

Extraction of methyl red from industrial wastewater using xylene as an extractant

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Abstract

A laboratory study on the liquid–liquid extraction system has been carried out for the removal and recovery of methyl red from aqueous solutions using xylene as an extractant. The concentration of methyl red has been studied in the range of 1.72×10^{-4} to 1.72×10^{-3} mol L⁻¹. The efficiency of dye extraction increased with increasing time of extraction. Distribution ratio is reasonably high ($D = 49$) even in the presence of inorganic salts. Extracted dye in the organic phase has been stripped into sodium hydroxide solution. The organic solvent is reused for reextraction of the dye from aqueous solution. The efficiency of reused organic solvent was maintained up to 10 runs. Loading capacity of dye has been found to be 14.32 mg. Under optimized conditions, real textile wastewater has been studied and the results are satisfactory.

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Keywords: Liquid–liquid extraction; Distribution ratio; Extractant; Strip; Methyl red; Reextraction

1. Introduction

Dyes are widely used in various industries, such as textiles, leather, plastic, paper and cosmetics, for coloring their final products. The release of colored wastewater from industry may produce an eco-toxic hazard and introduce potential danger of bioaccumulation, which may eventually affect humans through the food chain [1]. Azo dyes are the largest group of dyes used in industry [2]. The term azo dye is applied to synthetic organic colorants that are characterized by a nitrogen-to-nitrogen double bond: $-\text{N}=\text{N}-$ [3]. Durability of azo dyes causes pollution to the environment. Besides, some azo dyes are toxic and mutagenic [4]. Methyl red is an anionic azo dye [5]. It is well known that methyl red dye has been used in paper printing and textile dyeing [6] and it causes irritation of the eye, skin and digestive tract if inhaled/swallowed [7].

It is, therefore, essential to remove the dye from wastewater or treat it in such a way so as to minimize the damage to the environment and also to decolorize the water [8]. Textile wastewater contains residual dyes that are difficult to remove in conventional treatment plants [9].

Various methods have been used to remove dyes from aqueous solutions. The widely used methods include adsorption, coagulation, photocatalytic degradation, ozone treatment, electro Fenton's and hypochlorite treatment [10–19]. The physical methods are non-destructive and merely transfer the pollutants from one medium to another, thus giving secondary treatment [20]. Chemical methods are not economically viable due to high dosage and production of a large quantity of sludge [21–23].

In recent years, much attention has been focused on a separation technique such as solvent extraction or liquid–liquid extraction (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 [24]. The

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advantages of LLE include high throughput, ease of automatic operation and of scale up and high purification [25].

Lee et al. [24] reported the removal of dye from water using predispersed solvent extraction. In this study, kerosene was chosen as the organic solvent and solvent yellow 1 was used as the dye. The removal of anionic methyl orange dye from water was carried out in the presence of cationic hexadecyltrimethylammonium bromide surfactant. And the removal of cationic methylene blue dye was carried out in the presence of anionic sodium dodecylbenzene surfactant solution where amyl alcohol was used as the solvent [26]. Hu et al. [27] reported the recovery of strong acid dye from wastewater by solvent extraction, and multistage counter current extraction and stripping experiments were carried out. The reusability of the organic phase regenerated was tested. Removal of azo dyes from aqueous solutions using Calix [4] arene and β -cyclodextrin was investigated by LLE [28] and dichloromethane has been used as the extractant. The recoveries of methylene blue by LLE with propylene and 1,2-butylenes carbonates were significantly better compared with the cloud point technique. Cloud point technique yielded 10–49% recoveries in the concentration range of 0.01–0.25 mol L⁻¹, whereas LLE yielded almost 100% recoveries [29].

Muthuraman et al. [30] reported the extraction and recovery of methylene blue 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. 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. The solvent used was recycled [31]. The selective extraction and separation of textile anionic dyes from aqueous solution were also reported [32]. Tetra butyl ammonium bromide was used as a carrier and methylene chloride was used as a diluent. The extracted dye was back extracted into salicylic acid and sodium carbonate solution. The stripped solution upon acidification precipitated salicylic acid and the dye was recovered.

In the present study, the recovery of an anionic dye, methyl red, from an aqueous solution has been studied by LLE using xylene as an extractant. Parameters such as, pH in feed, NaOH concentration in strip, effect of time, individual dye concentration, aqueous to organic phase ratio, addition of inorganic salts and organic to aqueous phase ratio have also been studied.

2. Experimental

2.1. Materials

Xylene, methyl red, 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 λ_{\max} and its concentration. The pH of an aqueous solution was measured by a pH meter (WTW, Germany). A mechanical stirrer (IKD-KS 50, Germany) was used for agitation of solutions.

Xylene was used as an extractant. The dye solution was prepared in distilled water. Sodium hydroxide was used as the stripping agent and sulphuric acid was used to adjust pH.

2.2. Procedure

2.2.1. LLE of dye

The organic solvent [(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 a known time in a shaker at 100 rpm. The mixture was then transferred into a separating funnel. A sample of the aqueous solution at the bottom of the separating funnel was withdrawn for absorbance measurement of dye. The experimental set up was the same as that in an earlier work [30]. The wavelength of maximum absorption (λ_{\max}) for methylene red was 412 nm. The structure of the dye is shown in Fig. 1. The distribution ratio (D) and percentage of extraction (E) were calculated by the following equations

$$D = [\text{dye}]_{\text{org}} / [\text{dye}]_{\text{aq}} \quad (1)$$

$$E = 100 \times ([\text{dye}]_{\text{aq0}} - [\text{dye}]_{\text{aq}}) / [\text{dye}]_{\text{aq0}} \quad (2)$$

where $[\text{dye}]_{\text{org}}$ is the dye concentration in organic phase (mg L⁻¹), $[\text{dye}]_{\text{aq0}}$ the initial dye concentration of aqueous phase (mg L⁻¹), and $[\text{dye}]_{\text{aq}}$ the dye concentration of aqueous phase after extraction (mg L⁻¹).

In stripping, the loaded extractant (V_o mL) and the aqueous strippant (sodium hydroxide 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 the analytical parameters were performed in triplicate for each run. A confidence limit of 95% was taken for reliable results.

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.

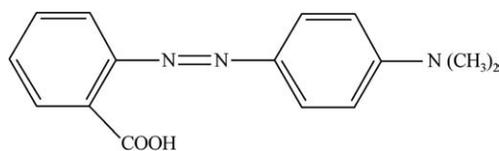


Fig. 1. Structure of methyl red.

3. Results and discussion

3.1. Extraction of methyl red

Anionic methyl red was extracted from aqueous solution using xylene as an extractant. In this section, the effects of pH, initial dye concentration, equilibration time, temperature effect, and loading capacity of dye were studied.

3.1.1. Effect of pH in the aqueous phase

The effect of pH on the extraction of methyl red was investigated at different values of pH in the aqueous phase ranging from 1 to 8 ± 0.2 at 25°C . The results show that extraction efficiency decreased with increasing pH. The maximum extraction of dye was noticed at $\text{pH } 2.5 \pm 0.1$ as shown in Fig. 2. At a $\text{pH} > 3$, the extraction efficiency decreased. The results suggest that at low pH, H^+ combines with dye and improves solubility in xylene. For further studies, it was decided to maintain the pH at 2.5 ± 0.1 at 25°C and the aqueous feed phase concentration was maintained at $1.72 \times 10^{-4} \text{ mol L}^{-1}$.

3.1.2. Effect of solvents

Various solvents such as benzene, toluene, xylene and hexane were tried for the extraction study. Among them, benzene, toluene and xylene extracted the dye very effectively. There was no extraction found in hexane (Table 1). Xylene was used for further studies, since it is less toxic compared to benzene and toluene. About 98% of the dye was stripped into xylene.

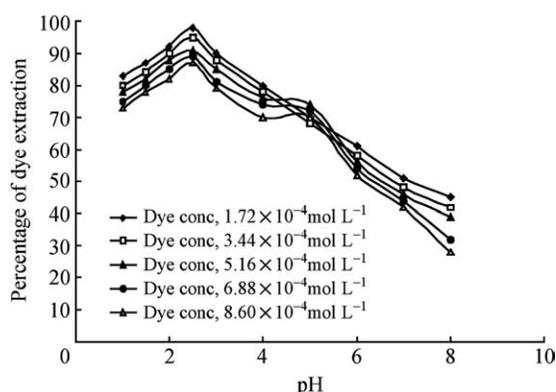


Fig. 2. Effect of pH in the feed solution. (Experimental conditions: volume of source phase = 25 mL, volume of organic phase = 25 mL, dye concentration 1.72×10^{-4} to $8.6 \times 10^{-4} \text{ mol L}^{-1}$, equilibration time = 5 min.)

Table 1
Effect of diluents on dye extraction efficiency.

Diluents	Dielectric constant (ϵ)	% of dye extraction
Hexane	2.02	No extraction
Toluene	2.24	85.3
Xylene	2.26	98.0
Benzene	2.28	96.5

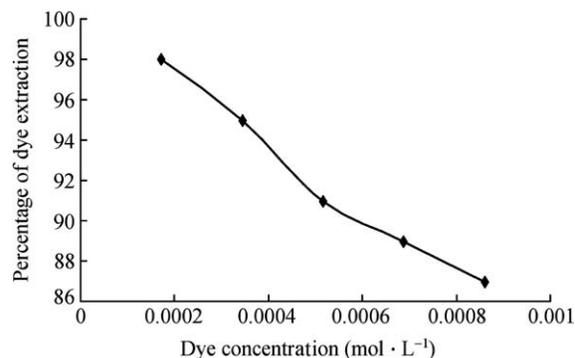


Fig. 3. Effect of initial dye concentration. (Experimental conditions: volume of source phase = 25 mL at $\text{pH } 2.5 \pm 0.1$, volume of organic phase = 25 mL, dye concentration = 1.72×10^{-4} to $8.6 \times 10^{-4} \text{ mol L}^{-1}$, equilibration time = 5 min.)

3.1.3. The effect of initial dye concentration in aqueous phase

Dye was extracted from freshly prepared aqueous solutions with concentration ranging from 1.72×10^{-4} to $1.72 \times 10^{-3} \text{ mol L}^{-1}$. From Fig. 3, the percentage of extraction efficiency decreased from 98% at $1.72 \times 10^{-4} \text{ mol L}^{-1}$ to 87% at $1.72 \times 10^{-3} \text{ mol L}^{-1}$. The percentage of extraction decreased with increasing initial dye concentration. It can be explained that at higher dye concentration, xylene was unable to completely extract the dye from the aqueous phase. However, the absolute amount of dye extracted increased with increase in dye concentration.

3.1.4. Effect of equilibration time

The organic and aqueous phases (xylene–methyl red) were equilibrated for a period of 1–15 min. The results are presented in Fig. 4. The maximum amount of dye was extracted at 5 min. Beyond 5 min, the extraction efficiency remained unchanged. For further studies, the equilibration time was fixed at 5 min.

3.1.5. Effect of temperature

The effect of temperature on extraction of dye from aqueous phase was studied. The extraction rate remained

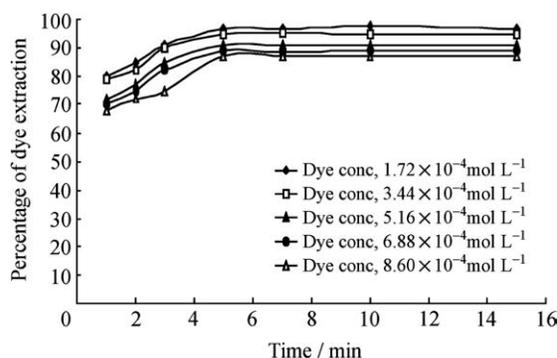


Fig. 4. Effect of equilibration time. (Experimental conditions: volume of source phase = 25 mL at $\text{pH } 2.5 \pm 0.1$, volume of organic phase = 25 mL, dye concentration = 1.72×10^{-4} to $8.6 \times 10^{-4} \text{ mol L}^{-1}$.)

unchanged at 98% from 18 to 28 °C. When the temperature was raised from 28 to 50 °C, the extraction efficiency of dye decreased. So, the effect of temperature is not significant at room temperature for extraction of dye from aqueous solution. Further studies were carried out at 27 °C.

3.1.6. Effect of extraction phase ratio

The volume phase ratio of aqueous to organic phase (A/O) was studied at 27 °C. The extraction efficiencies at different volume ratios are presented in Table 2. About 98% extraction efficiency was achieved from 1:1 to 5:1 A/O ratios; beyond 5:1 A/O ratio, the efficiency of extraction decreased. When the ratio was increased to 10:1, the extraction efficiency dropped from 97% to 90%. The A/O ratio from 1:1 to 5:1 yielded a higher percentage of dye removal from aqueous solution. This could be due to the higher free concentration of organic phase when the aqueous to organic phase ratio (A/O) is lower [30].

3.1.7. Loading capacity of xylene

A volume of 10 mL of xylene and 10 mL of methyl red (100 mg L⁻¹) was mixed and shaken at ambient temperature for 5 min. After extraction, the dye concentration in the raffinate was measured. After each stage of extraction, the accumulated dye content transferred into the organic phase was calculated. The results are shown in Fig. 5. After 11 runs of extraction, emulsion formation was noticed. It is clear from the figure that the loading capacity of xylene for extraction of dye from aqueous solution is 14.32 mg after 15 runs.

Table 2

Effect of extraction phase ratio on percentage of dye extraction with initial dye concentration of 1.72×10^{-4} mol L⁻¹.

Ratio (A/O)	Extracted dye (mol L ⁻¹)	% of dye extraction
1:1	1.68×10^{-4}	98.0
3:1	1.68×10^{-4}	98.0
5:1	1.68×10^{-4}	98.0
7:1	1.63×10^{-4}	95.0
10:1	1.54×10^{-4}	90.0

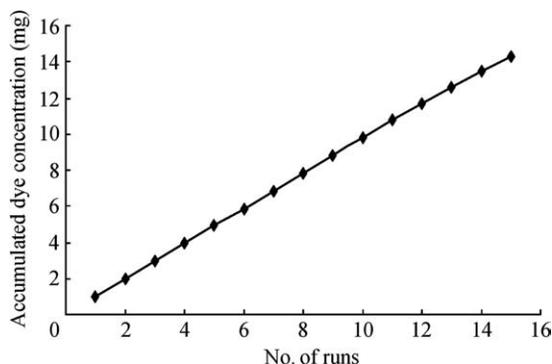


Fig. 5. Effect of loading capacity of dye in xylene. (Experimental conditions: volume of source phase = 10 mL at pH 2.5 ± 0.1 , volume of organic phase = 10 mL, dye concentration = 100 mg L⁻¹, equilibration time = 5 min.)

3.2. Stripping of loaded organic phase

In any extraction process, it is imperative to back extract the extracted species from the organic phase. Sodium hydroxide was used as the stripping agent. The effects of concentration of stripping agent, stripping phase ratio, stripping contact time and stripping temperature were studied.

3.2.1. Effect of stripping reagent concentration

The concentration of stripping reagent plays an important role in stripping dye from the loaded organic phase, and the results are shown in Fig. 6. Sodium hydroxide was used as the stripping agent and its concentration was varied from 0.001 to 0.1 mol L⁻¹. It can be seen from Fig. 6 that the stripping efficiency increased with increasing NaOH concentration. The maximum amount of dye was stripped into 0.05 and 0.1 mol L⁻¹ NaOH solutions. Further increase in NaOH concentration did not improve the efficiency of stripping. Hence, 0.05 mol L⁻¹ NaOH solution was chosen for further studies.

3.2.2. Effect of stripping phase ratio

The stripping phase ratio (organic to aqueous phase, O/A) is an important parameter in stripping processes. From Fig. 7, the percentage of stripping decreased with increas-

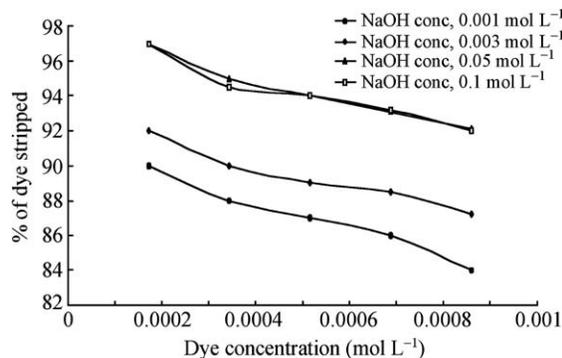


Fig. 6. Effect of stripping reagent concentration. (Experimental conditions: volume of source phase = 25 mL at pH 2.5 ± 0.1 , volume of organic phase = 25 mL, dye concentration = 1.72×10^{-4} to 8.6×10^{-4} mol L⁻¹, volume of stripping reagent = 25 mL.)

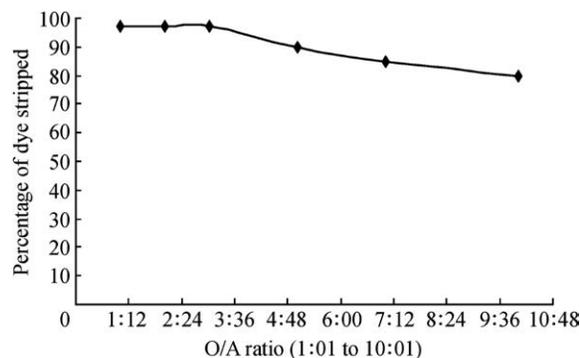


Fig. 7. Effect of stripping phase ratio. (Experimental conditions: volume of organic phase = 25 mL at pH 2.5 ± 0.1 , volume of organic phase = 25 mL, different volume ratio of stripping reagent.)

Table 3
Reusability of solvent.

No. of run	% of dye extraction
0	98
1	98
2	98
3	98
4	98
5	98
6	98
7	98
8	98
9	98
10	98
11	95
12	93
13	90
14	87
15	84

ing O/A ratio. The maximum stripping efficiency was found for the O/A ratio between 1:1 and 3:1. Beyond 5:1 O/A ratio, the efficiency of stripping decreased. This might be due to an insufficient quantity of stripping reagent to neutralize the acid in the organic phase. So, to use a small quantity of stripping agent, the phase ratio O/A of 3:1 was maintained.

3.2.3. Effect of stripping contact time

When a freshly loaded organic solution was used, the stripping efficiency did not increase with increased contact

time in the range of 5–20 min. Maximum stripping was obtained at 10 min. Beyond 10 min, the stripping efficiency remained unchanged. Hence, stripping contact time was fixed at 10 min.

3.2.4. Stripping system temperature

The stripping system temperature affects phase disengagement and stripping. The maximum stripping rate was obtained at lower temperature. At higher temperature, the stripping rate decreased. Xylene could dissolve into the aqueous phase at higher temperature, leading to increase in xylene loss from the organic phase [27]. Thus, the optimized stripping conditions are as follows: concentration of NaOH $5 \times 10^{-2} \text{ mol L}^{-1}$, phase ratio O/A 3:1, and the system temperature 27°C .

3.2.5. Reusability of solvent

Stripped organic solvent was reused to reextract methyl red from aqueous solution. It was found that 98% of dye was extracted at each run and extraction efficiency remained constant up to 10 runs. After 10 runs, the extraction efficiency slightly decreased. The results are presented in Table 3.

3.3. Flow sheet for recovery of methyl red

Based on the above results, a proposed flow sheet for removal and recovery of methyl red from industrial wastewater of methyl red concentration 950 mg L^{-1} is shown in Fig. 8.

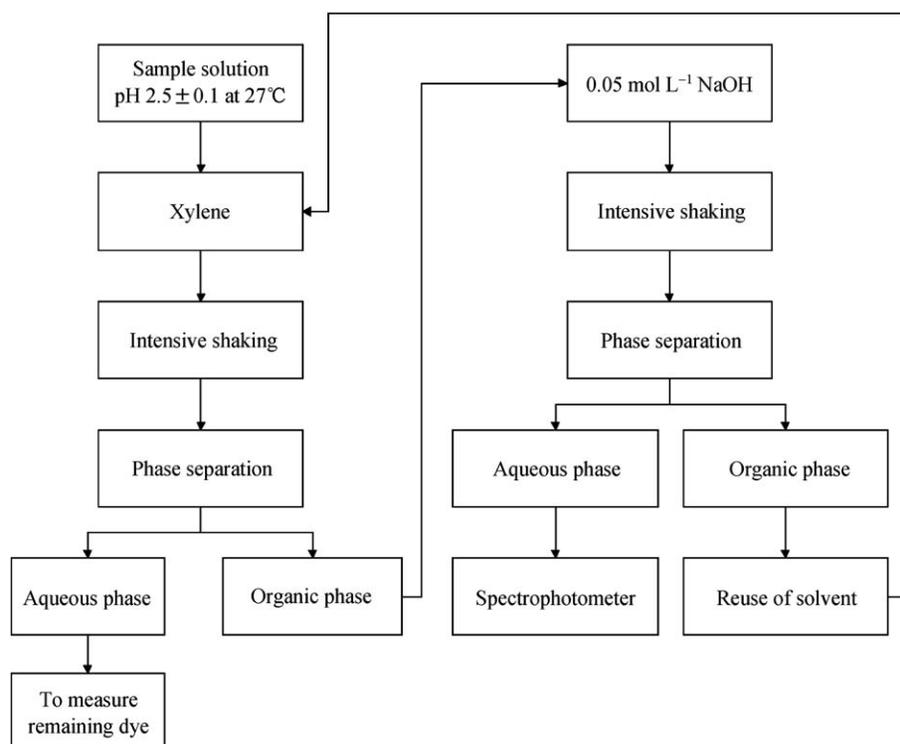


Fig. 8. A proposed flow sheet for extraction and recovery of dye from industrial wastewater.

4. Conclusion

Methyl red was extracted from aqueous solution by LLE and xylene was used as a carrier. Under optimum conditions and depending on initial dye concentration, dye extraction efficiency varied from 97% to 90% in 5 min at the aqueous to organic phase volume ratio (A/O) from 1 to 10. In addition, the loading capacity of xylene was checked. Stripping study was carried out at various concentrations (1×10^{-3} to 1×10^{-1} mol L⁻¹) of NaOH solution. It was found that 5×10^{-2} mol L⁻¹ NaOH solution was suitable for stripping. Stripped organic solvent could be reused up to 10 times without losing extraction efficiency. Under optimized conditions, real textile wastewater was treated, and it was found that extraction efficiency did not deviate much from that of synthetic solution.

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