) for quadratic model developed for liquid–liquid extraction of methyl red dye using benzene

Source	Percentage dye removal					Distribution coefficient					Solvent capacity				
	SS	df	MS	F-value	p-value	SS	df	MS	F-value	p-value	SS	Df	MS	F-value	p-value
Model	1753	9	194.8	5.83	0.033	6.68	9	0.742	5.80	0.033	1817	9	201.9	191.6	<0.05
A	602.3	1	602.3	18.02	0.008	2.30	1	2.30	17.97	0.008	934.2	1	934.2	886.6	<0.05
B	489.5	1	489.5	14.64	0.012	1.87	1	1.87	14.62	0.012	33.54	1	33.54	31.83	0.002
C	229.6	1	229.6	6.87	0.047	0.871	1	0.871	6.80	0.047	672.8	1	672.8	638.6	<0.05
AB	154.6	1	154.6	4.63	0.084	0.592	1	0.592	4.63	0.084	0.4096	1	0.4096	0.3888	0.560
AC	2.94	1	2.94	0.088	0.778	0.011	1	0.011	0.086	0.781	101.1	1	101.1	95.96	<0.05
BC	2.94	1	2.94	0.088	0.778	0.011	1	0.011	0.086	0.781	6.60	1	6.60	6.27	0.054
A ²	7.17	1	7.17	0.214	0.662	0.027	1	0.027	0.216	0.661	16.46	1	16.46	15.62	0.010
B ²	251.2	1	251.2	7.51	0.040	0.947	1	0.947	7.40	0.041	12.69	1	12.69	12.04	0.017
C ²	30.92	1	30.92	0.924	0.380	0.118	1	0.118	0.925	0.380	34.43	1	34.43	32.68	0.002
Residual	167.1	5	33.43			0.640	5	0.128			5.27	5	1.05		
Lack of fit	165.6	3	55.23	74.67	0.013	0.634	3	0.211	69.69	0.014	5.13	3	1.71	25.31	0.038
Pure error	1.48	2	0.739			0.006	2	0.003							
Cor total	1920	14				7.33	14								

SS—Sum of squares, df—Degree of freedom, MS—Mean square, A—Dye concentration in feed, B—Extraction time, C—Dye solution to solvent ratio

$$\begin{aligned} \text{Percentage dye removal } Y_1 = & -17.99 + 0.241 * A + 5.186 * B \\ & + 19.93 * C - 0.015 * A * B - 0.0214 * A * C \\ & - 0.086 * B * C - 0.0009 * A^2 - 0.082 * B^2 - 2.894 * C^2 \end{aligned} \quad (7)$$

$$\begin{aligned} \text{Distribution coefficient } Y_2 = & -1.111 + 0.0150 * A + 0.319 * B \\ & + 1.230 * C - 0.001 * A * B - 0.0013 * A * C \\ & - 0.0052 * B * C - 0.00005 * A^2 \\ & - 0.005 * B^2 - 0.179 * C^2 \end{aligned} \quad (8)$$

Table 4 Statistical significance for response factors for liquid–liquid extraction of methyl red dye using benzene

Statistical parameters	Percentage dye removal	Distribution coefficient	Solvent capacity
Standard deviation	5.78	0.357	1.03
Coefficient of variance (%)	9.47	9.51	5.18
Determination coefficient (R^2)	0.913	0.912	0.997
Adjusted R^2	0.756	0.755	0.991
Predicted R^2	0.591	0.587	0.954
PRESS	2654.16	10.16	82.43
AICc	153.7	70.26	101.87
BIC	105.8	22.34	53.95

$$\begin{aligned}
 \text{Solvent capacity } Y_3 = & -0.864 + 0.664 * A + 1.155 * B \\
 & + 11.28 * C - 0.0008 * A * B - 0.125 * A * C \\
 & - 0.128 * B * C - 0.0013 * A^2 \\
 & - 0.018 * B^2 - 3.053 * C^2
 \end{aligned}
 \tag{9}$$

Table 4 shows the analysis of variance (ANOVA) for quadratic model developed for liquid–liquid extraction of methyl red dye using benzene. From the ANOVA table, it is evident that the models were significant with high F -values of 5.83, 5.80 and 191.6 for percentage dye removal, distribution coefficient, and solvent capacity, respectively, and low p -values of <0.05 . ANOVA shows difference in significance of model terms for solvent capacity than percentage dye removal and distribution coefficient. For percentage removal and distribution coefficient, interactive terms and quadratic terms involving dye concentration in feed and dye solution to solvent ratio were not significant with p -values >0.05 . But, for solvent capacity, an interactive term involving dye concentration in feed and extraction time was not significant with p -value >0.05 . All the remaining terms are significant with p -value <0.05 . This means that linear terms are contributing more to the maximizing the responses. Also, it is evident that standard deviation of response values is 0.5029 which is less than $\pm 5\%$. Coefficient of variance (C.V.) of 6.25% implied that the experimental values are in accordance with the predicted values.

Table 4 shows the statistical significance for response factors for liquid–liquid extraction of methyl red dye using benzene. The deviation between experimental and predicted values were studied through standard deviation, coefficient of variation, determination coefficient (R^2), adjusted and predicted R^2 , PRESS, AICc and BIC.

Standard deviation, coefficient of variation, determination coefficient (R^2), difference between adjusted and predicted R^2 are used as model fitting parameters for response factors. They should be $<10\%$, between 5 and 10, >0.8 and <0.2 , respectively. PRESS, BIC and AICc are used as model comparison parameters for dependent variables. They should be minimum, maximum and minimum, respectively,

for statistical significance. Table 4 shows that all the criteria were satisfied by the models.

Effect of process parameters on percentage dye removal

Figure 1a shows the 3D interactive effect between dye concentration in feed and extraction time on percentage dye removal at constant dye solution to solvent ratio. The interactive effect was studied by varying dye concentration in feed from 20 to 100 ppm and extraction time from 10 to 30 min at dye solution to solvent ratio of 2 mL/mL. The dye removal of 46.28% was obtained at the lowest dye concentration in feed and extraction time of 20 ppm and 10 min, respectively. From this point, when the dye concentration in feed increased to 100 ppm, the dye removal enhanced to 48%.

Similarly, the dye removal increased to 80.57% at the dye concentration in feed and extraction time of 20 ppm and 30 min, respectively. The dye removal decreased to 57.42% when the dye concentration in feed further increased to 100 ppm at the extraction time and dye solution and solvent ratio of 30 min and 2 mL/mL. Also, the dye removal of 67.71% was obtained at extraction time of 20 min at the dye concentration in feed of 60 ppm. From the interactive effect between dye concentration in feed and extraction time at constant dye solution to solvent ratio, the optimal conditions were found to be dye concentration in feed and extraction time of 20 ppm and 30 min, respectively, to obtain dye removal of 80.57%.

Figure 1b shows the 3D interactive effect between dye concentration in feed and dye solution to solvent ratio on percentage dye removal at constant extraction time. The interactive effect was studied by varying dye concentration in feed from 20 to 100 ppm and dye solution to solvent ratio from 1 to 3 mL/mL at extraction time of 20 min. The dye removal of 69.42% was obtained at the lowest dye concentration in feed and dye solution to solvent ratio of 20 ppm and 1 mL/mL, respectively. From this point, when the dye

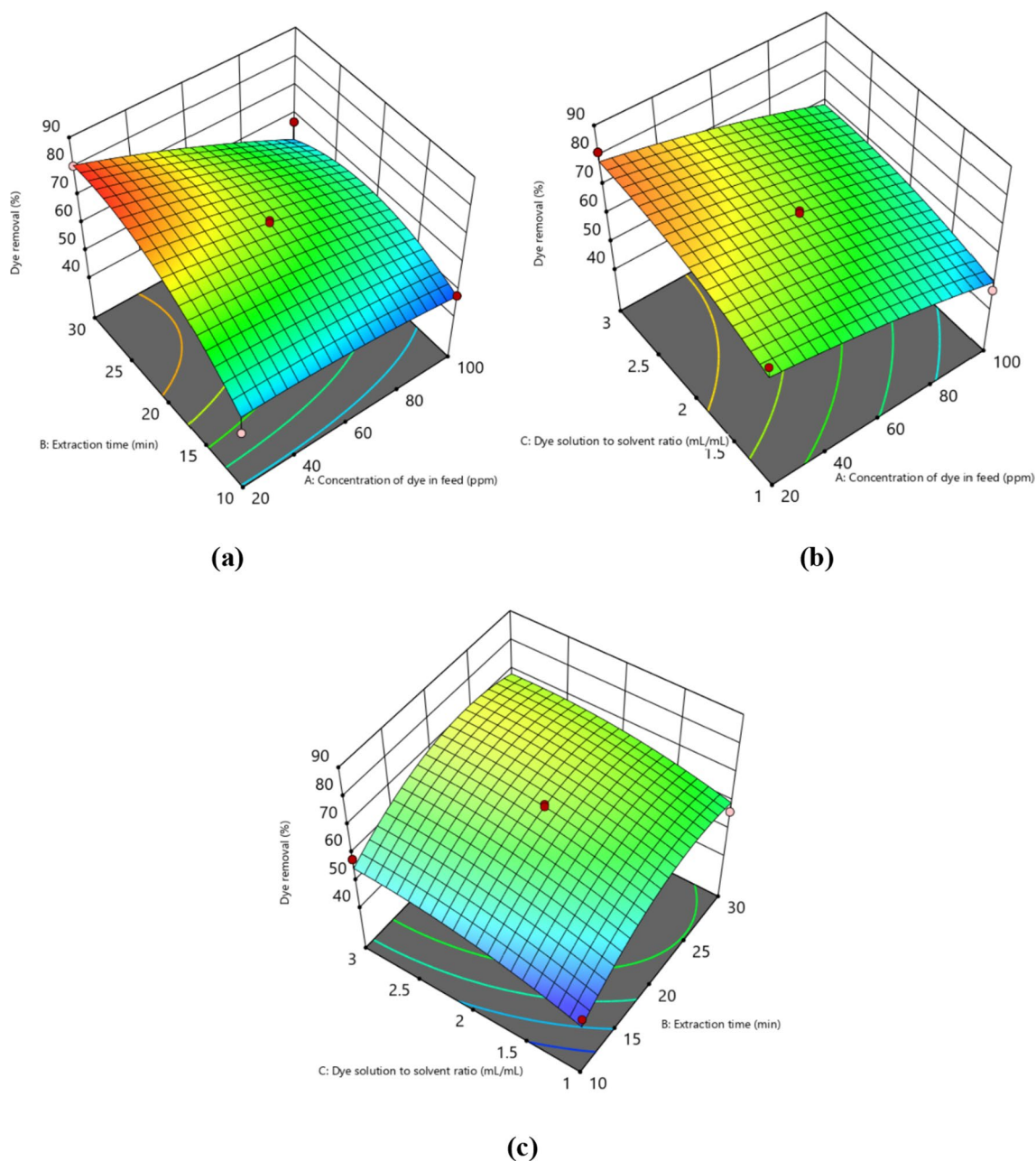


Fig. 1 Interactive effect of **a** dye concentration in feed and extraction time, **b** dye concentration in feed and dye solution to solvent ratio and **c** extraction time and dye solution to solvent ratio on percentage dye removal for liquid–liquid extraction of methyl red dye using benzene

concentration in feed increased to 100 ppm, the dye removal decreased to 47.14%.

Similarly, the dye removal increased to 81.42% at the dye concentration in feed and dye solution to solvent ratio of 20 ppm and 3 mL/mL, respectively. The dye removal decreased to 55.71% when the dye concentration in feed further increased to 100 ppm at the dye solution to solvent ratio and extraction time of 3 mL/mL and 20 min. Also, the dye

removal of 67.71% was obtained at dye solution to solvent ratio of 2 mL/mL at the dye concentration in feed of 60 ppm. From the interactive effect between dye concentration in feed and dye solution to solvent ratio at constant extraction time, the optimal conditions were found to be dye concentration in feed and dye solution to solvent ratio of 20 ppm and 3 mL/mL, respectively, to obtain dye removal of 81.42%.

Figure 1c shows the 3D interactive effect between extraction time and dye solution to solvent ratio on percentage dye removal at constant dye concentration in feed. The interactive effect was studied by varying extraction time from 10 to 30 min and dye solution to solvent ratio from 1 to 3 mL/mL at dye concentration in feed of 60 ppm. The dye removal of 45.42% was obtained at the lowest extraction time and dye solution to solvent ratio of 10 min and 1 mL/mL, respectively. From this point, when the extraction time increased to 30 min, the dye removal decreased to 56.57%.

Similarly, the dye removal increased to 58.28% at the extraction time and dye solution to solvent ratio of 10 min

and 3 mL/mL, respectively. The dye removal increased to 66% when the extraction time further increased to 30 min at the dye solution to solvent ratio and dye concentration in feed of 3 mL/mL and 60 ppm. Also, the dye removal of 67.71% was obtained at dye solution to solvent ratio of 2 mL/mL at the extraction time of 20 min. From the interactive effect between extraction time and dye solution to solvent ratio at constant dye concentration in feed, the optimal conditions were found to be extraction time and dye solution to solvent ratio of 20 min and 2 mL/mL, respectively, to obtain dye removal of 67.71%.

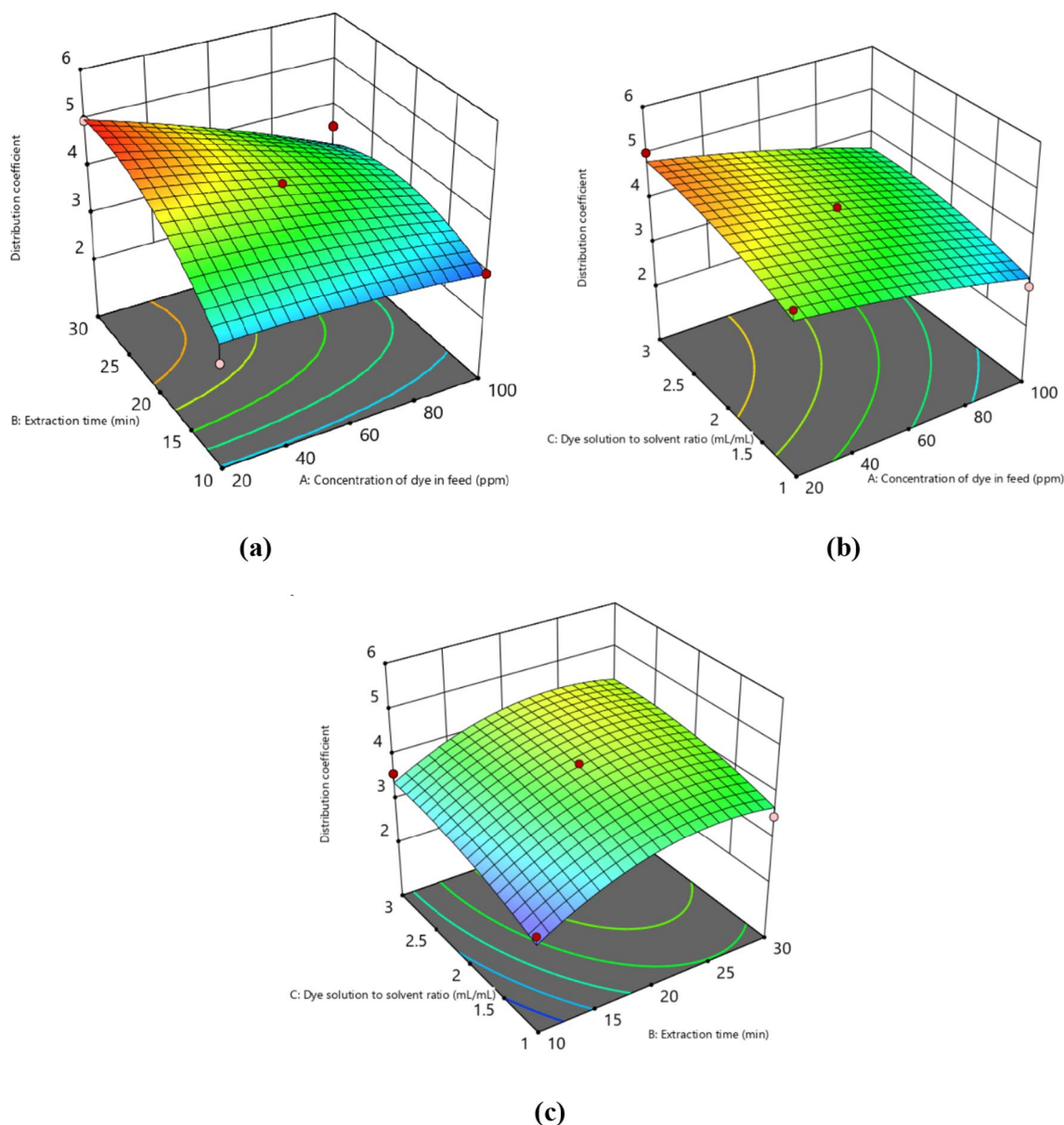


Fig. 2 Interactive effect of **a** dye concentration in feed and extraction time, **b** dye concentration in feed and dye solution to solvent ratio and **c** extraction time and dye solution to solvent ratio on distribution coefficient for liquid–liquid extraction of methyl red dye using benzene

Effect of process parameters on distribution coefficient

Figure 2a shows the 3D interactive effect between dye concentration in feed and extraction time on distribution coefficient at constant dye solution to solvent ratio. The interactive effect was studied by varying dye concentration in feed from 20 to 100 ppm and extraction time from 10 to 30 min at dye solution to solvent ratio of 2 mL/mL. The distribution coefficient of 2.85 was obtained at the lowest dye concentration in feed and extraction time of 20 ppm and 10 min, respectively. From this point, when the dye concentration in feed increased to 100 ppm, the distribution coefficient enhanced to 2.96.

Similarly, the distribution coefficient increased to 4.97 at the dye concentration in feed and extraction time of 20 ppm and 30 min, respectively. The distribution coefficient decreased to 3.54 when the dye concentration in feed further increased to 100 ppm at the extraction time and dye solution and solvent ratio of 30 min and 2 mL/mL. Also, the distribution coefficient of 4.17 was obtained at extraction time of 20 min at the dye concentration in feed of 60 ppm. From the interactive effect between dye concentration in feed and extraction time at constant dye solution to solvent ratio, the optimal conditions were found to be dye concentration in feed and extraction time of 20 ppm and 30 min, respectively, to obtain distribution coefficient of 4.97.

Figure 2b shows the 3D interactive effect between dye concentration in feed and dye solution to solvent ratio on distribution coefficient at constant extraction time. The interactive effect was studied by varying dye concentration in feed from 20 to 100 ppm and dye solution to solvent ratio from 1 to 3 mL/mL at extraction time of 20 min. The distribution coefficient of 4.28 was obtained at the lowest dye concentration in feed and dye solution to solvent ratio of 20 ppm and 1 mL/mL, respectively. From this point, when the dye concentration in feed increased to 100 ppm, the distribution coefficient decreased to 2.90.

Similarly, the distribution coefficient increased to 5.02 at the dye concentration in feed and dye solution to solvent ratio of 20 ppm and 3 mL/mL, respectively. The distribution coefficient decreased to 3.44 when the dye concentration in feed further increased to 100 ppm at the dye solution to solvent ratio and extraction time of 3 mL/mL and 20 min. Also, the distribution coefficient of 4.18 was obtained at dye solution to solvent ratio of 2 mL/mL at the dye concentration in feed of 60 ppm. From the interactive effect between dye concentration in feed and dye solution to solvent ratio at constant extraction time, the optimal conditions were found to be dye concentration in feed and dye solution to solvent ratio of 20 ppm and 3 mL/mL, respectively, to obtain distribution coefficient of 5.02.

Figure 2c shows the 3D interactive effect between extraction time and dye solution to solvent ratio on distribution coefficient at constant dye concentration in feed. The interactive effect was studied by varying extraction time from 10 to 30 min and dye solution to solvent ratio from 1 to 3 mL/mL at dye concentration in feed of 60 ppm. The distribution coefficient of 2.8 was obtained at the lowest extraction time and dye solution to solvent ratio of 10 min and 1 mL/mL, respectively. From this point, when the extraction time increased to 30 min, the distribution coefficient decreased to 3.49.

Similarly, the distribution coefficient increased to 3.59 at the extraction time and dye solution to solvent ratio of 10 min and 3 mL/mL, respectively. The distribution coefficient increased to 4.07 when the extraction time further increased to 30 min at the dye solution to solvent ratio and dye concentration in feed of 3 mL/mL and 60 ppm. Also, the distribution coefficient of 4.17 was obtained at dye solution to solvent ratio of 2 mL/mL at the extraction time of 20 min. From the interactive effect between extraction time and dye solution to solvent ratio at constant dye concentration in feed, the optimal conditions were found to be extraction time and dye solution to solvent ratio of 20 min and 2 mL/mL, respectively to obtain distribution coefficient of 4.17.

Effect of process parameters on solvent capacity

Figure 3a shows the 3D interactive effect between dye concentration in feed and extraction time on solvent capacity at constant dye solution to solvent ratio. The interactive effect was studied by varying dye concentration in feed from 20 to 100 ppm and extraction time from 10 to 30 min at dye solution to solvent ratio of 2 mL/mL. The solvent capacity of 4.62 mg/L was obtained at the lowest dye concentration in feed and extraction time of 20 ppm and 10 min, respectively. From this point, when the dye concentration in feed increased to 100 ppm, the solvent capacity enhanced to 24 mg/L.

Similarly, the solvent capacity decreased to 8.05 mg/L at the dye concentration in feed and extraction time of 20 ppm and 30 min, respectively. The solvent capacity decreased to 2.87 mg/L when the dye concentration in feed further increased to 100 ppm at the extraction time and dye solution and solvent ratio of 30 min and 2 mL/mL. Also, the solvent capacity of 20.31 mg/L was obtained at extraction time of 20 min at the dye concentration in feed of 60 ppm. From the interactive effect between dye concentration in feed and extraction time at constant dye solution to solvent ratio, the optimal conditions were found to be dye concentration in feed and extraction time of 20 ppm and 30 min, respectively, to obtain solvent capacity of 24 mg/L.

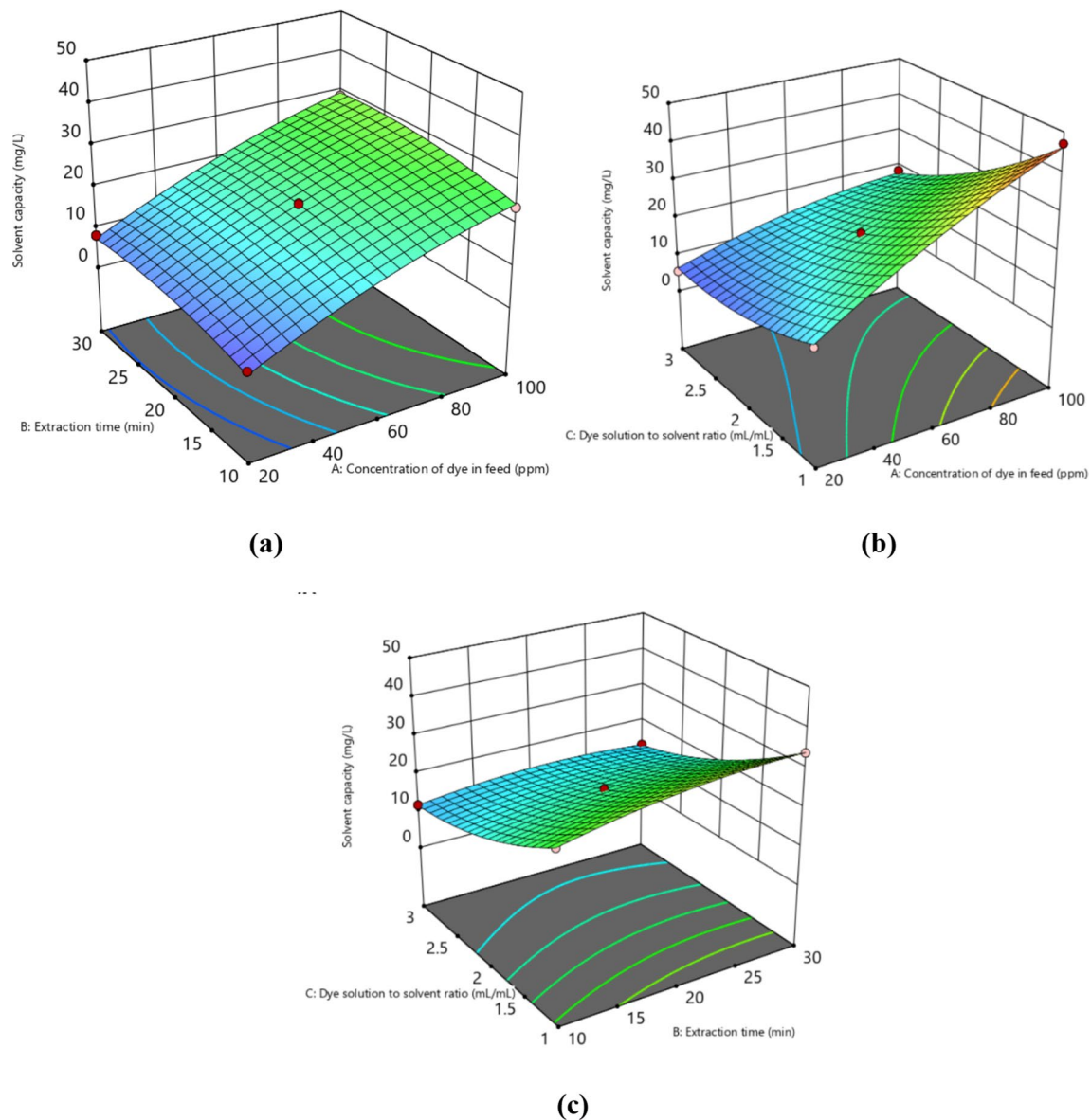


Fig. 3 Interactive effect of **a** dye concentration in feed and extraction time, **b** dye concentration in feed and dye solution to solvent ratio and **c** extraction time and dye solution to solvent ratio on solvent capacity for liquid–liquid extraction of methyl red dye using benzene

Figure 3b shows the 3D interactive effect between dye concentration in feed and dye solution to solvent ratio on solvent capacity at constant extraction time. The interactive effect was studied by varying dye concentration in feed from 20 to 100 ppm and dye solution to solvent ratio from 1 to 3 mL/mL at extraction time of 20 min. The solvent capacity of 13.88 mg/L was obtained at the lowest dye concentration in feed and dye solution to solvent ratio of 20 ppm and 1 mL/mL, respectively. From this point, when the dye concentration in feed increased to 100 ppm, the solvent capacity decreased to 47.14 mg/L.

Similarly, the solvent capacity decreased to 5.42 mg/L at the dye concentration in feed and dye solution to solvent ratio of 20 ppm and 3 mL/mL, respectively. The solvent capacity increased to 18.57 mg/L when the dye concentration in feed further increased to 100 ppm at the dye solution to solvent ratio and extraction time of 3 mL/mL and 20 min. Also, the solvent capacity of 20.31 mg/L was obtained at dye solution to solvent ratio of 2 mL/mL at the dye concentration in feed of 60 ppm. From the interactive effect between dye concentration in feed and dye solution to solvent ratio at constant extraction time, the optimal conditions were found

Table 5 Comparison of liquid–liquid extraction of various dyes using solvents

Dye	Solvent	Outcomes	Reference
Cibacron Red FN-R	Tetrabutylammonium bromide	90–100% removal	Muthuraman et al. (2012)
Astacryl Blue BG and Astacryl Golden Yellow	Salicylic acid with toluene	93–98% removal	Muthuraman (2011)
Golden yellow, Cibacron LSG-HC, Brown ERN, Levafix Red CA and Levafix Scarlet CA dyes	Tetrabutylammonium bromide	95–98% removal	Muthuraman and Teng (2010)
Astacryl golden yellow	Vegetable oils	95% removal	Muthuraman et al. (2009)
Methyl red	Xylene	98% removal and distribution coefficient = 49	Muthuraman and Teng (2009a, b)
Methyl red	Benzene	% removal = 81.28 and distribution coefficient = 40.64	Present study

to be dye concentration in feed and dye solution to solvent ratio of 20 ppm and 3 mL/mL, respectively, to obtain solvent capacity of 20.31 mg/L.

Figure 3c shows the 3D interactive effect between extraction time and dye solution to solvent ratio on solvent capacity at constant dye concentration in feed. The interactive effect was studied by varying extraction time from 10 to 30 min and dye solution to solvent ratio from 1 to 3 mL/mL at dye concentration in feed of 60 ppm. The solvent capacity of 27.25 mg/L was obtained at the lowest extraction time and dye solution to solvent ratio of 10 min and 1 mL/mL, respectively. From this point, when the extraction time increased to 30 min, the solvent capacity decreased to 33.94 mg/L.

Similarly, the solvent capacity decreased to 11.65 mg/L at the extraction time and dye solution to solvent ratio of 10 min and 3 mL/mL, respectively. The solvent capacity increased to 13.2 mg/L when the extraction time further increased to 30 min at the dye solution to solvent ratio and dye concentration in feed of 3 mL/mL and 60 ppm. Also, the solvent capacity of 20.31 mg/L was obtained at dye solution to solvent ratio of 2 mL/mL at the extraction time of 20 min. From the interactive effect between extraction time and dye solution to solvent ratio at constant dye concentration in feed, the optimal conditions were found to be extraction time and dye solution to solvent ratio of 20 min and 2 mL/mL, respectively, to obtain solvent capacity of 20.31 mg/L. Table 5 compares outcomes of liquid–liquid extraction of various dyes on solvents.

Conclusion

The presented work aimed to maximize the percentage dye removal, distribution coefficient and solvent capacity by varying dye concentration in feed (20–100 ppm), extraction time (10–30 min), and dye solution to solvent ratio (1–3 mL/mL) was examined at constant pH and temperature of 3 and

27 ± 2 °C. The optimal values show that the percentage dye removal, distribution coefficient, and solvent capacity of 81.28%, 4.33, and 21.7 mg/L were achieved at dye concentration in feed, extraction time, and dye solution to solvent ratio of 45 ppm, 27 min, and 1.5 mL/mL, respectively. The results showed the best goodness-of-fit between experimental and predicted values by Box–Behnken design. Thus, benzene could be the potential solvent for liquid–liquid extraction of methyl red dye from its aqueous solution.

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Authors contributions Conceptualization was done by PK and SS; methodology was done by PK and SS; software was done by SS; validation was done by PK; formal analysis was done by PK and SS; investigation was done by PK; data curation was done by PK; writing—original draft were done by PK and SS; writing—review and editing were done by PK, SS, and KT; supervision was done by SS; project administration was done by PK and SS.

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