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Recovery of methylene blue from aqueous solution by liquid–liquid extraction

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ABSTRACT

The aim of this study is the removal and recovery of methylene blue (MB) from wastewater. MB is one of the most commonly used substances for dyeing cotton, wood, and silk. Though MB is not strongly hazardous, it can cause some harmful effects where acute exposure to MB may cause increased heart rate, vomiting, shock, cyanosis, jaundice and quadriplegia and tissue necrosis in human. So, we selected the MB for solvent/liquid–liquid extraction study. MB is the cationic dye, so it requires an anionic carrier for extraction purpose. Salicylic acid acts as an anionic carrier in this study. Removal of MB using salicylic acid in benzene was studied. The efficiency of dye extraction increased with decreasing dye concentration. The extracted dye in the organic phase can be back-extracted into 1 M oxalic acid solutions. The experimental parameters examined were salicylic acid concentration, effects of diluents, effect of pH, effect of initial dye concentration, effect of equilibrium time, aqueous to organic phase ratio, and various stripping agents. Real effluent was also studied under optimized condition and satisfactory result has been found.

Keywords: Extraction; Methylene blue; Wastewater; Salicylic acid; Stripping; Recovery

1. Introduction

Among different pollutants of aquatic ecosystem dyes are a large and important group of chemicals. They are widely used in industries such as textile, paper, rubber, plastic, cosmetic, etc. to color the products. These dyes are invariably left in the industrial waste and consequently discharged mostly to surface water resources. Dyes even in low concentration are visually detected and affect the aquatic life and food web. These colored compounds are not only aesthetically displeasing but also inhibiting sunlight into streams and affecting photosynthetic reaction [1]. Once the dye has contaminated the water, its removal by conventional wastewater treatment method is particularly difficult because many dyes are stable to light and oxidizing agent and are resistant to aerobic biooxidation [2]. More than 700,000 tons of dyes and pigments are produced over the world annually. An estimated 10–20% of dyes used are lost in residual liquors through exhaustion and washing operations [3]. Various industries use different types of organic dyes and dye intermediates. Approximately, 15% of the dyes produced throughout the world are lost during the dyeing process and the resulting wastewater and colored dye effluent pose a major threat to the surrounding ecosystem, unless processed in the correct manner [4]. The most widely used industrial

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dyes are azo dyes, which constitute 60–70% of all produced dyestuffs [5]. Azo dyes are the largest group of dyes used in industry [6]. Various methods have been used to remove dyes from aqueous solutions. The widely used methods include adsorption, coagulation, flocculation, biosorbent, thermolysis, photocatalytic degradation, photocatalytic mineralization, ozone treatment, electro-Fenton's, hypochlorite treatment, and physicochemical combined process and electrocoagulation method is also effective to remove dyes from aqueous solutions [7–24]. The physical methods are non-destructive and merely transfer the pollutants from one medium to another, thus giving secondary treatment [25]. Chemicals methods are not economically viable due to high dosage and production of large quantity of sludge [26–28]. Removal of anionic and cationic organic dyes from aqueous solutions by liquid–liquid extraction (LLE) using reverse micelles was proposed by Pandit and Basu [29] who studied the separation of organic dyes such as methyl orange, methylene blue (MB), cibacrome 4G, and cibacrome 6B from wastewater using CGA. Hexa tetra methyl ammonium bromide and sodium dodecyl benzene sulfonate were used as surfactants for the generation of CGA [30].

Removal of MB by carbon derived from peach stones by H_3PO_4 activation was studied [31]. Separation of MB from aqueous solution by micellar-enhanced ultra filtration was also reported [32]. Photocatalytic degradation of MB was also investigated [33–35]. Various techniques like precipitation, ion-exchange, chemical oxidation, and adsorption have been used for the removal of toxic pollutant from wastewater [36–38]. MB is a common pollutant material in textile wastewater and is frequently used in dye houses and textile industries. The removal of MB from aqueous solutions using low-cost materials (e.g. agricultural wastes) has been investigated by some other researchers [39]. The structure of MB is relatively stable compared with other dyes, so the traditional treatment methods used for dyeing wastewater cannot degrade it effectively, which made it our experimental object [40]. Thus, the removal of MB from industrial effluents has become one of the major environmental concerns. In recent years, much attention has been focused on a separation technique such as solvent extraction or LLE and liquid membrane. LLE is based on the principle that a solute can distribute itself in a certain ratio between immiscible solvents, and the extraction process depends on its mass transfer rate [41]. LLE offers significant advantages in toxicological analysis such as preconcentration of toxic substances, simplicity, low cost, and compatibility with analytical systems. Removal of azo dyes from aqueous solutions using Calix [4] arene and β-cyclodextrin was investigated by LLE [42]. Muthuraman et al. reported the extraction and recovery of MB from industrial wastewater by LLE, using benzoic acid as the extractant. Under optimized conditions, 99% of the dye was extracted from aqueous solutions and the extracted dye in the organic phase was back-extracted into sulphuric acid solutions [43]. Similarly, golden yellow low salt anionic-type dye was extracted and recovered from aqueous solutions by the solvent extraction method using tri-n-butyl phosphate as the carrier. The extracted dye was stripped into 0.01 mol L^{-1} sodium hydroxide solutions and the solvent used was recycled [44]. Thiazine dye, MB, forms 1:1 ion-associate with salicylic acid in aqueous phase and the ion-associate can be extracted in a series of non-polar non-coordinating solvent systems [45].

Salicylic acid is a diprotic acid with pKa value 2.97 and 13.4 in aqueous medium corresponding to the dissociation of carboxylic acid and phenolic groups, respectively [46]. From the electrochemical point of view, this molecule can be considered as a phenol substituted in ortho position [47]. Salicylic acid is sparingly soluble in water and the solution is colorless.

In the presence study, the extraction of a cationic dye namely MB while it makes an ion-pair with salicylic acid in a sequence of non-polar solvent benzene as extractant and also some other influencing parameters such as effect of pH, effect of carrier concentration, effect of dye concentration, effect of salt and stripping agent concentration etc., was also thoroughly studied and reported here.

2. Experimental

2.1. Materials

Benzene, salicylic acid, and MB were obtained from Merck and used without further purification. The following inorganic acids and organic solvents such as salicylic acid (≥99.8%), MB (98%), oxalic acid (99%), sulphuric acid (98%), nitric acid (70%), hydrochloric acid (35.4%), benzene (≥99%), toluene (98%), hexane (99%), and xylene (99%) were used without further purification.

All chemicals used were in analytical reagents grade and aqueous solutions were prepared in double distilled water.

2.2. Apparatus and measurements

A UV visible spectrophotometer (Elico Sl 159, India) was used to find out λ_{max} and measure dye concentration in the raffinate phase and strip solution.

pH meter (Elico Li 120, India) was used to measure pH of aqueous solutions. For agitation of solution, a shaker was used (IKD-KS 50, India). Systronics Electrophoresis 606 was used to find out whether the dye is cationic or anionic.

2.3. Preparation of MB solution

The MB dye used was discovered by Caro in 1878. MB is a cationic dye. Its IUPAC name is 3,7-bis (dimethylamino)-phenothiazin-5-ium chloride. MB, the basic dye composed of heterocyclic aromatic chemical compound used in this present study, is a monovalent cationic dye. It is classified as CI basic blue 9, CI solvent blue 8, and CI 52015. It has a molecular formula $C_{16}H_{18}N_3ClS$ and molecular weight of 319.85 g/mol. The maximum wavelength of this dye is 662 nm. The properties and structure of MB dye presented in Table 1.

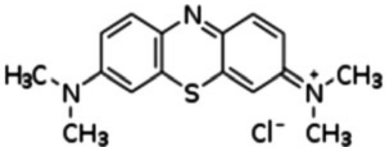
The MB used was of analytical grade so it was used without further purification. A stock solution of 1,000 mg L^{-1} was prepared by dissolving an appropriate quantity of MB in a liter of deionized water. The working solutions were prepared by diluting the stock solution with deionized water to give the appropriate concentration of the working solutions [48].

2.4. Procedure

2.4.1. LLE of dye

The organic solvent (benzene + salicylic acid) used for extraction was added to the prepared dye aqueous solutions of known concentration in a glass-stoppered bottle and the glass-stoppered bottle was shaken at 100 rpm for 5 min in a shaker. The solution was then transferred into a separating funnel. Sample of aqueous solution at the bottom of the separating funnel was taken for absorbance measurement of dye. The wavelength of maximum absorption (λ_{max}) for MB was 662 nm. The distribution ratio (D) and percentage of extraction (E) were calculated as per the following equations:

Table 1
Properties of MB dye

Properties	
Suggested name	Methylene blue
IUPAC name	3,7-bis(dimethylamino)-phenothiazin-5-ium chloride
CI name	Basic blue 9
CI number	52015
Molecular formula	$C_{16}H_{18}N_3SCl$
Molecular weight, g/mol	319.85
λ_{max} (nm)	662 (measured value)
Chemical structure	

$$D = [\text{dye}]\,\text{org}/[\text{dye}]\,\text{aq} \tag{1}$$

$$E = 100\{[\text{dye}]\,\text{aq0} - [\text{dye}]\,\text{aq}\}/[\text{dye}]\,\text{aq0} \tag{2}$$

where [dye] org: dye concentration in the organic phase (mg/L); [dye] aq0: initial dye concentration in the aqueous phase (mg/L); and [dye] aq: dye concentration of aqueous phase after extraction (mg/L) [49].

In stripping, the loaded extractant and the aqueous strippant (acid solution) were added together into a glass-stoppered bottle and shaken at 100 rpm for 5 min in a shaker. The content was then transferred into a separating funnel. The aqueous strippant was taken for dye concentration measurements. All the experiments were run in duplicate and analytical parameters were performed in triplicate for each run. Confidence limit of 95% was taken for reliable results.

3. Results and discussion

3.1. Effect of pH in the aqueous phase

The effect of pH is most important parameter to study because wastewater-containing dyes is discharged at different pH. The influence of pH on the extraction efficiency was studied for a wide range of pH from 1 to 9.0 and the results are shown in the Fig. 1. The pH was adjusted using 0.01 N H_2SO_4 and 0.01 N NaOH. Extraction of cationic dye MB from the aqueous solution was studied using 7.24×10^{-2} mol/L salicylic acid at 1:1 aqueous to organic phase (A/O) ratio with initial pH range from 1 to 9.0 ± 0.1 and the dye concentration of 20 mg/L. Maximum extraction efficiency was noticed as follows: 93% for 20 mg/L, 82.5% for 40 mg/L, 73% for 60 mg/L, 68.5% for 80 mg/L, and 51.5% for 100 mg/L at pH 7.0. Further increases in pH did not increase the extraction efficiency. However, at higher pH value of 10–14, the dye is not extracted. Because, at alkaline pH, extractant gets negative charge and the dye is negative too. Thus, in alkaline medium, repulsion takes place between the extractant and the base. On the other hand, when the pH is increasing in the feed solution, dye molecules might be changed from its original structure. Thus, in

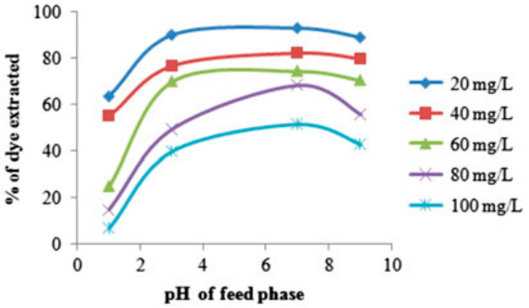


Fig. 1. Effect of pH in the aqueous phase (experimental conditions: volume of feed phase = 10 mL, extractant concentration = 7.24 × 10^{-2} M, volume of organic phase = 10 mL, A/O ratio = 1:1, dye concentration = 20 mg/L, and equilibration time = 3 min).

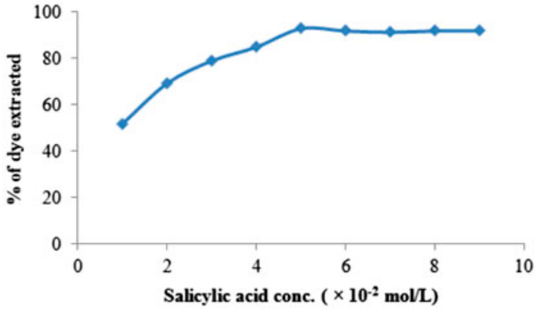


Fig. 2. Effect of extractant concentration (experimental conditions: volume of feed phase = 10 mL at pH 7.0 ± 0.1, volume of organic phase = 10 mL, A/O ratio = 1:1, dye concentration = 20 mg/L, and equilibration time = 3 min).

acidic medium, the extractant may get positively charged, thus making H^+ions compete effectively with dye cations causing a decrease in amount of dye extracted. At the pH increases 3–7, extractant may get negatively charged, which enhances the positively charged dye cations through electrostatic force of attraction. The results show that there is only slight increase and decrease in the dye extraction percentage when the pH was varied. Thus, the effect of the pH can be considered no effect on dye extraction. The percentage of dye extraction was about 93%. Thus, the further experiment to study the other parameters was carried out at pH 7 ± 0.1.

3.2. Effect of extractant concentration

The effect of extractant concentration on the percentage extraction and distribution ratio (D) of the dye was investigated in the range of 2.17 × 10^{-2}–6.516 × 10^{-1} mol/L of salicylic acid. The experimental data for the percentage of extraction vs. [extractant] are plotted in Fig. 2. The percentage of extraction increased with increase in concentration of salicylic acid. Maximum extraction of 93% for 20 mg/L, 82.5% for 40 mg/L, 73.0% for 60 mg/L, 68.5% for 80 mg/L, and 51.5% for 100 mg/L occurred at salicylic acid concentration of 7.24 × 10^{-2} mol/L. Further increase in the extractant concentration did not improve the extraction efficiency. It is interesting to note that in the absence of salicylic acid, no extraction of dye occurred in the organic phase. This confirms that salicylic acid is effective in extracting cationic dye. Hence, the subsequent extraction studies were conducted using 7.24 × 10^{-2} mol/L of extractant. The reaction mechanism for extracting the dye is given in Fig. 3.

The extraction mechanism of dyes can be explained as follows:

(1) The extraction of cationic dye from feed solution into the presence of anionic salicylic acid carrier can form as ion-pair complex [Dye^+ $(C_6H_4OH\,COO)^-$].

(2) The applicability of this ion-association process has been tested for a number of phenolic precursors. It has been observed that MB can form an ion-associate with salicylic acid.

(3) The resulting neutral ion-paired complex is preferentially distributed into the organic phase.

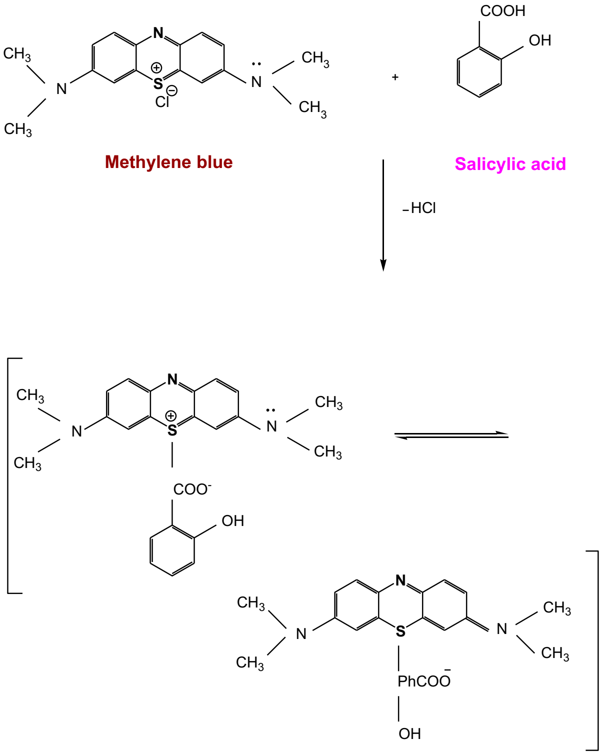


Fig. 3. Mechanism of MB.

3.3. *Effect of diluents*

The extraction of cationic dye from aqueous solution using 7.24 × 10^{-2} mol/L salicylic acid in various solvents such as benzene, toluene, xylene, and hexane was tried for the extraction study. The results also clearly demonstrate that the diluents such as benzene, xylene, and toluene having low dielectric constant show high extraction of cationic dyes. Among them, benzene, toluene, and xylene extracted the dye very effectively. No extraction was found in hexane. The maximum extraction efficiency was noticed as follows: 93.0% for benzene, 87.6% for toluene, and 68.9% for xylene at 20 mg/L initial dye concentration. Among the benzene derivatives, the extraction increased in the order: benzene > toluene > xylene from aqueous solution. The extraction efficiency slightly varied with the nature of diluents used in this study. Table 2 shows the extraction efficiency of different diluents.

3.4. *Effect of dye concentration*

The extraction efficiency of various initial concentrations of cationic dye in the aqueous phase (10 mL) was determined at pH 7.0 ± 0.1 contacted with organic layer (10 mL) containing 7.24 × 10^{-2} mol/L of salicylic acid. When efficiency of extraction decreased, the dye concentration increased. At initial dye concentration of 20 mg/L, 93% extraction was obtained. The aqueous phase (Raffinate) was analyzed for dye concentration and dye transferred into organic phase was calculated. At higher initial dye concentration in the aqueous phase, the extraction efficiency decreased because, in higher concentration, dye has higher energy and high color. So, salicylic acid is not able to completely remove the dye in aqueous phase. However, the absolute amount of dyes extracted, increased with increase of initial dye concentration. Fig. 4 shows the extraction efficiency of different dye concentration.

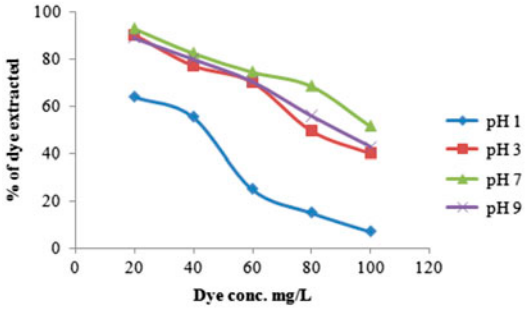


Fig. 4. Effect of dye concentration (experimental conditions: volume of feed phase = 10 mL at pH 7.0 ± 0.1, volume of organic phase = 10 mL, A/O ratio = 1:1, extractant concentration = 7.24 × 10^{-2} M, and equilibration time = 3 min).

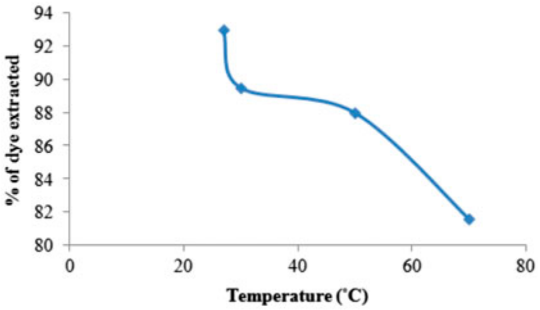


Fig. 5. Effect of temperature (experimental conditions: volume of feed phase = 10 mL at pH 7.0 ± 0.1, volume of organic phase = 10 mL, A/O ratio = 1:1, extractant concentration = 7.24 × 10^{-2} M, dye concentration = 20 mg/L, and equilibration time = 3 min).

3.5. *Effect of temperature*

Fig. 5 shows the effect of temperature on extraction of dye from aqueous phase. The extraction was studied from 27 to 70°C at pH 7.0 ± 0.1. When the temperature was raised from 30 to 70°C, the extraction rate decreased. Maximum extraction of 93% for 27°C, 89.5% for 30°C, 88.0% for 50°C, and 81.6% for 70°C occurred at 20 mg/L initial dye concentration. When temperature increased, the physical bonding between the organic compounds (including dyes) and negative charge of the extractant weakened. Besides, the solubility of MB also increased with increase in temperature and, therefore the dye was more difficult to extract. The result may be attributed to that changing temperature could change the equilibrium capacity of the extractant for a particular dye. And, the dye energy also increased. So, the effect of temperature on extraction was not very significant at room temperature. Further studies were carried out at 27°C.

Table 2
Effect of diluents on extraction of dye efficiency

Diluents	% of dye extraction
Hexane	No extraction
Toluene	87.6
Xylene	68.9
Benzene	93.0

3.6. *Equilibrium time*

To study the effect of equilibration time at different time intervals, different dye concentration was studied from 3 to 7 min. Fig. 6 shows the extraction efficiency of various concentration of dye at different time intervals. The amount of cationic dye (MB) extracted into the organic phase containing 7.24 × 10^{-2} mol/L of salicylic acid in benzene. The extraction efficiency increased with increasing equilibration time. Maximum extraction of 93% for 20 mg/L, 82.5% for 40 mg/L, 73.0% for 60 mg/L, 68.5% for 80 mg/L, and 51.5% for 100 mg/L was achieved from 3 to 7 min. Further increases in the time did not increase the extraction efficiency. Hence, an equilibration time of 3 min is recommended for further studies.

3.7. Effect of (A/O) ratio

The A/O ratio varied from 1:1 to 10:1 was used to study the effect of phase ratio on extraction with an initial dye concentration 20 mg/L. About 93% extraction efficiency was achieved from 1:1. When the A/O volume ratio was increased to 2:1–10:1, the percentage of extraction decreased. Maximum extraction of 93% for 1:1 ratio, 67% for 2:1 ratio, 57.62% for 3:1 ratio, 37.9% for 4:1 ratio, 32.6% for 5:1 ratio, and 20.0% for 6:1 ratio was achieved at 20 mg/L initial dye concentration. The 1:1 yielded a higher percentage of dye removal from aqueous solution. The organic phase was maintained at 10 mL in each experiment. The A/O ratio effect is shown in Fig. 7. Beyond 2:1 A/O ratio, the extraction efficiency of dyes decreased because the extractant was not able to extract the dye in higher amount from aqueous phase. This may be due to the availability of salicylic acid extractant. The percentage of extraction was highest when A/O ratio of 1:1 applied. For further studies, it was decided to maintain 1:1 (A/O) ratio.

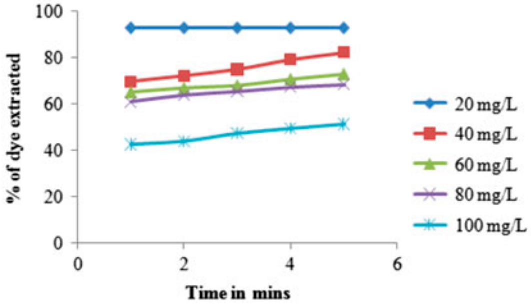


Fig. 6. Effect of equilibrium time (experimental conditions: volume of feed phase = 10 mL at pH 7.0 ± 0.1, volume of organic phase = 10 mL, A/O ratio = 1:1, extractant concentration = 7.24 × 10–2 M, and dye concentration = 20 mg/L).

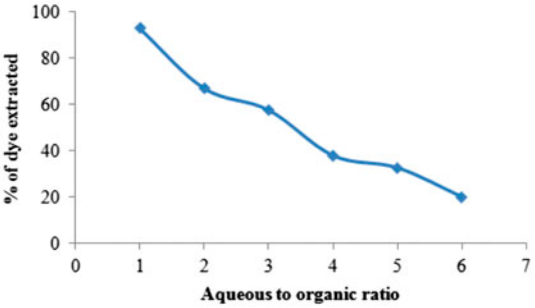


Fig. 7. Effect of (A/O) ratio (experimental conditions: volume of feed phase = 10 mL at pH 7.0 ± 0.1, extractant concentration = 7.24 × 10^{-2} M, dye concentration = 20 mg/L, and equilibration time = 3 min).

3.8. Effect of salt concentration

In the actual industrial textile dye bath effluent, the dye contains salts like sodium chloride and sodium sulfate. To study the influence of sulfate and chloride concentration on dye extraction, dye solutions with different concentrations of sodium chloride and sodium sulfate were prepared and extracted at pH 7.0 ± 0.1. The results are presented in Table 3, which show that the extraction efficiency of dyes remained unchanged when sodium chloride was present in the dye solution. The maximum extraction efficiency of 82.0% for 5 g/L, 85.0% for 10 g/L, 85.3% for 25 g/L, 86.9% for 50 g/L, 88.0% for 75 g/L, and 93.0% for 100 g/L was achieved at sodium chloride present in the aqueous solution. In contrast, the percentage of extraction increased slightly with increasing sodium sulfate concentration. Maximum extraction efficiency of 89.0% for 5 g/L, 90.0% for 10 g/L, 91.0% for 25 g/L, 93.0% for 50 g/L, 93.7% for 75 g/L, and 95.3% for 100 g/L was achieved when sodium sulfate present in the aqueous solution. It can be seen that the percentage removal of dye was not affected with increase in sodium chloride and sodium sulfate concentrations up to 100 g/L in the aqueous source phase.

Table 3
Effect of salt concentration in aqueous feed phase on extraction efficiency

Salt concentration (g/L)	Na_2SO_4 percentage of extraction (MB)	NaCl percentage of extraction (MB)
5	89.0	82.0
10	90.0	85.0
25	91.0	85.3
50	93.0	86.9
75	93.7	88.0
100	95.3	93.0

Table 4
Effect of stripping agents on percentage of dye stripping from organic phase

Stripping agent	Percentage of stripping
Sulphuric acid (1M)	72.1
Hydrochloric acid (1M)	66.5
Nitric acid (1M)	59.0
Oxalic acid (1M)	93.1
Acetic acid (1M)	55.4
Sodium hydroxide (1M)	26.0
Potassium hydroxide (1M)	45.9
Sodium bicarbonate (1M)	65.9
Sodium carbonate (1M)	71.5

3.9. Effect of stripping reagents

In extraction processes, it is very imperative to back-extract the extracted dye from the organic phase. Various strong and weak acids and strong and weak bases are used in this study; such as sulphuric acid, nitric acid, hydrochloric acid, oxalic acid, acetic acid, sodium hydroxide, sodium carbonate, sodium bicarbonate, potassium hydroxide have been tried as stripping agents. Among them, oxalic acid was best to strip the dye from loaded organic phase because the weak acid easily recovers the dye from the loaded organic phase. Table 4 shows the percentage of stripping compared to other acids and bases. Maximum extraction efficiency of 72.1% for 1 M $H_2SO_4,$ 66.5% for 1 M HCl, 59.0% for 1 M nitric acid, 55.4% for 1 M acetic acid, 93.1% for 1 M oxalic acid, 26.0% for 1 M sodium hydroxide, 45.9% for 1 M potassium hydroxide, 65.9% for 1 M sodium bicarbonate, and 71.5% for 1 M sodium carbonate was achieved at 20 mg/L initial dye concentration. Hence, 1 M oxalic acid was found to be suitable for stripping of the extracted dye. The maximum amount of dye (93%) was stripped within 3 min. Further increase in time did not improve stripping efficiency. Further studies were carried out using 1 M oxalic acid as stripping agent. The mechanism of stripping has been explained as follows:

$$[(C_6H_4OHCOOH)_{org} + [Dye]_{aq^+} = [(C_6H_4OHCOO)^-(Dye)^+_{org} + HCl^-$$

$$[(C_6H_4OHCOO)^-(Dye)^+_{org} + (C_2H_2O_4)_{aq} = [(C_6H_4OHCOOH)_{org} + [Dye]^+_{aq}HC_2O_{4^-}$$

3.10. Effect of stripping contact time

The stripping contact time was determined for the system containing 10 mL of loaded organic phase and 10 mL of stripping agent (1 M Oxalic acid) equilibrated with increase in contact time in the range of 1–3 min. The maximum stripping efficiency was found to be 93% at 3 min. This indicates that the stripping reaction was very fast. Further increase in contact time did not improve stripping efficiency. Hence, 3 min was selected as stripping contact time.

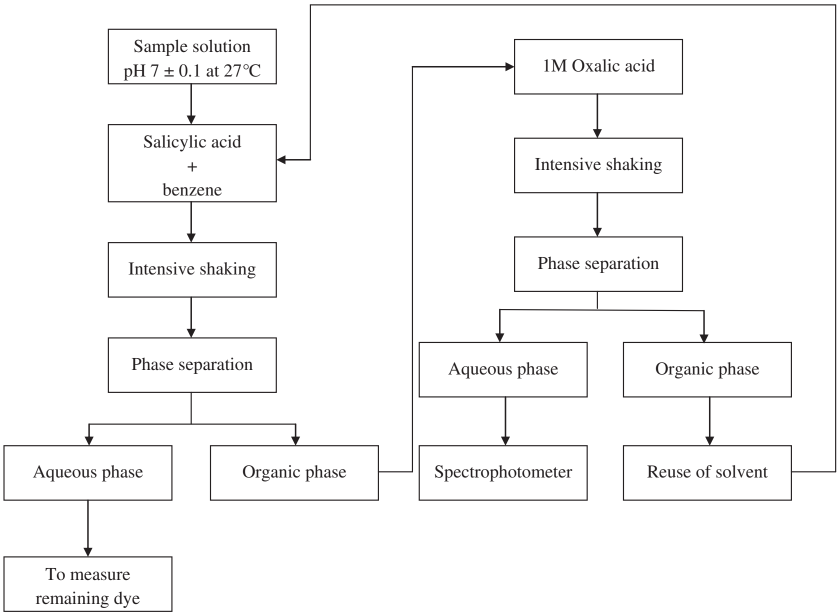


Fig. 8. A proposed flow sheet for extraction and recovery of dye from industrial wastewater.

3.11. Application of the developed solvent extraction or LLE for industrial wastewater

The developed solvent extraction or LLE system was tested for applicability to real industrial wastewater. Under optimized condition (feed phase = 20 mg/L at pH 7 ± 0.1, extractant concentration = 7.24×10^{-2} mol/L, equilibrium time = 3 min, strip phase = 1 M oxalic acid, A/O ratio = 1:1), the textile dye waste was extracted and the extracted dye was stripped into the oxalic acid solution. It was noticed that the extraction and stripping were not affected by various type of salts present in textile wastewater. Based on the above data, a proposed flow sheet for extraction and recovery of dye from industrial wastewater is given in Fig. 8.

4. Conclusions

The LLE method offers a simple approach for selective extraction of cationic dye for removal and recovery. Salicylic acid is able to extract more than 93% of cationic MB dye from aqueous solution in a short time of 3 min. The extraction efficiency of dye decreases with increasing concentration of dye. The extracted dye was successfully stripped into oxalic acid solution from loaded organic phase. The maximum extraction efficiency was obtained at pH 7.0 ± 0.1. The A/O ratio 1:1 is maintained in this study. Under optimized condition, industrial wastewater also tested and the result was found to be satisfactory.

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