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Extraction of methylene blue from aqueous solution by pickering emulsion liquid membrane using cellulose as eco-friendly emulsifier: optimization and modeling studies

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ABSTRACT

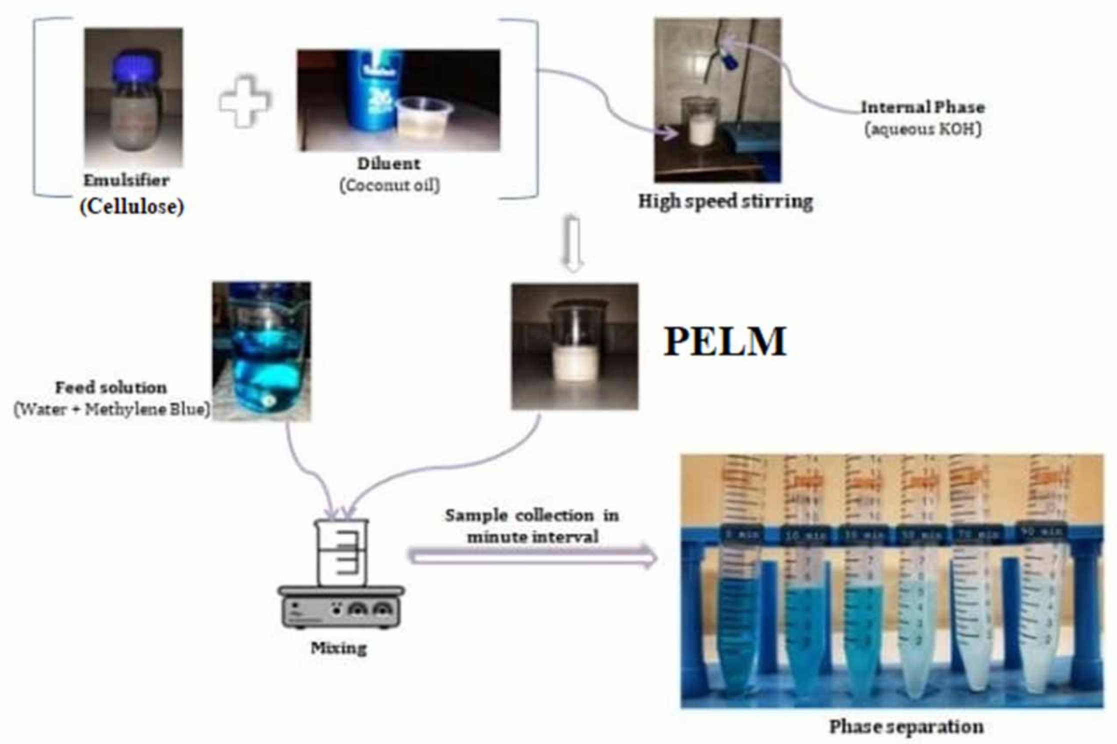
In the present investigation cellulose, a naturally occurring biopolymer, was used as an eco-friendly emulsifier for the removal of methylene blue (MB) from simulated wastewater using emulsion liquid membrane. Coconut oil, a green diluent, was used as an organic phase in preparing a pickering emulsion liquid membrane (PELM) the extraction of dye. The PELM was prepared by loading with aliquat 336 as extractant, potassium hydroxide (KOH) as internal phase, and edible coconut oil as the diluent. The effect of the process parameters such as dye concentration, internal phase concentration, emulsifier concentration, organic phase to aqueous phase (O/A) ratio, stirring speed (RPM) were studied using Box-Behnken design and response surface method. The results showed that more than 92% of MB were successfully extracted around 120 min. Hence, it could be concluded that cellulose can be used as a promising emulsifying agent in the PELM preparation for the removal of MB from wastewater.

Key words: biopolymer, dye, emulsion liquid membrane, extraction, optimization, wastewater

HIGHLIGHTS

- Cellulose was employed as a novel emulsifier in pickering emulsion liquid membrane.
- Green synthesis of pickering emulsion liquid membrane was carried out using coconut oil as diluent.
- Statistical tool was employed for optimization of the parameters.
- At optimum condition a maximum dye removal of 90% was attained.

GRAPHICAL ABSTRACT



INTRODUCTION

The only planet containing life is Earth, and the survival of that life is dependent on a variety of natural circumstances. Water, air, and soil are three of the most important resources for our survival. Water is necessary to sustain life since it provides and forms essential elements for our survival, and water makes up 70% of our bodies. Not only that, but it provided us with the necessary minerals and resources to keep our existence going (Dwivedi 2017). Pollution has become a significant issue in the twenty-first century. These pollutions can be of different forms like water pollution, air pollution, soil pollution, and so on (Mia *et al.* 2019). Water pollution is a serious problem since it can have a direct impact on human health and lifestyle by compromising the availability of potable water and the sanitation process (Schwarzenbach *et al.* 2010). Textile, fabric, cosmetics, leather, paper, food, tannery, and pharmaceutical items consume a lot of dyes, which has a negative impact on water bodies (Slama *et al.* 2021). These textile and garment sectors, which are integral sectors of the economy, are worth of almost a trillion dollars, represent around 7% of global exports, and employ around 35 million people worldwide (Desore & Narula 2018). The textile industry, rough and ready at approximately 108 billion dollars, is likely to achieve a market of 223 billion dollars by 2021 (http://www.ibef.org/industry/textiles.aspx; Accessed: 26.07.2017) as agriculture is contributing nearly 11% of Indian employment of exports (Sarkar *et al.* 2017). It offers direct employment to over 35 million people in India (Hasanuzzaman & Bhar 2016).

Previously, the dyes used to be naturally manufactured, but now the synthetic dyes, which have various colour mediators like direct, reactive, vat, sulfide, azo, acid, and cationic dyes, cause contamination in the effluents discharged from the industries (Chandanshive *et al.* 2017). A series of experiments and research are being conducted for the treatment of such effluents to smoothly dispose of them or to recover and reuse the chemicals and salvage the treated water. The textile effluents have higher chemical oxygen demand (COD), biochemical oxygen demand (BOD), dissolved solids, suspended solids, and other toxic heavy metals because of the presence of the different reaction groups (Hassan *et al.* 2012) in the plants, fishes, microbes, mollusks, and cultured mammalian cells as well (Chandanshive *et al.* 2017). They hamper the water body ecosystem by preventing light from entering the water, causing a reduced rate of photosynthesis and also affecting dissolved oxygen levels, which is an important factor for the entire marine biota (Lellis *et al.* 2019). For the human body, dye toxicity includes the introduction of synthetic substances into the system, causing irritation and aggravation. This ended up causing skin disorders, irritable or blocked noses, sniffling, and aching eyes (Manzoor & Sharma 2019). The dye that is used in industry can be divided into some categories, (Muthuraman & Teng 2009a) like anionic dyes, cationic dyes, direct dyes, reactive dyes, or dispersed dyes (Mohammed *et al.* 2020)

Methylene blue (cationic dye) is a highly soluble, synthetic aromatic azo dye used commonly in the textile and printing industries for different dyeing purposes. It has one or more azo ($-N=N-$) groups and sulfonic (SO_3^-) as functional groups (Sarkar *et al.* 2017). It is used as an indicator and stabilizer in the chemical industry. Even if methylene blue is not very perilous, it shows acute toxicity and can be harmful if a person is exposed to MB and ends up having vomiting, increased heart rate, cyanosis, jaundice, shock, sneezing, and quadriplegia and tissue death in humans (Muthuraman & Teng 2009a).

Hence, for water body treatment, many physical treatment procedures have been studied like crystallization, sedimentation, or gravity separation to remove dyes from wastewater, including conventional methods like reverse osmosis, electrodialysis, solvent extraction, electrolysis, ion exchange, adsorption, etc. (Mohammed *et al.* 2020). There are also many conventional techniques of dye exclusion like physical, chemical, and biological ways to treat wastewater to different degrees. Physico-chemical methods like flocculation/coagulation/precipitation (Verma *et al.* 2012), catalytic and photocatalytic degradation of dye (Chakrabarti & Dutta 2004), adsorption (Crini 2006), U-V photolysis, oxidation, ozonation (Wu & Wang 2001), membrane filtration (Madhura *et al.* 2018), sonolysis techniques, and advanced oxidation processes (AOP) are available to treat contaminated wastewaters. Alternative modes like nano, micro, ultra-filtration, reverse osmosis, and biological methods (Daneshvar *et al.* 2007) are used to remove dye too. But, even though these processes can remove the colour from dye effluents, there are some drawbacks regarding toxicity which complicate the system of removals (Gupta & Suhas 2009). The main disadvantage is the lack of importance on the recovery of bio-hazardous pollutants, which can be upturned but with an additional cost (Kurniawan *et al.* 2006).

As a substitution, researchers are interested in the emulsion liquid membrane (ELM) process (Shokri *et al.* 2020) as this process can isolate these pollutants by isolating them using a phase concept, as this system uses extraction and stripping collectively in one stage (Cahn & Li 1974) and purifies and concentrates the solute in another stage (Ahmad *et al.* 2011; Lu *et al.* 2019). It is a liquid–liquid extraction process that has shown a positive response recovering various acids/bases, metals and dyes (Kusumastuti *et al.* 2018), hydrocarbons, and inorganic species; as the membrane possesses a high interfacial area for mass transfer, it can eliminate substrates selectively and concentrate them by using small amount of organic solvent (Ahmad *et al.* 2011). The ELM technique, being a simple mechanism having speedy extraction, high selectivity, high effectiveness, exclusion, and recovery of the needed species in one step, along with the stability with low energy and the high contact surface, has given it an advantage over other techniques (Kislik 2010).

Emulsions are multi-phasic arrangements having three parts: the oil (organic) phase, the water phase, and the emulsifier. The phases are dispersed into one another in the form of droplets, and the emulsifier (surfactant) plays a major role in stabilizing the emulsion solution. We can either have oil-in-water (O/W) or water-in-oil (W/O) emulsions depending on the dispersed phase we obtain, where the solubility of the emulsifier plays an important role (Ivanova *et al.* 2016). The system follows three steps; firstly, the di-phasic emulsion O/W is prepared by mixing the membrane phase and aqueous internal phase, where the oil droplets are diffused into the water. Second, the feed phase is prepared, which comes in contact between the emulsion and the continuous phase at the interfacial contact, forming a multi-phasic water-in-oil-in-water (W/O/W) system. Finally, the extraction is done by resolving the emulsion and external phases, and then the demulsification step is done by recovering the membrane phase (Hachemaoui *et al*. 2010). In the removal step, the dye of our desire is passed on through the difference in the concentration of the external feed phase and the internal receiving phase. The intermediate oil (organic) phase acts as a membrane by providing resistance. The main disadvantage of this process is the swelling of droplets, which causes breakage of emulsion, hence decreasing the efficiency (Ahmad *et al.* 2011).

In emulsion liquid membrane (ELM), the organic phase (membrane phase) consists of emulsifiers (we used cellulose in our study), normally a low viscous liquid, diluents (oil), and carrier (aliquat 336) in some cases. The properties looked for in a diluent (organic solvent) include non-toxicity, low viscosity, cost-effective, non-caustic properties, and the ability to remove species with high efficiency (Parhi 2013). Coconut oil is an organic oil which is very much available in the southern part of India, making it a cost-effective, non-toxic, viscous liquid compared to other diluents that are normally used like kerosene, heptane, etc. (Shokri *et al.* 2020). The emulsifier (surfactant) stabilizes the receiver phase and is discrete in the membrane phase, forming fine droplets which later form small globules in the feed phase (Zaheri & Davarkhah 2017). It, being absorbed by the droplet surface, stabilizes the system by forming a protective interfacial layer which prevents the droplets from mixing together and maintains the physicochemical state of emulsion droplets. The emulsifier (stabilizer) acts as a thickening agent that helps to improve the viscosity of the continuous phase and, as a result, droplet collision and sedimentation velocity decrease (Zembyla *et al.* 2020).

Biopolymers (non-surface active (polysaccharides) or surface-active (proteins)) can also be used as emulsifiers by integrating them into the interfacial region of emulsion droplets by directly adsorbing them into the interface during the process of droplet development and stabilization or by interacting with other emulsifiers or biopolymer layers already present at the interface (Zembyla *et al.* 2020). These polymers are non-toxic, economical, and stable in nature. In the pickering emulsion liquid membrane (PELM) system, they increase the stability of emulsion by slowing down droplet movement by escalating the viscosity of the liquid membrane (continuous) phase. Not only that, the polymers also decrease the surface tension by forming a fine film coating around the oil droplets individually and causes the reduction of coalescence and hence the rate of creaming (Maphosa & Jideani 2018).

Mostly, all the experiments that have been conducted until now have used chemically synthesized surfactants. Even though these surfactants show positive results over dye removal, they can be toxic or cause an adverse effect on nature or on the human body. Bio-surfactants are based on renewable materials, can be easily degraded, show low toxicity, and are relatively stable under a wide range of physiochemical environments. Cellulose is one of the most abundant biopolymers in nature, which makes it relatively cost-effective and makes the entire extraction process green.

To date, no work has been reported using cellulose biopolymer as an eco-friendly emulsifying agent in stabilizing the PELM. Interestingly, several researchers have demonstrated the ability of cellulose particles to self-assemble at oil–water interfaces and stabilize o/w emulsions without the aid of surfactants. So, it is believed that the amphiphilic character of cellulose resides in its crystalline organization at the elementary brick level, and cellulose nanocrystals thus have both hydrophilic and hydrophobic edges that are preferentially wetted by water and oil phases, respectively. Therefore, the present study is to investigate the extraction of MB from aqueous solution using cellulose as an eco-friendly emulsifying agent. Box–Behnken experimental design was employed for the optimization of important operational parameters during the extraction process.

Many revisions have been conducted using different methods of experimental designs optimized to study the conditions to get the most screening efficiency by optimizing the effective parameters. For this reason, the screening design is done using the Box–Behnken design model to determine important parameters and their most favourable values.

MATERIALS AND METHODS

Reagents and chemicals

Potassium hydroxide (KOH) was obtained from HiMedia Laboratory Pvt. Ltd, Nashik, India. Aliquat 336, 88% (tricaprylylmethylammonium chloride) was bought from Sisco Research Laboratory Pvt. Ltd, Maharashtra, India. Glacial acetic acid was obtained from Thermo Fisher Scientific. Cellulose (purified) was procured from Kemphasol, Mumbai and methylene blue from Finar Limited, Ahmedabad, India respectively. Methanol was obtained from Merck. All the chemicals were used without further treatment. The coconut oil is purchased from a local shop.

Preparation of cellulose solution

2 g cellulose was added into 20 mL of 85 wt% phosphoric acid which was cooled at 5 °C, and the solution was kept stirring for 12 h until the cellulose was completely dissolved (Alves *et al.* 2016).

Preparation of feed solution

Methylene blue (MB) was used as the model dye for the experiment. The stock solution of 1 mg/mL was prepared by dissolving 0.25 g of dye in 250 mL of distilled water. The trial solutions (50 mL) for experiments of different concentrations were prepared by diluting the stock solution. The maximum absorbance of MB was to be 660 nm.

PELM preparation

20 mL of coconut oil was and added along with 5% aliquat 336 and different concentration of the emulsifier (cellulose, varied from 0.75 (w/v)%–1.25 (w/v)%) in a glass beaker. The internal phase solution was prepared using KOH at different concentrations in distilled water. The liquid membrane was prepared by adding the internal phase with the help of the burette, drop by drop, keeping the mixture stirred at a fixed rpm to the organic phase containing oil, carrier, and emulsifier. The final

volume was around 45 to 50 mL. The system was stirred for about 20 min to get a white, homogeneous solution, resulting in a stable emulsion.

Dye extraction

Around 50 mL dye (MB)-containing feed solution was put in a beaker and the solution was kept on stirring using a magnetic stirrer, keeping the speed in the range of 200–600 rpm. Around 10 mL (1/5th of feed) of the steady liquid emulsion (milky homogeneous emulsion) was slowly added to the feed solution. Over time, the emulsion liquid slowly began to disperse. At every 10 min interval, samples were drawn and kept in a test tube. The organic phase was unconnected automatically due to the difference in gravity, and the lighter membrane phase was rising as the upper phase. After settlement, emulsion, which is the extract phase, settled on the top and the raffinate was observed in the bottom of the test tube. The lower raffinate phase had a clear solution which was analyzed for the remaining dye as the treated water using the spectrophotometric (UV-VIS spectrophotometer) method at 660 nm wavelength as λmax. The extraction of dye is calculated as,

$$\text{Extraction (\%)} = \frac{(Co - Ct)}{Co} \times 100 \tag{1}$$

where,

Co = the initial dye concentration
Ct = the concentration of dye at time t.

Breakage

The ratio between the volume of internal product phase leaked into the *external feed phase (*V_{leak}*) via splitting* and *the starting volume of the emulsion (*V_e*)* determines emulsion breakage.

$$\text{Breakage} = \frac{V_{leak}}{Ve} * 100 \tag{2}$$

According to the material balance derived from the feed phase pH at any point before or after contact, the *volume (*V_{leak}*)* is computed as (León *et al.* 2017),

$$\mathrm{V_{leak}} = \mathrm{V_f}\frac{10^{\mathrm{pHf,0}} - 10^{\mathrm{pHf,t}}}{10^{\mathrm{pHf,t}} - 10^{\mathrm{pHp,0}}} \tag{3}$$

where,

V_f = the initial feed phase volume,
$pH_{f,0}$ *and* $pH_{f,t}$ = the pH in the feed phase at time 0 and at time t, respectively
$pH_{p,0}$ = the initial pH of in the emulsion

Experimental design

Box–Behnken factorial design

In the study of the removal of dye using PELM, many factors have direct or indirect influence on the efficiency of the removal process. Therefore, Minitab Statistical Software Version 21.1.0 was used to design experiments to decrease the number of experiments to be conducted to optimize the experiment and reduce cost (Shokri *et al.* 2020).

A five-factor Box–Behnken factorial design was considered for optimizing the MB removal. The response surface methodology (RSM) is a compilation of mathematical and statistical practices that models the process and helps to analyse the response because of different parameters of interest, and hence, it is a proper statistical method for studying a variety of factors and their interactions among them by reducing the number of experiments and providing the least error of the experiments (Daraei *et al.* 2019; Shokri *et al.* 2020; Sujatha & Rajasimman 2021). Box–Behnken design model (BBD) is a common practice of factorial designs to understand RSM design (Jerold & Sivasubramanian 2018).

The experimental data with the known parameters planned by BBD were analyzed by the response surface methodology (Nam *et al.* 2018) using Minitab and is fits the following second-order polynomial model (Equation (4)):

$$Y = \beta_0 + \sum_{i=1}^{k} \beta i X i + \sum_{i=1}^{k} \beta ii (Xi)^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta ij XiXj + e_0 \quad (4)$$

where,

Y = the predicted response,
β_0, βi, βii, βij, = coefficients calculated from regression
Xi *and* Xij = independent variables in coded levels
β_0, = constant coefficient,
k, = number of factors (independent variables)
e_0 = model error

Table 1 is used to note the examined levels of each of the affecting parameters.

Artificial neural network

The 46 samples were used for the ANN study using the MATLAB R2022a version. The ANN study was done using an in-build toolbox called 'Neural Network Fitting.' These 46 data sets are separated into training, validation and test sets, arbitrarily, with 70% training, 15% validation and 15% test data ratio (He *et al.* 2019).

It has been found out that, a neural network with three layers – input layer, hidden layer, and output layer can work as a continuous function on a non-unbounded region. In this three layer neural network, five inputs have been used: emulsifier conc., KOH conc., dye conc., O/A, and RPM and the removal % is used as output. The neuron number of the hidden layer was determined using the equation,

$$N_{hid} = 2N_{in} + 1 \quad (5)$$

where,

N_{hid} = the number of hidden neurons
N_{in} = the number of input neurons

Thus, a 5–11–1 artificial neural network arrangement has been used for the study.

RESULT AND DISCUSSION

Extraction mechanism

In the ELM, the dye molecules are transported from the external feed phase to the internal stripping phase through the liquid organic phase with or without the help of a carrier. The dye must be suspended in the oil membrane and pass through to enter into the internal phase. If the dye is not able to pass through, then a carrier molecule can be used. This should be in charge of the passing of the molecule through the membrane by binding with the dye particles.

Table 1 | The affecting parameters and the examined levels for each parameter

Parameter	Unit	Lower limit	Upper limit
Dye conc.	PPM	5	10
Internal phase conc.	M	0.6	1
Cellulose conc.	% (w/v)	0.75	1.25
O/A[a]	–	1	5
RPM	–	200	600

[a]Organic phase to aqueous phase ratio.

Coconut oil is an efficient membrane along with the carrier aliquat 336 to transport the MB dye molecules across the membrane towards the stripping phase and hence the removal of unwanted dye by the liquid–liquid extraction process (Muthuraman & Teng 2009b).

Design of experiments

The five factors that influence the extraction processes were identified and a series of experiments were conducted to optimize the five parameters, such as emulsifier conc. (A), KOH conc. (B), dye conc. (C), O/A (D) and RPM (E). These experiments ran according to the design of the Box–Behnken experimental model for the removal of MB using cellulose. These particular factors and their levels are shown in Table 2.

Screening of parameters

From Figures 1 and 2, the Pareto chart and normality chart with ($\alpha = 0.05$) 95% confidence, we can conclude (from Figure 1) that the volume ratio of organic to the aqueous phase (O/A), emulsifier concentration, internal phase concentration, and dye

Table 2 | The levels of studied affecting parameters

Parameter	Unit	Factor code	Level of factors Low (−1)	Mid (0)	High (+1)
Cellulose concentration	w/v, %	A	0.75	1.0	1.25
KOH (internal phase) concentration	M	B	0.6	0.8	1.0
Methylene blue (dye) concentration	Ppm	C	5	7.5	10
Volume ratio of organic to aqueous phase (O/A)	–	D	1	3	5
RPM	–	E	200	400	600

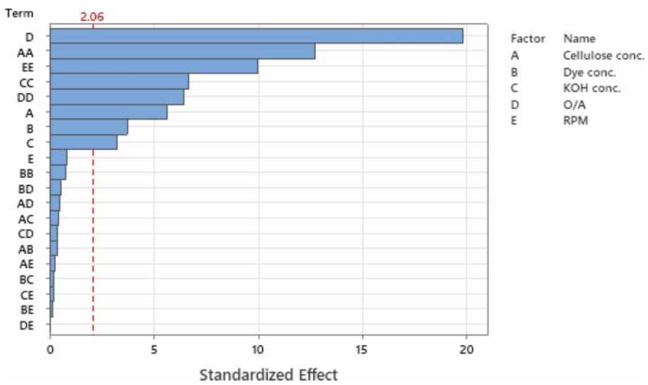


Figure 1 | Pareto chart for screening of parameters in removal (%) of methylene blue from feed by PELM process.

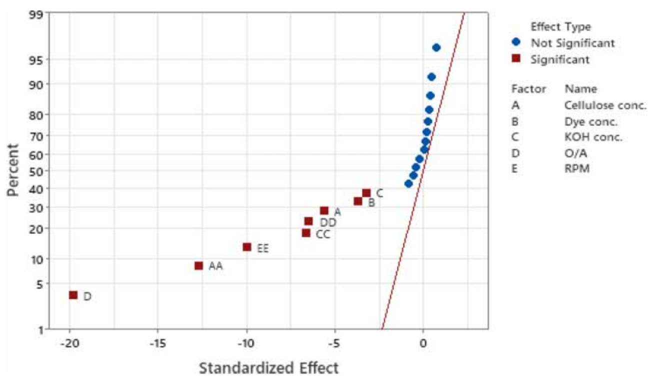


Figure 2 | Normality plot of standardized effect for the parameters in removal (%) of methylene blue from by PELM process.

concentration in the feed were the more important parameters compared, which affected MB removal percentage. From the normal plot (from Figure 2), the three mentioned parameters are far from the linear axis, which shows the significance of removing the dye. The order of weightage of parameters to influence the result is noted from these plots as volume ratio of organic to aqueous phase (O/A)> surfactant concentration > internal phase concentration > dye concentration in feed > stirring speed (RPM) (Sujatha & Rajasimman 2021).

From the main plots observed in Figure 3, it can be stated that emulsion concentration, internal phase concentration, dye concentration/feed phase concentration, and stirring speed have a balanced contrast effect, which shows a positive effect to a point, and then the removal rate decreases. The dye concentration/feed phase concentration was less significant in the level measured for the dye removal process compared to the internal phase concentration and stirring speed, which had a more prominent effect on dye removal. And, with an increase in dye concentration, the removal rate decreases.

The volume ratio of the organic to the aqueous phase (O/A) was an imperative parameter for the PELM process. Hence, an emulsion droplet has a comparably larger surface area, so it can be said that it can extract dye molecules from a comparably larger volume of feed solution. The volume ratio of the organic to the aqueous phase (O/A) has effects on the dye extraction process, enhancing the stability of droplets and emulsion structure (Dâas & Hamdaoui 2010). From the main effect plots, it can be concluded that an increase in O/A ratio from 1 to 5 decreases the extraction process rate, as the resistance for the dye to pass through the organic membrane increases. The O/A ratio showed the most considerable effect on dye extraction in contrast to all other parameters.

Statistical analysis

Using the Box–Behnken experimental model for the removal of MB, different groupings of the factors (emulsifier conc. (A), KOH conc. (B), dye conc. (C), O/A (D) and RPM (E)) are done and the obtained results are shown in Table 3. Table 3

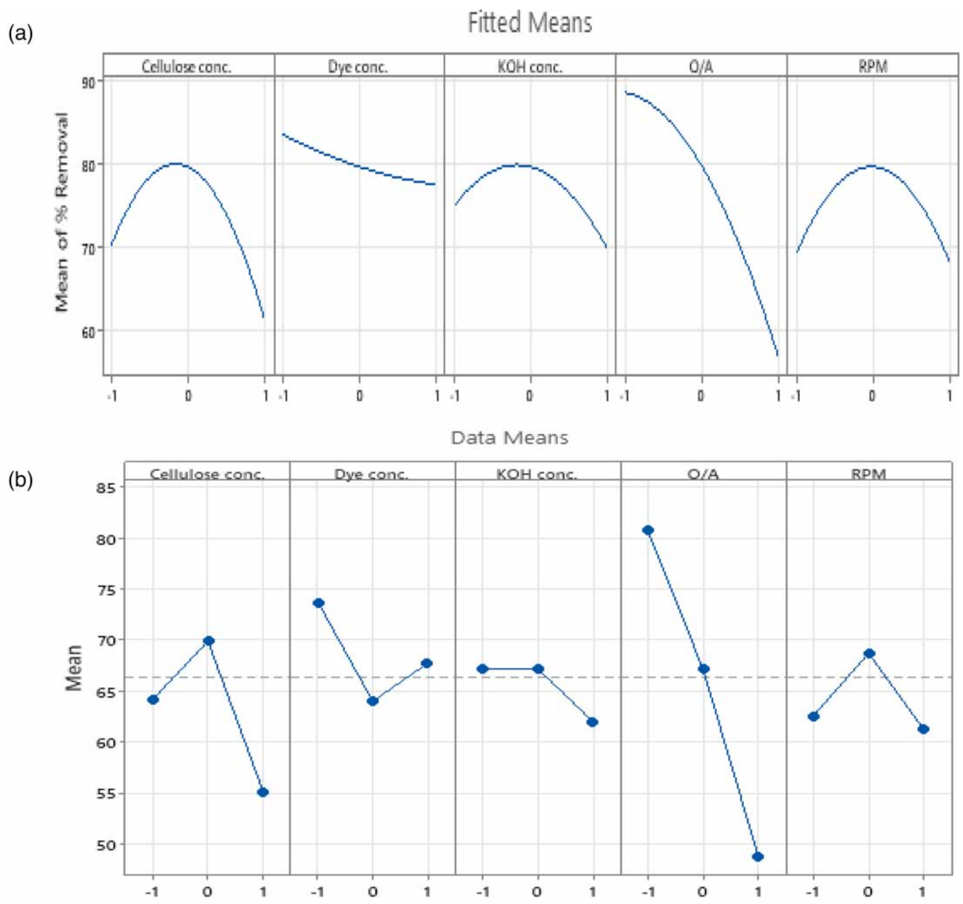


Figure 3 | Main effect plot for methylene blue removal based on (a) fitted means and (b) data means.

Table 3 | The statistical results of the BBD for methylene blue extraction using cellulose as surfactant by pickering emulsion liquid membrane process

St No.	Cellulose concentration	KOH (internal phase) concentration	Methylene blue (dye) concentration	Volume ratio of organic to aqueous phase (O/A)	RPM	% removal (Y)
1	1.25	0.8	7.5	1	400	68.709
2	1.0	0.6	7.5	5	400	52.225
3	1.25	0.8	7.5	5	400	41.361
4	1.0	1.0	7.5	3	200	59.097
5	1.0	1.0	7.5	1	400	72.36
6	1.0	0.8	10	3	200	64.928
7	1.0	0.8	7.5	3	400	79.613
8	0.75	0.8	7.5	3	600	56.516
9	1.0	0.6	7.5	3	200	65.161
10	1.0	0.8	7.5	5	200	45.157
11	1.0	0.8	10	3	600	64.568
12	1.0	0.8	7.5	3	400	79.613
13	1.0	1.0	7.5	3	600	57.161
14	1.25	0.8	7.5	3	600	45.29
15	1.25	0.8	10	3	400	63.309
16	0.75	0.8	5	3	400	70.261
17	1.0	0.6	10	3	400	72.662
18	1.0	0.8	7.5	5	600	44.503
19	1.0	0.8	10	5	400	52.516
20	1.0	0.8	10	1	400	87.455
21	1.0	0.8	7.5	3	400	79.613
22	1.25	1.0	7.5	3	400	53.806
23	0.75	0.8	7.5	5	400	48.298
24	1.0	0.8	5	1	400	92.049
25	1.25	0.8	7.5	3	200	46.839
26	1.0	1.0	10	3	400	69.065
27	1.0	1.0	7.5	5	400	45.942
28	1.0	1.0	5	3	400	72.869
29	1.0	0.6	5	3	400	77.739
30	1.25	0.8	5	3	400	64.174
31	0.75	0.6	7.5	3	400	66.968
32	0.75	0.8	10	3	400	67.176
33	1.0	0.8	7.5	3	400	79.613
34	1.25	0.6	7.5	3	400	57.677
35	1.0	0.6	7.5	3	600	64.387
36	0.75	0.8	7.5	3	200	59.742
37	1.0	0.8	5	3	200	76.522
38	1.0	0.8	7.5	3	400	79.613
39	1.0	0.8	5	3	600	75.304
40	1.0	0.8	7.5	1	600	82.269
41	1.0	0.8	7.5	1	200	83.181

(*Continued.*)

Table 3 | Continued

St No.	Cellulose concentration	KOH (internal phase) concentration	Methylene blue (dye) concentration	Volume ratio of organic to aqueous phase (O/A)	RPM	% removal (Y)
42	1.0	0.8	5	5	400	60.688
43	0.75	0.8	7.5	1	400	78.748
44	0.75	1.0	7.5	3	400	65.935
45	1.0	0.6	7.5	1	400	81.095
46	1.0	0.8	7.5	3	400	79.613

summarizes the experimental runs for tentative dye removal using PELM, showing the extraction results. The results were evaluated by ANOVA using the same software.

For the regression analysis, the coefficients of Equation (4) were obtained.

The final form of the second-order polynomial model for dye extraction could be presented as follows:

$$\begin{aligned} Y =& 79.61 - 4.530\,A - 2.995\,C - 2.605\,B - 15.948\,D - 0.664\,E - 13.86A{*}A + 0.85\,C{*}C \\ &- 7.25\,B{*}B - 7.05\,D{*}D - 10.87\,E{*}E + 0.55\,A{*}C - 0.71\,A{*}B + 0.78\,A{*}D + 0.42A{*}E \\ &+ 0.32\,C{*}B - 0.89\,C{*}D + 0.21C{*}E + 0.61B{*}D - 0.29B{*}E + 0.06D{*}E \end{aligned} \tag{6}$$

where,

Y = removal efficiency of removal percentage of methylene using PELM
A = Emulsifier concentration
B = KOH concentration in internal phase solution
C = methylene blue solution concentration
D = O/A ratio
E = stirring speed, RPM

Effect of the main parameters

The observed dye extraction percentage, the impact of the key parameters on dye extraction effectiveness, and the interaction of the influencing parameters are all shown in Figure 4.

The percentage of dye removal and the effects of the different process parameters can both be seen in Figure 4 and can be inferred to interact with one another and have an impact on the removal percentage. According to the interaction plot, the removal rate increases until a certain point, at which point the balance between the effects of the emulsion concentration, internal phase concentration, dye concentration, and stirring speed decreases. The internal phase concentration and stirring speed, which had a more significant impact on dye removal, were more significant factors in the dye removal process than the dye concentration. Furthermore, the removal rate decreases as dye concentrations rise. It is evident that more extraction occurs when the stirring speed is increased from 200 to 400 RPM. The extraction rate, however, falls as the increase continues. The reason for this is that even though smaller, more surface-area-rich droplets are formed at higher speeds, which should result in positive mass transfer, efficiency still declines because high speed also adversely affects the constancy of the emulsion droplets and eventually leads to breakage. Up to a certain concentration, the extraction rate also increases as the dye concentration in the feed increases.

When the KOH concentration is between 0.6 and 0.8 M, there is a high dye removal. The extraction procedure is slowed down by a further increase in KOH concentration to 1.0 M. This could be a result of too much KOH causing the emulsion's droplets to swell, which in turn causes the liquid membrane to degrade.

The O/A ratio is crucial to the PELM process because, in addition to slowing down the extraction rate, it also affects how the emulsion droplet's structure changes (Dâas & Hamdaoui 2010). The extraction rate drops and dye transfer stops as the O/A ratio rises from 1 to 5, which may be due to the emulsion's increased viscosity, which causes the internal phase droplets to

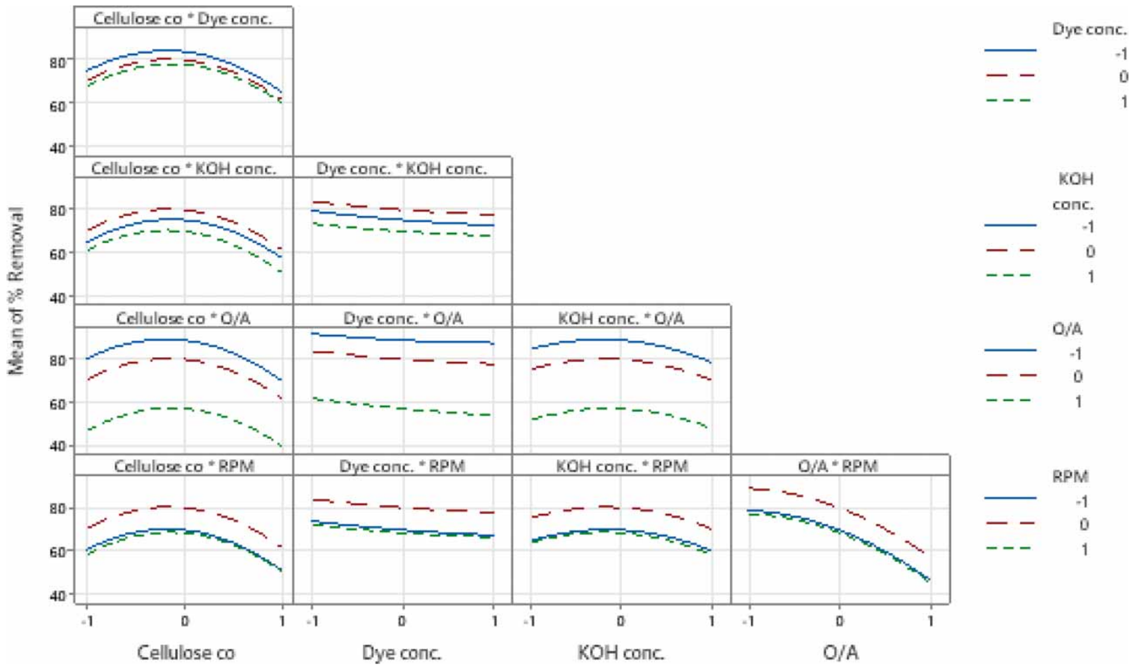


Figure 4 | Plot of main effects and their interactions vs. dye extraction (%).

swell. The amount of dye transported to the stripping phase is consequently reduced as the thickness of the droplets thickens and the contact area between the feed and the emulsion decreases (Daraei *et al.* 2019).

Box–behnken statistical analysis

The result ANOVA shown in the above Table 4 implies the effect of individual parameters and their interactions, and this model also investigates the relationship between the response values and one or more independent variables. The ANOVA model also takes into account the possible effects of the parameters and if the data sets are feasible or not (Sujatha & Rajasimman 2021).

Low probability (<0.05) and high F values signify the precision of the model. From Table 4, it is noted that the Model F-value of 35.41 is significant and values of '*P*' less than 0.05 implement the importance of terms. In this case, the linear effects of A, B, C, and D and square effects of A*A, B*B, D*D, and E*E were found to be effective for dye removal using the PELM process. A high R-sq value of 0.9659 (96.59%) gives us an idea about the legitimacy of the model foretold by BBD for dye removal (Daraei *et al.* 2019).

The R-sq = 0.9659 (96.59%) means 96.59% of the variations for dye removal percentage can be clarified by the independent variables. Theoretically, the difference between values of the adjusted R2 and predicted R2 must be less than 0.2 for the model to be acceptable (Mourabet *et al.* 2011). If they are not, there may be a problem with either the data or the model. From Table 5 it can be observed that the predicted R-sq for dye extraction% is 0.8636 (86.36%), and the adjusted R-sq is 0.9659 (96.59%). Hence, it can be concluded that the model has high precision and is approved by the earlier studies conducted (Mesli & Belkhouche 2018).

Response surface plot and contour plot

The contour and 3D surface plots are shown in Figures 5–8 and illustrate how the efficiency of the removing dye can be affected by altering two variables where the third factor is kept constant at the central point characterized by the software. According to Figures 5 and 6, the highest percentage of dye removal was achieved using 1.0 (w/v) % of cellulose. Any concentration lower or higher makes the emulsion droplets unstable and, hence, the extraction percentage decreases.

Figures 5 and 7 demonstrate that with the rise of KOH from 0.6 to 0.8 M, the rate of removal enhances. At concentrations of more than 0.8 M, it causes the swelling of the globules and instability of the emulsion system, and the extraction rate decreases.

Table 4 | Analysis of variance (ANOVA) for response surface quadratic model

Source	DF	Adj sum of square	Adj mean square	F-Value	*P*-Value
Model	20	7,345.91	367.30	35.41	0.000
Linear	5	4,657.19	931.44	89.80	0.000
A	1	328.33	328.33	31.65	0.000
B	1	108.57	108.57	10.47	0.003
C	1	143.56	143.56	13.84	0.001
D	1	4,069.67	4,069.67	392.34	0.000
E	1	7.06	7.06	0.68	0.417
Square	5	2,676.72	535.34	51.61	0.000
A*A	1	1,676.04	1,676.04	161.58	0.000
B*B	1	458.27	458.27	44.18	0.000
C*C	1	6.28	6.28	0.61	0.444
D*D	1	433.25	433.25	41.77	0.000
E*E	1	1,031.84	1,031.84	99.48	0.000
2-Way Interaction	10	12.00	1.20	0.12	0.999
A*C	1	1.23	1.23	0.12	0.733
A*B	1	2.01	2.01	0.19	0.663
A*D	1	2.41	2.41	0.23	0.634
A*E	1	0.70	0.70	0.07	0.797
C*B	1	0.41	0.41	0.04	0.845
C*D	1	3.20	3.20	0.31	0.584
C*E	1	0.18	0.18	0.02	0.895
B*D	1	1.50	1.50	0.14	0.707
B*E	1	0.34	0.34	0.03	0.858
D*E	1	0.02	0.02	0.00	0.968
Error	25	259.32	10.37		
Lack-of-fit	20	259.32	12.97	*	*
Pure error	5	0.00	0.00		
Total	45	7,605.23			

Table 5 | Model summary regarding standard deviation (SD) and coefficient of the model determination (R^2) values

SD	R-sq	R-sq(adj)	R-sq(pred)
3.22068	96.59%	93.86%	86.36%

For the O/A phase ratio, we can see from Figures 6 and 7 that an increase in the O/A ratio shows an adverse effect on removal efficiency. It can be reasoned that in the organic phase the stability of the emulsion droplet increases too much, which causes more confrontation for the dye to pass through, hence showing poor performance (Das *et al.* 2008). Hence, O/A = 1 is used to get a homogeneous emulsion solution that shows the best dye-removing performance.

The optimum values to get the maximum dye removing performance were projected by Minitab software using an in-built optimizer tool, and the result was found in Figure 9. From the figure, the optimum values for maximum dye removal were analysed as follows: cellulose concentration: 0.947 (w/v) %, KOH concentration: 0.753 M, dye concentration: 5 ppm, O/A ratio: 1 and stripping speed: 390 RPM.

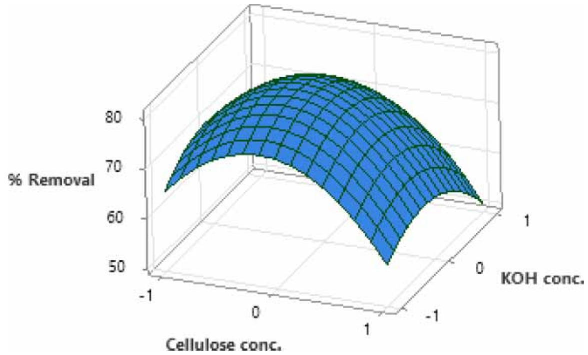


Figure 5 | 3D plot of dye removal showing the effects of cellulose conc. and KOH conc. (A/O ratio = 1; Dye conc. = 0.075 ppm; RPM = 400).

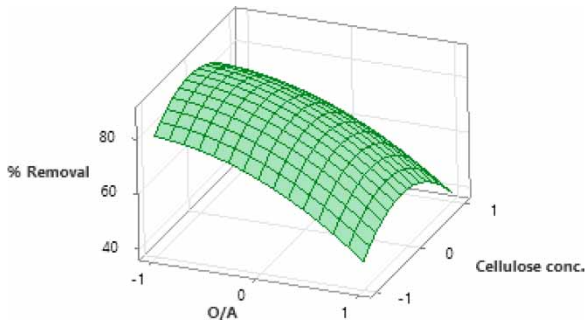


Figure 6 | 3D plot of dye removal showing the effects of cellulose conc. and O/A (KOH conc. = 0.8M; dye conc. = 0.075 PPM; RPM = 400).

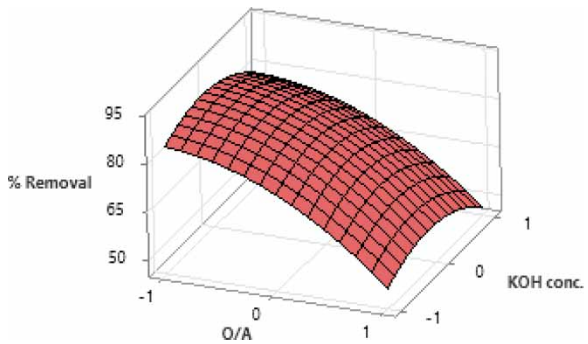


Figure 7 | 3D plot of dye removal showing the effects of O/A and KOH conc. (cellulose conc. = 1.0 (w/v) %; dye conc. = 0.075 ppm; RPM = 400).

Breakage study

From Figure 10, it can be said the emulsion is stable for around 120 min. After that, the emulsion starts to break because of swelling or leakage.

Kinetic study of dye extraction by PELM

To determine the rate constants and applicability of the order, data from dye extraction by the PELM method at the optimal conditions were obtained from the time tests that were conducted. The kinetic study was carried out using the equations below (Gurel & Buyukgungor 2016).

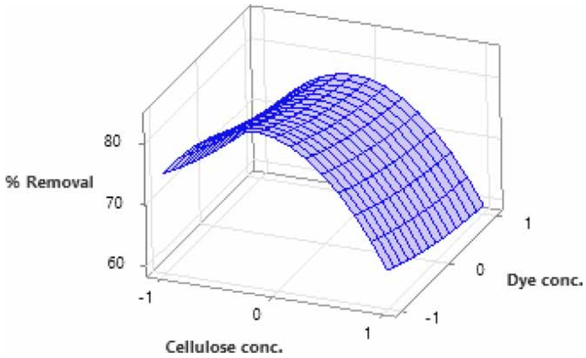


Figure 8 | 3D plot of dye removal showing the effects of dye conc. and cellulose conc. (KOH conc. = 0.8 M; O/A = 1; RPM = 400).

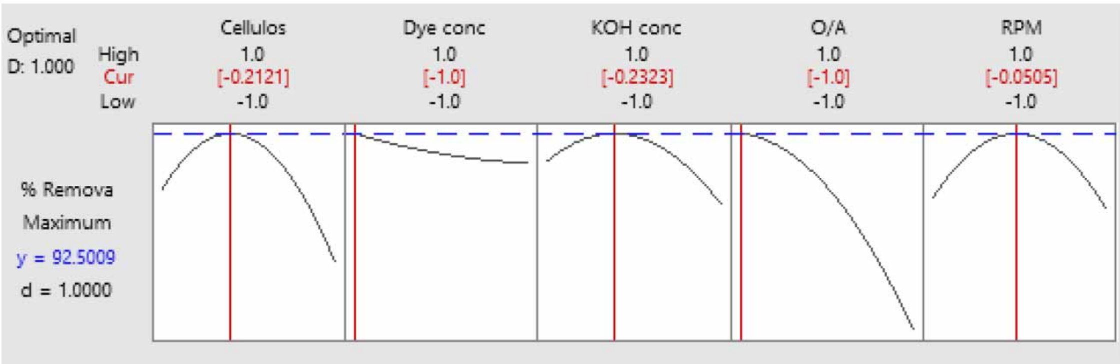


Figure 9 | Optimizer plot for dye removal by PELM process.

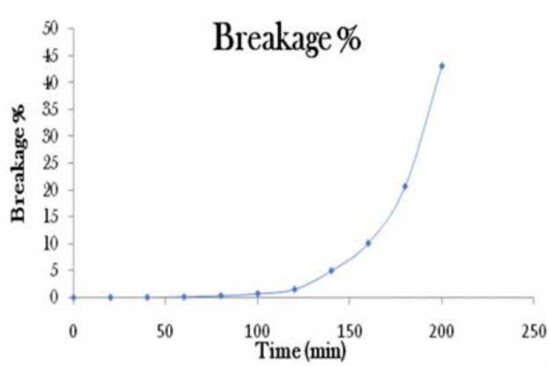


Figure 10 | Breakage of emulsion over time (parameters: cellulose conc. = 1.0 (w/v) %; KOH conc. 0.8 M; speed 400 rpm; dye conc. 10 μg/ml; O/A (vol/vol) = 1).

We know,

The zero order rate equation is,

$$C_t = C_o - kt \tag{7}$$

The first order rate equation is,

$$\ln C_t = \ln C_o - kt \tag{8}$$

The second order rate equation is,

$$(1/C_t) = (1/C_o) + kt \quad (9)$$

where,

C_t = the methylene blue concentration at time t
C_o = the initial methylene blue concentration
t = time
k = reaction rate constant

The kinetic data is tabulated in Table 6. Figure 11(a)–11(c) summarizes the output of the kinetic study using the zero, first, and second reaction models. Table 6 includes the constants which have been calculated as well as the R^2 values. The first-order reaction having the highest R^2 value implies that the extraction process follows the first-order reaction. A uniform percentage of the dye removal per time interval is observed in the first-order kinetics. The amount of dye in the solution determines the rate of disposal. During the PELM process, the proportion of MB varies with time, as shown by the kinetic model curve in Figure 11(b).

According to the kinetic profile in the plot, during the initial stage, the rate of removal of MB from the feed solution was considerable. Then, as the experiment continued, the extraction rate decreased after a certain time and eventually became stable at roughly 70 min, comparable to the optimum dye extraction. A similar kind of result was observed during the recovery of tungsten from printed circuit board recycling unit wastewater by ELM process (Avinash & Prashant 2015) in which the extraction was maximum at initial stage and the kinetic data followed first-order reaction. The transfer of MB from the feed phase was rapid at the initial stage attributed to a high concentration gradient at the early stage of the extraction process (Sujatha & Rajasimman 2021).

Artificial neural network (ANN) study

The artificial neural network (ANN) is a computational model which mimics the neural network of the human brain during data processing. It has a powerful non-linear reflection potential that can properly anticipate the target value, and also a high self-adaptive and self-learning ability; and also it is a multi-layered linear neural network having great non-linear prediction ability, computational efficiency, and low latency, and is now the most commonly accepted method. As a result, it's normally employed in technological methods for non-linear applications and approximations.

The Levenberg–Marquardt algorithm is used for the regression analysis as this algorithm is fast and precise and the resulting network will have better stability.

Figure 12(a)–12(d) show the correlation coefficient R of the regression plot of expected output and the network prediction outputs from the training data set, validation data set, test data set, and overall data set. The dotted line at 45° in the plots corresponds to an ideal case, R = 1, which means calculated outputs = targets (Y = T). These scatter plots show how the data points are from the dotted line and correspond to outliers. The solid coloured line stands for the finest linear fit of regression between the outputs and targeted values (He *et al.* 2019).

The R-value is an important suggestion of the relation between the calculated output values and target values. In the regression plots, the closer the value of R is to 1, the higher the accuracy of the model (Angelo 2015).

Figure 12(a)–12(d) provides an idea about the R values for the training data set, validation data set, test data set, and overall data set are 0.99977, 0.96005. 0.96725 and 0.98702, respectively. MATLAB neural network fitting toolbox proposes that

Table 6 | Data from the kinetic analysis

Order of reaction	R^2 value	Rate constant value
Zero order	0.869	0.162 sec – 1
First order	0.925	0.034 (Mol sec) – 1
Second order	0.681	0.012 (Mol/sec)

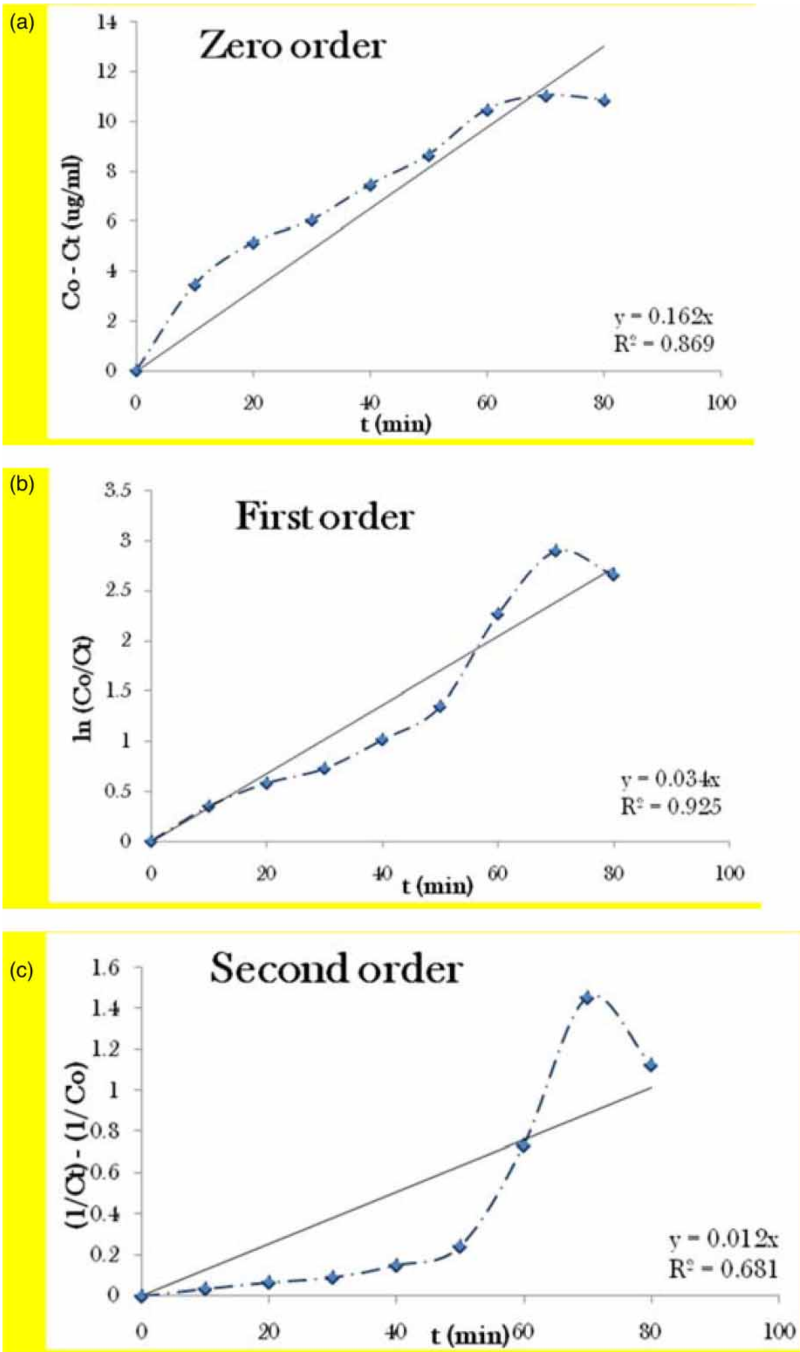


Figure 11 | (a) Zero order; (b) first order; and (c) second order.

R-value greater than 0.9, gives the acceptance of the model. Hence, it can be said that these artificial neural network models can be used to forecast extraction sufficiency and validation with a high degree of generalization without overfitting.

CONCLUSION

The PELM is a recent concept using an emulsifying agent introduced to treat a sample wastewater body by dissolving methylene blue in the water. A series of experiments were conducted using the Box–Behnken design method to study the efficiency of different parameters on dye extraction and optimize those data of varying parameters to achieve the highest dye removal.

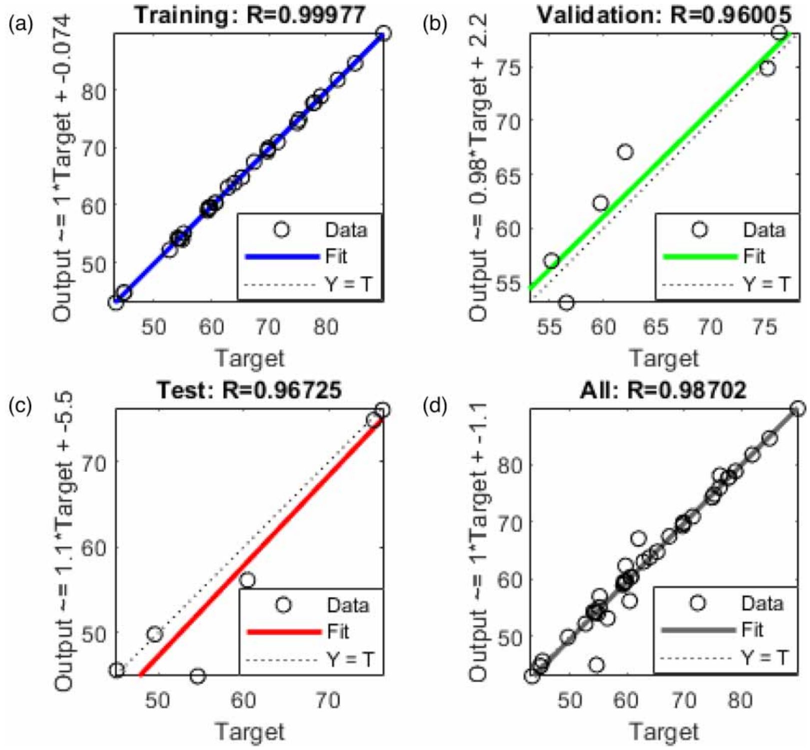


Figure 12 | Correlation coefficient R: (a) training data set, (b) validation data set, (c) test data set, and (d) overall data set.

Their interaction and optimization curves are studied to attain the best possible values of each parameter to get the highest dye removal. The model recommended 0. 947 (w/v) % cellulose concentrations, 0.753 M KOH concentration as internal phase and equal amounts of organic and aqueous phase (O/A ratio) PELM and feed solution containing 5 ppm MB to reach the highest (92.50%) dye removal. The breakage is less than 2% when the extraction time is less than 120 min. The extraction process is validated by the ANN model. From these results, we can say that coconut oil is non-toxic, biodegradable, cost-effective and easily available and cellulose, an easily available biopolymer an emulsifier to remove dye from water. For this study, different bio, edible or waste oil can also be used along with different biopolymers.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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