# Extraction and recovery of methylene blue from industrial wastewater using benzoic acid as an extractant

G. Muthuraman, Tjoon Tow Teng*, Cheu Peng Leh, I. Norli

*School of Industrial Technology, Universiti Sains Malaysia, Penang 11800, Malaysia*

## ARTICLE INFO

## ABSTRACT

Liquid–liquid extraction (LLE) of methylene blue (MB) from industrial wastewater using benzoic acid (extractant) in xylene has been studied at 27 °C. The extraction of the dye increased with increasing extractant concentration. The extraction abilities have been studied on benzoic acid concentration in the range of $0.36$–$5.8 \times 10^{-2}$ M. The distribution ratio of the dye is reasonably high ($D = 49.5$) even in the presence of inorganic salts. Irrespective of the concentration of dye, extraction under optimal conditions was 90–99% after 15 min of phase separation. The extracted dye in the organic phase can be back extracted into sulphuric acid solution. The resultant recovered organic phase can be reused in succeeding extraction of dye with the yield ranging from 99 to 87% after 15 times reused, depending on the concentration of the initial feed solution. Experimental parameters examined were benzoic acid concentration, effect of diluent, effect of pH, effect of initial dye concentration, effect of equilibration time, various stripping agents, aqueous to organic phase ratio in extraction, organic to aqueous phase ratio in stripping and reusability of solvent.

## 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 colour 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 coloured compounds are not only aesthetically displeasing but also inhibiting sunlight into streams and affecting photosynthetic reaction [1]. It is estimated that more than 100,000 commercially available dyes with over $7 \times 10^5$ tons of dyestuff are produced annually [2]. Methylene blue (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 will cause increased heart rate, vomiting, shock, cyanosis, jaundice, and quadriplegia and tissue necrosis in humans [3]. The advantages and disadvantages of some methods of dye removal from wastewater are given in Table 1 [4].

Removal of MB by carbon derived from peach stones by $H_3PO_4$ activation was studied [5]. Adsorption of MB by algal biomass based materials was also reported [6]. Kavitha and Namasivayam [7] also used coir pith activated carbon. The adsorption capacity was found to be 5.87 mg/g by Langmuir isotherm for the particle size of 250–500 $\mu$m. In these cases disposal of spent activated carbon is a problem. Micellar enhanced ultra filtration (MEUF) is one possible method to remove organic dyes from water. Even though MEUF method is not yet applied on an industrial scale, many studies have shown that it is a suitable method for the retention of metal ions [8,9], anions [10], and organic pollutants [11,12]. Separation of MB from aqueous solution by micellar enhanced ultra filtration was also reported [13].

Electrochemical degradation of MB was studied by Panizza et al. [14]. Photo catalytic degradation of MB was also investigated [15,16]. Removal and recovery of dye stuffs (DSs) using ion exchange method was proposed by MonaNaim and Yehia [17]. Electrochemical oxidation of dye wastewater was studied by various researchers [18,19]. Sundrarajan et al. [20] reported that ozonation is efficient in decolorization of exhausted dye bath effluent containing conventional reactive dyes. Ozone treatment was used on acid red 18, acid orange 7, acid orange 10 and acid red 73 by Muthukumar et al. [21]. For all the dyes two successive recycling processes were carried out. Ozonation method does not remove total dissolved solids (TDS), but it reduces chemical oxygen demand (COD) of the effluent.

Membrane separation process plays an increasing role in the reduction and/or recovery of DSs. Fouling of membrane is a problem in this case [22]. Removal of anionic and cationic organic dyes

* Corresponding author. Tel.: +60 4 6532215; fax: +60 4 6573678.
*E-mail addresses:* ttteng@usm.my, sooksan@eng.usm.my (T.T. Teng).

**Table 1**
Advantages and disadvantages of the current methods of dye removal from industrial effluent [4]

| Physical/chemical methods | Advantages | Disadvantages |
|---|---|---|
| Fenton's reagent | Effective decolourization of both soluble and insoluble dyes | Sludge generation due to $Fe^{2+}$ used |
| Ozonation | Applied in gaseous state no alternative of volume | Short half life (20 min) of ozone |
| Photochemical | No sludge production | Formation of by products |
| NaOCl | Initiate and accelerates azo bond cleavage | Release of aromatic amines and adsorption of organic halides |
| Electrochemical destruction | Breakdown compounds are non hazards | High cost |
| Activated carbon | Good adsorbent due to cellular structure | Very expensive and disposal of spent |
| Peat | Good adsorbent due to cellular structure | Specific surface areas of adsorbent are lower than activated carbon |
| Wood chips | Good sorption capacity for acid dyes | Requires long retention time |
| Silica gel | Effective removal for basic dyes | Prevent commercial application |
| Ion exchange | Regeneration, no adsorbent loss | Not effective all types of dyes |

from water by liquid–liquid extraction (LLE) using reverse micelles was proposed by Pandit and Basu [23]. Removal of methyl orange and methylene blue dyes from water using colloidal gas aphrons (CGA) was reported by Basu and Malpani [24]. Roy et al. [25] studied the separation of organic dyes such as methyl orange, methylene blue, cibacrome 4G, cibacrome 6B from wastewater using CGA. Hexa tetramethyl ammonium bromide and sodium dodecyl benzene sulphonate were used as surfactants for the generation of CGA.

Aqueous bibasic system (ABS) consists of two immiscible phases formed when certain water soluble polymers are mixed with one another or with certain inorganic salts in specific concentration [26]. ABS composing of dodecyl trimethyl ammonium hydroxide and sodium dodecyl sulphates was reported to be able to extract methyl orange and porphyry dyes [27].

Liquid–liquid extraction method is used for the purification enrichment separation and analysis of various compounds in mixtures. It is based on the principle that a solute can distribute itself in a certain ratio between immiscible solvents. Therefore, the selection of both a diluent and an extractant determines equilibrium for a given system and the efficiency of extraction process depends on its mass transfer rate [28]. The advantage of solvent extraction includes high through put, ease of automatic operation and of scale up and high purification [29]. The main factors affecting LLE process are, organic to aqueous phase ratio, salt concentration, nature of solvent, salting effect and some of the interference mechanisms.

In the present study, the efficiency of liquid–liquid extraction of a cationic dye namely, methylene blue using benzoic acid prepared in xylene as extractant was studied. The dye extraction and stripping extracted dye were investigated and operating conditions were optimized. Further recovery of dye and stripping reagents were also studied.

## 2. Experimental

### 2.1. Materials

Benzoic acid, xylene, methylene blue, sulphuric acid, sodium hydroxide, sodium chloride, nitric acid and hydrochloric acid, were obtained from Merck. All chemicals used in this study were of AR grade.

A UV–visible spectrophotometer (Spekol 1200, Analytical Jena, Germany) was used to measure the absorbance of the dye and to establish its $\lambda_{max}$ and its concentration. pH of an aqueous solution was measured by a pH meter (WTW, Germany). For agitation of solutions a mechanical stirrer was used (IKD-KS 50, Germany).

Benzoic acid was used as extractant and dissolved in xylene. The dye solution was prepared in distilled water. Sulphuric acid was used as stripping agent and sodium hydroxide was used to adjust pH.

### 2.2. Procedure

#### 2.2.1. Liquid–liquid extraction of dye

The organic solvent [(benzoic acid + xylene) ($V_o$ mL)] used for extraction was added to the prepared aqueous dye solution ($V_a$ mL) in a glass-stoppered bottle and the glass-stoppered bottle was shaken for known time in a shaker at 100 rpm. 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 ($\lambda_{max}$) for methylene blue was 650 nm. The experimental setup is shown in Fig. 1. The distribution ratio ($D$) and percentage of extraction ($E$) were calculated as per the following equations

$$D = \frac{[dye]_{org}}{[dye]_{aq}} \tag{1}$$

$$E = 100 \times \frac{[dye]_{aq0} - [dye]_{aq}}{[dye]_{aq0}} \tag{2}$$

where $[dye]_{org}$ is the dye concentration in the organic phase (mg/L), $[dye]_{aq0}$ is the initial dye concentration of aqueous phase (mg/L), $[dye]_{aq}$ is the dye concentration of aqueous phase after extraction (mg/L).

In stripping, the loaded extractant ($V_o$ mL) and the aqueous strippant (acid solution) were added together into a glass-stoppered bottle and shaken at 100 rpm. 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.
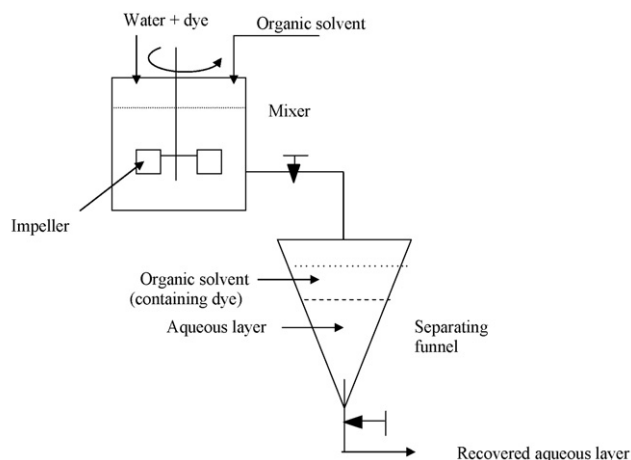


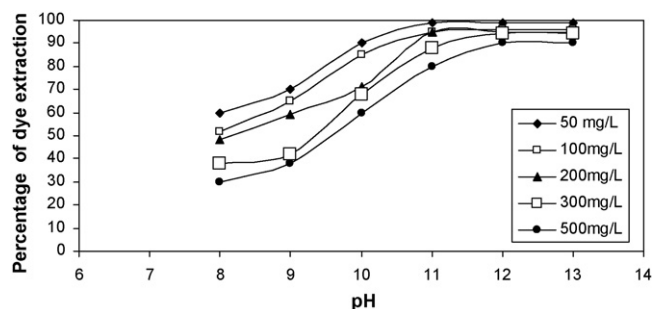**Fig. 1.** Schematic experimental setup for liquid–liquid extraction for removal of dye from aqueous solution.

**Fig. 2.** Effect of pH in the feed solution (experimental conditions: volume of source phase = 25 mL, volume of organic phase = 25 mL, extractant concentration $2.9 \times 10^{-2}$ M, equilibration time = 10 min).

The extraction and stripping processes were repeated on aqueous dye solutions in which inorganic salts were added to study the effect of the presence of these salts.

## 3. Results and discussion

### 3.1. Effect of pH of source phase

The effect of pH of the source phase on the efficiency of dye extraction is shown in Fig. 2. Aqueous solutions of different concentrations were maintained in the range of pH 7–13 to study dye extraction efficiency. Maximum extraction efficiency was noticed
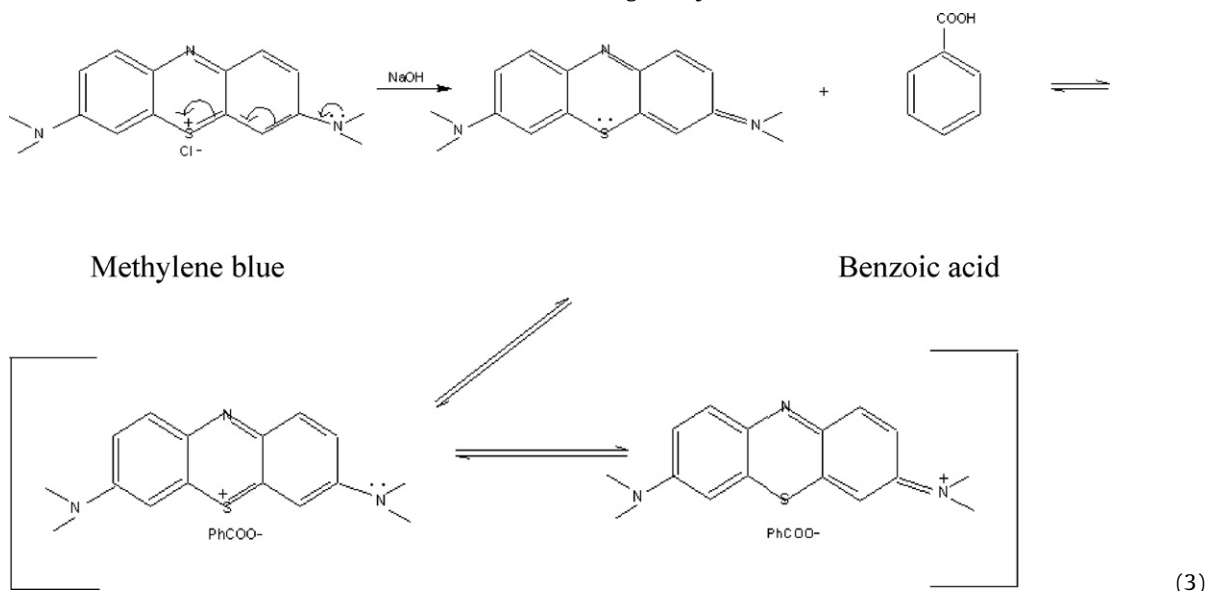
**Table 2**
Effect of extractant concentration

| Extractant concentration ($M \times 10^2$) | Percentage of dye extraction | Distribution ratio ($D$) |
|---|---|---|
| 0 | 0 | 0 |
| 0.36 | 55.3 | 27.6 |
| 0.72 | 62.3 | 31.1 |
| 1.45 | 85.7 | 42.8 |
| 2.91 | 99.0 | 49.5 |
| 5.81 | 99.0 | 49.5 |

Extraction phase ratio 1:1.

in extractant concentration did not show considerable effect on extraction efficiency. It is interesting to note that in the absence of benzoic acid no extraction of dye occurred in the organic phase. This confirms that benzoic acid is effective in extracting cationic dye. Hence in the succeeding test the extractant benzoic acid concentration was fixed at $2.9 \times 10^{-2}$ M.

To determine the nature of the extracted dye, dye solutions of different concentrations were extracted by fixed concentration of benzoic acid ($2.9 \times 10^{-2}$ M). The distribution ratio ($D$) of dye was calculated at fixed concentration of benzoic acid. The plot of log extracted dye versus log feed concentration ($mg\,L^{-1}$) (Fig. 3) gives a straight line with a slope value of 1.0356 indicating that dye to extractant concentration ratio was best at 1:1 and suggesting formation of 1:1 complex. It can then be assumed that 1 mol of benzoic acid can best extract 1 mol of cationic dye [22]. The reaction for extracting the dye is as follows.



Methylene blue                    Benzoic acid

(3)

as follows: 99% for 50 mg/L, 96% for 100 mg/L, 95% for 200 mg/L, 94% for 300 mg/L and 90% for 500 mg/L, respectively. It can be seen that percentage of dye extraction increased with increasing pH of aqueous solution. The results reveal that the maximum extraction of dye had occurred in the pH range 10–13. For further studies, it was decided to maintain the extraction at pH $12 \pm 0.1$.

### 3.2. Effect of extractant concentration

The effect of benzoic acid concentration on distribution ratio ($D$) of the dye was next investigated in the concentration range of $0.36 \times 10^{-2}$ to $5.8 \times 10^{-2}$ M. Table 2 shows that the efficiency of dye extraction increased with increasing benzoic acid concentration. Maximum extraction of 99% occurred at benzoic acid (50 mg/L) concentration of $2.9 \times 10^{-2}$ M. Further increase (beyond $2.9 \times 10^{-2}$ M)
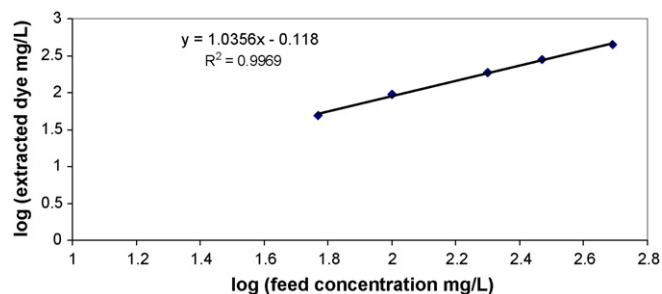


**Fig. 3.** Distribution ratio (experimental conditions: volume of source phase = 25 mL at pH $12 \pm 0.1$, volume of organic phase = 25 mL, extractant concentration $2.9 \times 10^{-2}$ M, equilibration time = 10 min).

**Table 3**
Effect of diluents on dye extraction efficiency

| Diluents | Percentage of dye extraction |
|---|---|
| Hexane | 5.0 |
| Methylene chloride | 70.1 |
| Toluene | 95.0 |
| Xylene | 99.0 |
| Benzene | 75.3 |

Extraction phase ratio 1:1.

### 3.3. Effect of diluents

The extraction was carried out in different diluents such as toluene, xylene, benzene, dichloromethane and hexane from aqueous solution at pH $12 \pm 0.1$. Benzoic acid solubility in hexane was poor. In toluene and xylene, high extraction percentages of dye were obtained compared to dichloromethane and benzene (Table 3). Succeeding tests were carried out using xylene as diluent since it is less toxic compared to benzene and dichloromethane. About 99% of dye was extracted into the solvent.

### 3.4. Effect of dye concentration

The effect of initial dye concentration on the extraction process was tested at $2.9 \times 10^{-2}$ M of benzoic acid in xylene. It can be seen from Fig. 4 that the percentage of dye extraction decreased with initial dye concentration. At initial dye concentration of 50 mg/L, 99% extraction was obtained. With further increase in dye concentration the percentage of extraction of dye decreased. However, the absolute amount of dye extracted, increased with increase of initial dye concentration.

### 3.5. Effect of equilibration time

The amount of dye extracted into organic phase at different times (up to 15 min) was studied. Fig. 5 shows that at 3 min maximum extraction was 95% at initial dye concentration of 50 mg/L. The extraction efficiency of dye increased with increase in equilibration time. Maximum extraction (99%) at initial dye concentration of 50 mg/L was achieved at 10 min. After 10 min, almost all dye was transported to the organic phase and hence an equilibrium period of 10 min is recommended.

### 3.6. Effect of temperature

Fig. 6 shows the effect of temperature on extraction of dye from aqueous phase. It can be seen that the extraction rate remained unchanged at 99% from 20 to 28 °C. When the temperature was raised from 28 to 50 °C, the extraction rate decreased. So the effect
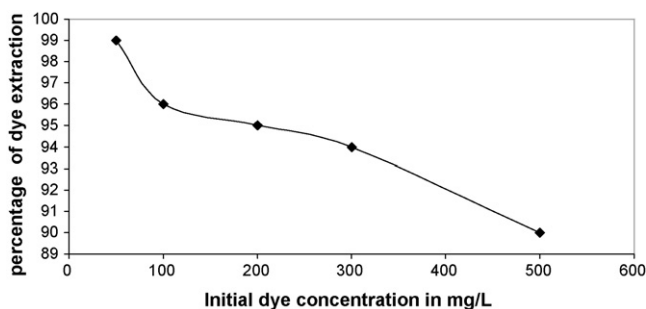
**Fig. 4.** Effect of dye concentration (experimental conditions: volume of source phase = 25 mL at pH $12 \pm 0.1$, volume of organic phase = 25 mL, extractant concentration $2.9 \times 10^{-2}$ M, equilibration time = 10 min).
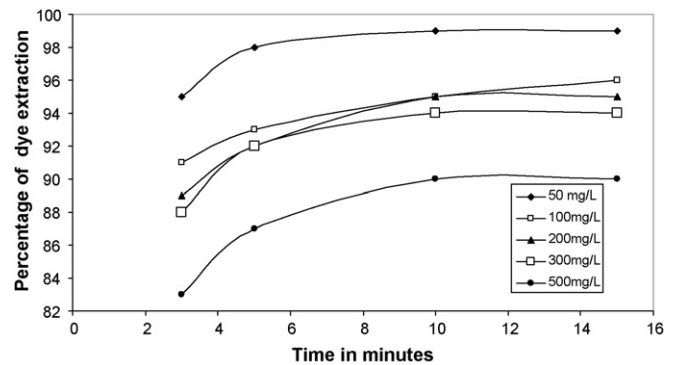
**Fig. 5.** Effect of equilibration time (experimental conditions: volume of source phase = 25 mL at pH $12 \pm 0.1$, volume of organic phase = 25 mL, extractant concentration $2.9 \times 10^{-2}$ M).
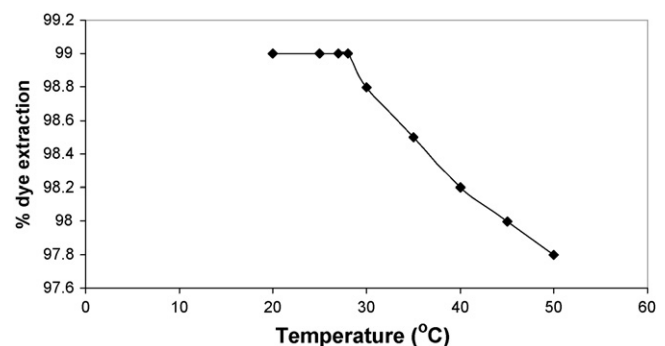
**Fig. 6.** Effect of temperature (experimental conditions: volume of source phase = 25 mL at pH $12 \pm 0.1$, volume of organic phase = 25 mL, extractant concentration $2.9 \times 10^{-2}$ M, equilibration time = 10 min).

of temperature on extraction was not very significant at room temperature. Further studies were carried out at 27 °C.

### 3.7. Effect of extraction phase ratio

The phase volume ratios (aqueous to organic phase volume) of 1:1, 5:1, 10:5, 15:1 were used to study the effect of phase ratio on extraction with initial dye concentration from 50 to 500 mg/L. The results are presented in Table 4. From Table 4 it is evident that for the ratio of 15:1 the removal efficiency dropped from 75 to 63% when initial dye concentration changed from 50 to 500 mg/L. When the ratio was reduced to 5:1 the removal efficiency changed from 92 to 81%. For the ratio of 1:1 the percentage of dye removal changed from 99 to 90%. The ratio 1:1 yielded high percentage of dye removal probably because the free concentration of benzoic acid in the organic phase is higher when the aqueous to organic phase ratio (A/O) is lower.

**Table 4**
Effect of extraction phase ratio on percentage of dye extraction with initial dye concentration from 50 to 500 mg/L

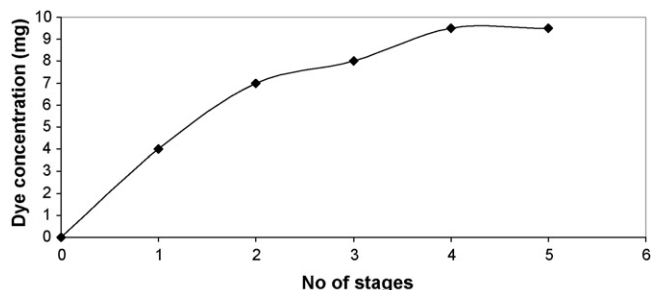| Ratio (A/O) | Extracted dye (mg/L) | | | | | Percentage of dye extraction | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 50 | 100 | 200 | 300 | 500 | 50 | 100 | 200 | 300 | 500 |
| 1:1 | 49 | 96 | 190 | 282 | 450 | 99 | 96 | 95 | 94 | 90 |
| 5:1 | 46 | 90 | 176 | 258 | 405 | 92 | 90 | 88 | 86 | 81 |
| 7:1 | 43 | 85 | 166 | 240 | 360 | 87 | 85 | 83 | 80 | 75 |
| 10:1 | 40 | 77 | 150 | 216 | 340 | 80 | 77 | 75 | 72 | 68 |
| 15:1 | 37 | 72 | 140 | 204 | 315 | 75 | 72 | 70 | 68 | 63 |

**Fig. 7.** Effect of loading capacity of dye for benzoic acid (experimental conditions: volume of source phase = 25 mL at pH 12 ± 0.1, volume of organic phase = 25 mL, extractant concentration $2.9 \times 10^{-2}$ M, dye concentration 50 mg/L, equilibration time = 10 min).

### 3.8. Loading of dye in benzoic acid

Benzoic acid ($2.91 \times 10^{-2}$ M) in 25 mL of xylene diluent was used for extraction at ambient temperature of 27 °C for 15 min with equal volume of aqueous solution containing 50 mg/L of dye. The aqueous phase was analyzed for dye concentration after each stage of extraction and cumulative dye content transferred into organic phase was calculated. The plot of cumulative dye content per $2.91 \times 10^{-2}$ M benzoic acid versus number of stages is depicted in Fig. 7. After five stages, emulsion was noticed. This might be because the extractant was unable to extract dye from the feed solution. It is clear from Fig. 7 that the loading capacity of benzoic acid in xylene for extraction of dye from aqueous solution was 9–9.5 mg of dye per $2.91 \times 10^{-2}$ M of extractant.

### 3.9. Effect of salt concentration

In the actual textile dye bath effluent the dye waste contains salts like sodium chloride and sodium sulphate. To understand the influence of sulphate and chloride concentration on dye extraction, dye solutions with different concentrations of sodium chloride and sodium sulphate were prepared and tested at pH 12 ± 0.1. Table 5 shows the effect of sodium chloride and sodium sulphate on percentage removal of dye from aqueous solutions in the presence of benzoic acid as an extractant and at pH 12 ± 0.1. It can be seen that the percentage removal of dye was not affected with increase in sodium chloride and sodium sulphate concentrations up to 5000 mg/L in the aqueous source phase.

**Table 5**
Effect of salt concentration on percentage of dye extraction with initial dye concentration from 50 to 500 mg/L

| Concentration of anions (mg/L) | Percentage of dye extraction | | | | |
|---|---|---|---|---|---|
| | 50 | 100 | 200 | 300 | 500 |
| Chloride | | | | | |
| 1000 | 99.0 | 96.0 | 95.0 | 94.0 | 90.0 |
| 2000 | 99.0 | 95.9 | 95.0 | 94.1 | 90.1 |
| 3000 | 98.9 | 96.0 | 95.2 | 94.0 | 90.0 |
| 4000 | 99.0 | 96.0 | 94.0 | 94.0 | 90.1 |
| 5000 | 98.9 | 96.1 | 95.1 | 94.0 | 90.1 |
| Sulphate | | | | | |
| 1000 | 99.0 | 95.8 | 95.0 | 94.0 | 90.0 |
| 2000 | 99.0 | 96.0 | 95.0 | 94.0 | 90.1 |
| 3000 | 98.0 | 96.0 | 94.7 | 94.0 | 90.1 |
| 4000 | 99.0 | 96.0 | 95.0 | 93.8 | 90.0 |
| 5000 | 99.0 | 96.0 | 95.0 | 94.0 | 90.0 |

**Table 6**
Effect of stripping agents on percentage of dye stripping

| Stripping agent | Percentage of stripping |
|---|---|
| HCl (0.5N) | 80.0 |
| HCl (1.0N) | 80.0 |
| HNO$_3$ (0.5N) | 35.0 |
| HNO$_3$ (1.0N) | 35.0 |
| H$_2$SO$_4$ (0.5N) | 90.0 |
| H$_2$SO$_4$ (1.0N) | 96.0 |
| H$_2$SO$_4$ (2.0N) | 96.0 |

Extraction phase ratio 1:1.

### 3.10. Effect of stripping reagents

In extraction processes, it is very imperative to back extract the extracted dye from the organic phase and allow recycling of the organic solvent without loss of efficiency. Various inorganic acids such as HCl, HNO$_3$ and H$_2$SO$_4$ were used as stripping agent in this study. Sulphuric acid stripped the dye very well from the organic phase (Table 6) compared to other inorganic acids. It means that the presence of H$_2$SO$_4$ in the stripping phase helped the dye by converting the dye hydrophilic moiety [30]. Hence 1N H$_2$SO$_4$ was found to be suitable for stripping of the extracted dye. The maximum amount of dye (96%) was stripped within 10 min. Further increase in time did not improve stripping efficiency.

### 3.11. Effect of stripping phase ratio

The stripping phase ratio (organic to aqueous) is an important factor in stripping process. From Fig. 8, the percentage of dye stripping increased with decreasing phase ratio (O/A). When O/A = 1/1–2/1, at fixed 1N H$_2$SO$_4$, the stripping rates were higher than 95%. However, when the ratio O/A was greater than 3/1, the efficiency of stripping decreased. This might be because the quantity of stripping reagent was not enough to neutralize the alkali in the organic phase. Thus, a phase ratio O/A of 2/1 was maintained.

### 3.12. Effect of stripping contact time

The stripping efficiency did not increase with increasing contact time in the range 3–10 min, when a freshly loaded organic solution was used. This indicates the stripping was very fast and the stripping reaction was completed within 5 min and 96% of the dye was stripped from the loaded organic phase. When contact time was increased, no further stripping was achieved.

### 3.13. Reusability of solvent

The stripped organic solvent was reused for MB dye extraction under the optimized condition and the results are presented in
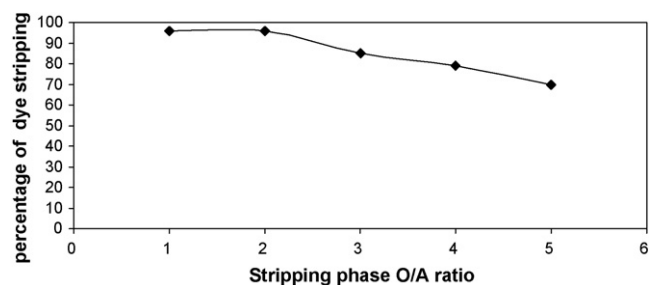


**Fig. 8.** Effect of stripping phase ratio (experimental conditions: volume of source phase = 25 mL at pH 12 ± 0.1, volume of organic phase = 25 mL, extractant concentration $2.9 \times 10^{-2}$ M, dye concentration 50 mg/L, volume of stripping reagent 12.5 mL).

**Table 7**
Reusability of solvent

| No. of stage | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Percentage of dye extraction | 99 | 99 | 99 | 99 | 99 | 99 | 99 | 99 | 99 | 99 | 96 | 93 | 91 | 89 | 87 |

Extraction phase ratio 1:1.

Table 7. The extraction efficiency of dye did not decrease up to 10 cycles. After 10 cycles, it was found that 87% MB dye was extracted into the solvent. This might be due to loss of benzoic acid during the stripping of dye. When $0.35 \times 10^{-2}$ M of benzoic acid was added to the recycled organic solvent the extraction increased to 99%.

### 3.14. Application of the developed LLE for textile wastewater

The developed liquid–liquid extraction system was tested for applicability to the real textile wastewater from a local textile industry. The wastewater was alkaline in nature (pH $12.5 \pm 0.1$). Under optimized condition (volume of source phase = 25 mL, dye concentration 60 mg/L, volume of organic phase = 25 mL, extractant concentration = $2.9 \times 10^{-2}$ M, equilibration time = 10 min, volume of stripping reagent = 12.5 mL, residual dye concentration in the source phase was 3 mg/L) the textile dye waste was extracted very well and the extracted dye stripped into sulphuric acid solution. It was noticed that the extraction and stripping were not affected by various types of salts present in the textile wastewater. Based on the above data, a proposed flow sheet for extraction and recovery of dye from industrial wastewater is given in Fig. 9.

## 4. Conclusions

The method presented offers a simple approach for selective extraction of cationic dye for removal and recovery.

- Benzoic acid in xylene is able to extract more than 99% of cationic dye from aqueous solution in a short time of 10 min.
- The extraction efficiency of dye was not affected in the presence of salts like NaCl and $Na_2SO_4$.
- Stripping efficiency of dye reduced with organic to aqueous phase ratio.
- Stripping reaction was completed within 5 min and 96% of the dye was stripped from loaded organic phase.
- Solvent (benzoic acid + xylene) can be reused as many as 10 times without loss of efficiency.
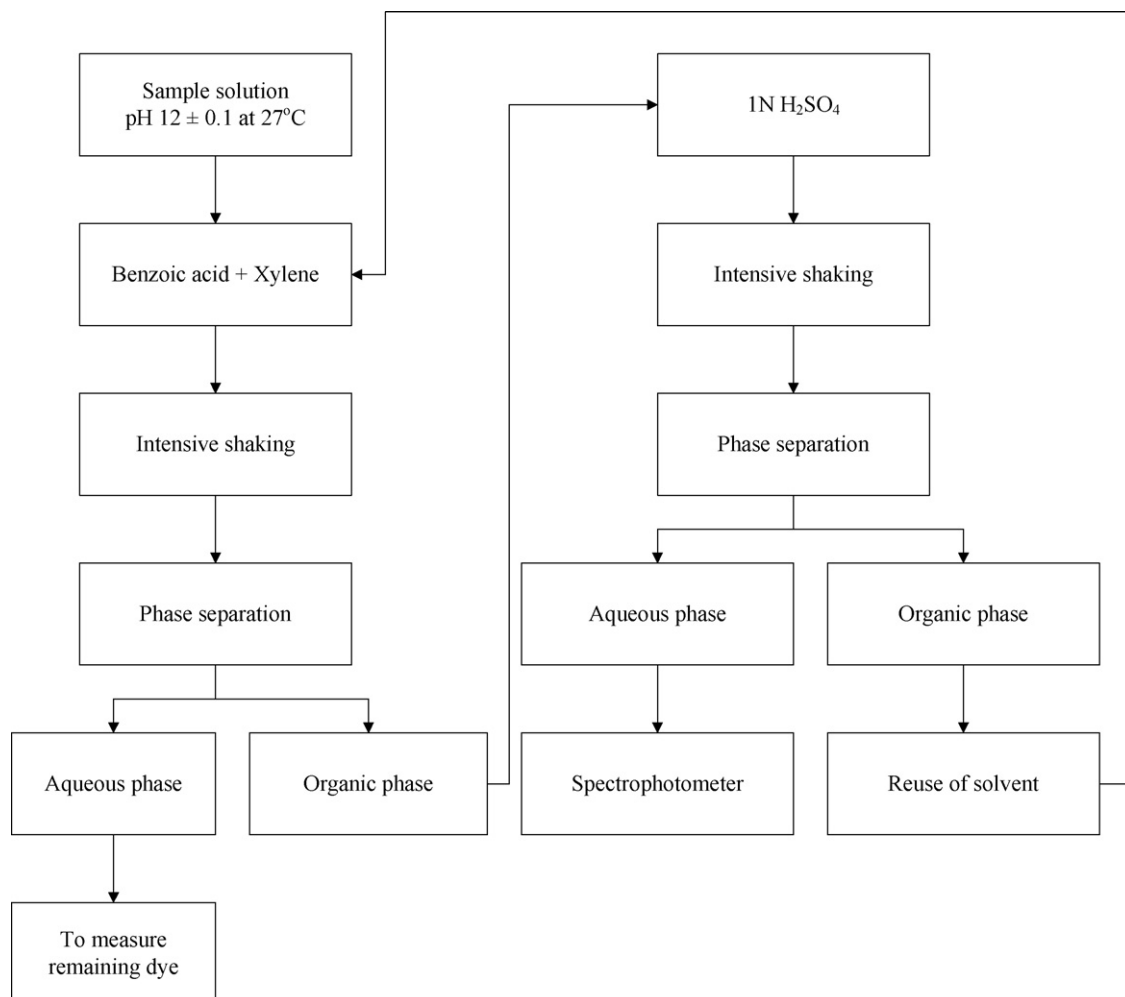
### Acknowledgement

Fig. 9. A proposed flow sheet for extraction and recovery of dye from industrial wastewater.

## References

[1] P.K. Malik, Use of activated carbon prepared from sawdust and rice husk for adsorption of acid dyes: a case study of yellow 36, Dyes Pigment 56 (2003) 239–249.

[2] J.W. Lee, S.P. Choi, R. Thiruvenkatachari, W.G. Shim, H. Moon, Evaluation of the performance of adsorption and coagulation processes for the maximum removal of reactive dyes, Dyes Pigment 69 (2006) 196–203.

[3] K.V. Kumar, A. Kumaran, Removal of methylene blue by mango seed kernel powder, J. Biochem. Eng. 27 (2005) 83–93.

[4] T. Robinson, G. Mc Mullan, R. Marchant, P. Nigam, Remediation of dyes in textile effluent a critical review on current treatment technologies with a proposed alterative, Bioresour. Technol. 77 (2001) 247–255.

[5] A.A. Amina, S.B Girgis, A.N Fathy, Removal of methylene blue by carbon derived from peach stones by $H_3PO_4$ activation batch and column studies, Dyes Pigment 76 (2008) 282–289.

[6] J.P. Vitor Vilar, M.S. Cidalia Botelho, A.R. Rui Boaventura, Methylene blue adsorption by algal biomass based materials: biosorbents characterization and process behaviour, J. Hazard. Mater. 147 (2007) 120–132.

[7] D. Kavitha, C. Namasivayam, Experimental and kinetic studies on methylene blue adsorption by coir pith carbon, Bioresour. Technol. 98 (2007) 14–21.

[8] S.D. Christian, J.F. Scamborn, Surfactant Based Separation Process Surfactant Science Series, vol. 33, Marcel Dekker, New York, 1989, 29 pp.

[9] A. Hafiane, I. Issid, D. Lemordant, Counterion binding on micelles an ultrafiltration study, J. Colloid Interface Sci. 142 (1991) 167–178.

[10] L. Gzara, M. Dhahbi, Removal of chromate anions by micellar enhanced ultrafiltration using cationic surfactants, Desalination 137 (2001) 241–250.

[11] H. Adam Czak, K. Matema, R. Urbariski, J. Szymanowski, Ultrafiltration of micellar solutions containing phenols, J. Colloid Interface Sci. 218 (1999) 359–368.

[12] S.R. Jadhav, N. Verma, A. Sharma, P.K. Battacharya, Flux and retention analysis during micellar enhanced ultrafiltration for the removal of phenol and aniline, Sep. Purif. Technol. 24 (2002) 541–557.

[13] N. Zaghbani, A. Hafiane, M. Dhahbi, Separation of methylene blue from aqueous solution by micellar enhanced ultrafiltration, Sep. Purif. Technol. 55 (2007) 117–124.

[14] M. Panizza, A. Barbucci, R. Ricotti, G. Cerisola, Electrochemical degradation of methylene blue, Sep. Purif. Technol. 54 (2007) 382–387.

[15] Lorena L. Garza-Tovar, Leticia M. Torres-Martínez, D. Bernal Rodríguez, R. Gómez, G. del Angel, Photocatalytic degradation of methylene blue on Bi2MnbO7 (M = Al, Fe, In, Sm) sol·gel catalysis, J. Mol. Catal. A Chem. 247 (2006) 283–290.

[16] S. Lakshmi, R. Renganathan, S. Fujita, Study on $TiO_2$ mediated photo catalytic degradation of methylene blue, J. Photo Chem. Photobiol. A Chem. 88 (1995) 163–167.

[17] M. MonaNaim, M.El.Abd. Yehia, Removal and recovery of dyestuff from dyeing wastewater, Sep. Purif. Methods 31 (2002) 171–228.

[18] Marco Panizza, Giacomo Cerisola, Removal of colour and COD from wastewater containing acid blue 22 by electrochemical oxidation, J. Hazard. Mater. 153 (2008) 83–88.

[19] R. Pelegrini, P. Peralta Zalmurade, R. De Andrade Adalgisa, J. Reyes, N. Duron, Electrochemically assisted photo catalytic degradation of reactive dyes, Appl. Catal. B 22 (1999) 83–90.

[20] M. Sundararajan, G. Vishnu, K. Joseph, Ozonation of light shaded exhausted reactive dye bath for reuse, Dyes Pigment 75 (2007) 273–278.

[21] M. Muthukumar, D. Sargunamani, M. Senthilkumar, N. Selvakumar, Studies on decolouration, toxicity and possibility of recycling of acid dye effluents using ozone treatment, Dyes Pigment 64 (2005) 39–44.

[22] G. Muthuraman, K. Palanivelu, Selective extraction and separation of textile anionic dyes from aqueous solution by tetra butyl ammonium bromide, Dyes Pigment 64 (2005) 251–257.

[23] P. Pandit, S. Basu, Removal of organic dyes from water by liquid–liquid extraction using reverse micelles, J. Colloid Interface Sci. 245 (2002) 208–214.

[24] S. Basu, P.R. Malpani, Removal of methyl orange and methylene blue dye from water using colloidal gas aphrons effect of processes parameters, Sep. Sci. Technol. 36 (2001) 2997–3013.

[25] D. Roy, K.T. Valsaraj, S.A. Kottai, Separation of organic dyes from wastewater by using colloidal gas aphrons, Sep. Sci. Technol. 27 (1992) 573–658.

[26] R.D. Roger, B.D. Nauer, Partitioning behavior of group 1 and 2 cations in poly (ethylene-glycol) based aqueous bibasic systems, J. Chromotogr. B 680 (1996) 237–241.

[27] Y. Akama, A. Tong, M. Ito, S. Tanaka, The study of positioning mechanism of methyl orange in an aqueous two phase system, Talanta 48 (1999) 1133–1137.

[28] D.W. Lee, W.H. Hong, K.Y. Hwang, Removal of an organic dye from water using a predispersed solvent extraction, Sep. Sci. Technol. 25 (2000) 1951–1962.

[29] X.J. Yang, A.G. Fane, K. Soldenhoff, Comparison of liquid membrane processes for metal separations permeability, stability and selectivity, Ind. Eng. Res. 42 (2003) 392–402.

[30] G. Muthuraman, K. Palanivelu, Transport of textile dye in vegetable oils based supported liquid membrane, Dyes Pigment 70 (2006) 99–104.