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Reactive Dye Removal from Simulated Wastewater using Tetrabutyl Ammonium Bromide as an Extractant

Norasikin Othman[a*], Noor Sa'ida Nafisah Mohd Aziz[a], Norlisa Harruddin[a]

[a]*Centre of Lipid Engineering and Applied Research (CLEAR), Department of Chemical Engineering, Faculty of Chemical Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bharu, Johor, Malaysia*

*Corresponding author: norasikin@cheme.utm.my

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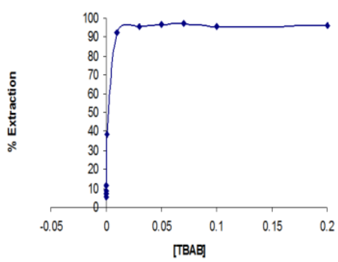
Graphical abstract



Abstract

Dyes caused serious environmental pollution and health problem in many ways. Many dyes have toxic effects on aquatic life and also on humans. Liquid-liquid extraction process is one of the alternatives for dye removal from wastewater. Removal of remazol red 3BS from simulated textile wastewater using tetrabutyl ammonium bromide has been studied at room temperature with total operation time of 18 hours. Several parameters have been studied such as pH, diluents, initial dye concentration, extractant concentration and stripping agents toward the extraction process of the dye. The results show only small effects of pH on the extraction percentage. The best diluent for the extraction is dichloromethane with the percentage of 98%. The percentage of extraction is maximum (97%) at 0.07M of TBAB concentration with the distribution ratio of D= 34.65. Salicylic acid in Na_2CO_3 with the ratio of 1:2 gives the highest percentage of stripping process. It shows a good performance for liquid-liquid extraction of remazol red 3BS for both removal and recovery processes.

Keywords: Reactive dye; textile wastewater; liquid-liquid extraction; dye removal

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1.0 INTRODUCTION

Industries in textile production are very common in most countries and have been expanded in the Middle East and Far East recently [1]. This industries obviously used colorants, as known as dyes to color the fabrics. Increasing demand for better quality and greater quantity of textile goods has resulted in the development of new types of fibres, fabrics and dyes. The removal of color synthetic organic dyestuff from waste effluents becomes environmentally important. It is rather difficult to treat dye effluent because of their synthetic origins and their mainly aromatic structure, which are biologically non-degradable.

The alternative applicable treatment for the removal of color varies considerably depending upon the type of dye wastewater. Many significant physical, chemical and biological treatment methods are employed for treating dye wastewater such as membrane filtration, photodegradation, adsorption, coagulation-flocculation, ion exchange, advanced oxidation, flotation, chemical reduction, ozonation, electrochemical and biological treatment [2, 3, 4].

According to Daneshvar *et al.* [5], the effective methods are by using activated carbon or oxidation process but the cost are really high, since an alternative method which using electrical energy in the process was used. This process has a fast rate of pollutant removal, simplicity in operation, low operating and equipment cost. Meanwhile, Removal of anionic and cationic organic dyes from water by liquid-liquid extraction using reverse micelles was proposed by Pandit and Basu [6].

Liquid-liquid extraction method (LLE) or solvent extraction method is used for the purification, enrichment, separation and analysis of various compounds in mixtures. These are 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 the equilibrium for a given system and efficiency of the extraction process depends on its mass transfer rate [7].

The advantage of solvent extraction includes high through put, ease of automatic operation and of scale up, and high purification. In the present study, solvent extraction of anionic dyes namely Remazol Red 3BS using tetrabutyl ammonium bromide (TBAB) prepared in methylene chloride (dichloromethane) as carrier was studied.

2.0 MATERIALS AND METHODS

2.1 Materials

Tetrabutyl ammonium bromide (TBAB), kerosene (Acros Organic S), Xylene, sodium carbonate (Na_2CO_3), dichloroethane (CH_2Cl_2), sulfuric acid (H_2SO_4)(MERCK KGaA), NaOH, $NaHCO_3$, n-dodecane (GCE Laboratory Chemicals), HNO_3, HCl (J.T Baker), and Salicylic Acid (Ficher Chemical) were used in this study. All the chemicals are the analytical grade reagents. Textile reactive-azo dye which is Remazol Red 3BS was supplied by Perusahaan Nozi Batik, Kuala Terengganu (Malaysia).

The equipment required to measured absorbance was UV/VIS spectrophotometer (Cole Parmer 1100RS). TBAB was used as extractant and dissolved in dichloromethane. Sodium carbonate in salicylic acid was used as stripping agent and NaOH and H_2SO_4 were used to adjust the pH. The pH of an aqueous solution was measured by a pH meter (Delta 320, Germany). For agitation of solutions a mechanical shaker was used (IKA-KS 130 Basic, Germany). The dye solution was prepared in distilled water.

2.2 Liquid-liquid Extraction of Dye

The organic solvent (TBAB + CH_2Cl_2) used for extraction was added to the prepared aqueous remazol red 3BS dye solution in a conical flask and the conical flask was shaked at 320 rpm for 18 hours. The solution was then transferred into a separating funnel and an additional time was taken to make it to be settled for about 15 min. Sample of aqueous solution at the top of the separating funnel was taken for absorbance measurement of dye.

The concentration of remazol brilliant red 3BS dye remaining in the aqueous phase was then being determined spectrophotometrically at $\lambda_{max} = 511$ nm . The distribution ratio (D) and percentage of extraction (E) were calculated using Equations 1 and 2.

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

$$E = \left(\frac{[dye]_{aq0} - [dye]_{aq}}{[dye]_{aq0}}\right) x100 \quad (2)$$

Where;
$[dye]_{org}$ is the dye concentration in the organic phase (ppm),
$[dye]_{aq0}$ is the initial dye concentration of aqueous phase (ppm),
$[dye]_{aq}$ is the dye concentration of aqueous phase after extraction (ppm).

For stripping part, the loaded extractant and the aqueous strippant (acid solution) were added together into a conical flask and shaked at 320 rpm within 18 hours. The mixture was then being transferred into a separating funnel and waited for another 15 min for phase separation. The aqueous strippant was taken for dye concentration measurements. All the experimental parameters were performed in three replicates for each run.

3.0 RESULTS AND DISCUSSION

3.1 Effect of pH of Feed Phase

The effect of pH of the source phase on the efficiency of dye extraction is shown in the Figure 1. Aqueous solutions were maintained in the range of pH 2–12 to study dye extraction efficiency. The results had been revealed that there were only small effects of the changes of pH towards the dye extraction. Therefore, the effect of pH from 2 to 12 can be considered as negligible in this study due to its minimal fluctuation. This is in agreement with Nerud *et al*. [8] and Bali *et al*. [9] which stated that the rate of decolorization was not affected by pH in the range of 3-9 and that the system has an advantage over the Fenton Oxidation system which is highly pH dependent. For further study, it is decided to maintain the pH at 7 ± 0.1 or in the other word; without any pH adjustment.

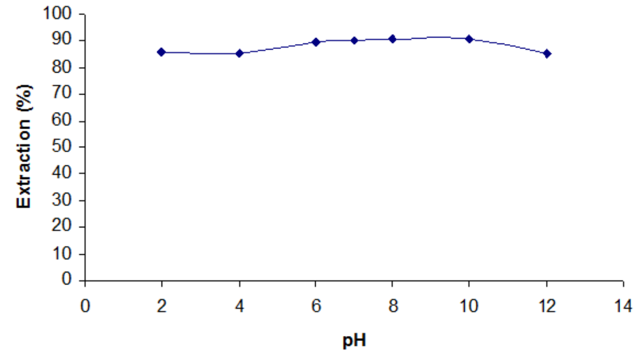

Figure 1 Effect of pH on dye extraction (Experimental conditions: dye concentration-100ppm; TBAB concentration- 0.7M; volume of aqueous-10mL; volume of organic-10mL)

3.2 Effect of Diluents on Dye Extraction

The effect of diluents towards the extraction efficiency of remazol red 3BS dye is shown in Figure 2. The results revealed that the extraction were high with dichloromethane and chloroform due to their percentage of 98% and 99% respectively. The graph showed that there were very minimal extraction found with other solvents such as kerosene, n-dodecane, toluene and xylene. This is due to the polarity of these solvents, which the polarity of both dichloromethane and chloroform were higher than the other solvents to be good solvents [10].

However, chloroform is more toxic and carcinogenic than dichloromethane and it has been replaced by dichloromethane and other solvents in most industrial degreasers and paint removers [11]. Therefore, CH_2Cl_2 was chosen as the best solvent in this study and thus subsequent studies were carried out with CH_2Cl_2 as the solvent.

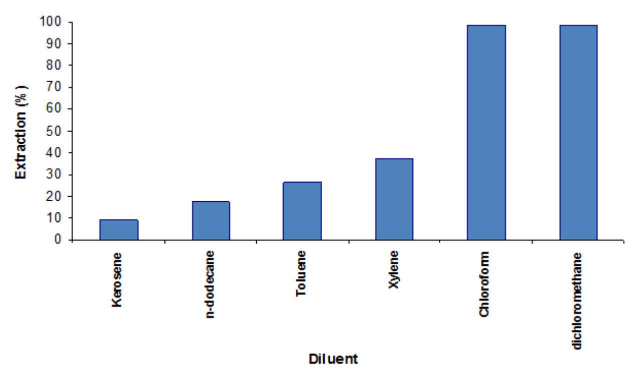

Figure 2 Effect of diluent on extraction of dye (Experimental conditions: dye concentration-100ppm; TBAB concentration- 0.7M; pH of aqueous- 7 ± 0.1; volume of aqueous-10mL; volume of organic-10mL)

3.3 Effect of TBAB Concentration on Dye Extraction

The effect of tetra butyl ammonium bromide concentration on distribution ratio (D) of the dye was investigated in the concentration range of 5.0×10^{-6} M to 0.2 M. Figure 3 shows that the percentage of dye extraction is increased with increasing of tetra butyl ammonium bromide (TBAB) concentration. In order to determine the stoichiometric reaction of dye and carrier, the distribution ratio (D) of dye was calculated at different molar concentrations of TBAB.

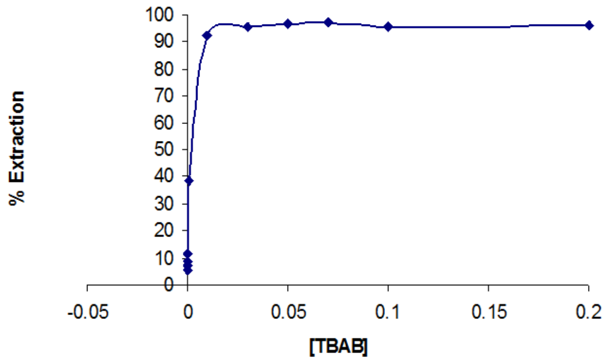

Figure 3 Effect of extractant (TBAB) concentration on the extraction of dye (Experimental conditions: dye concentration-100ppm; volume of aqueous-10mL; volume of organic-10mL; diluent used-dichloromethane)

Figure 4 shows the plot of log D versus log [TBAB] that gives a straight line with the slope of 0.75 indicating that dye to carrier ratio was 1:1 and forms 1:1 ratio complex. Thus, it can be assumed that 1 mole of TBAB extracts 1 mole of dye. One $(Dye)^-$ molecule combines with one tetra butyl ammonium cation to form an ion-pair as evident from 1:1 stoichiometry of the extracted complex. The reaction for extracting the dye is shown in Figure 5.

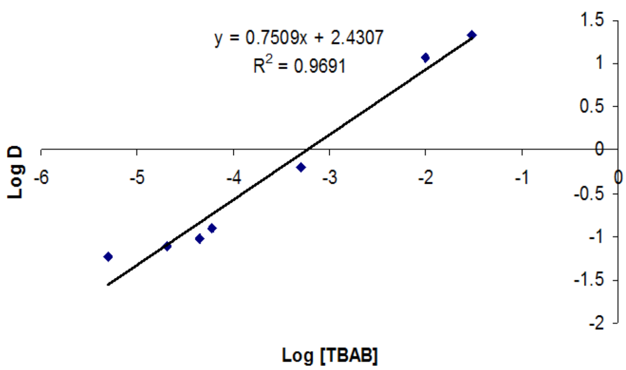

Figure 4 Effect of extractant (TBAB) concentration on the distribution ratio (D) of dye (Experimental conditions: dye concentration-100ppm; volume of aqueous-10mL; volume of organic-10mL; diluent used-dichloromethane)

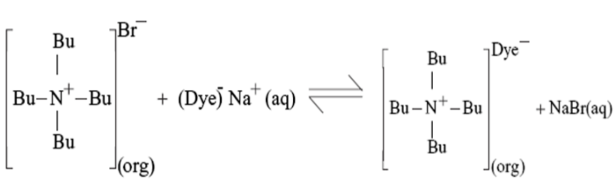

Figure 5 The reaction mechanism of dye extraction

The behavior of the extraction with the increasing of TBAB concentration is clearly shown in Figure 6 for the low concentration part. In the absence of TBAB, the dye would not be extracted in organic phase, prove that positively charged TBAB cation is necessary to extract the anionic dye. In the presence of TBAB, the extraction process had increased slowly for very low concentration of TBAB because the amount of TBAB is not enough to extract the dye. The extraction is start increasing rapidly when the concentration of TBAB was 4.5×10^{-5} because the amount of TBAB is appropriate to initiate the reaction.

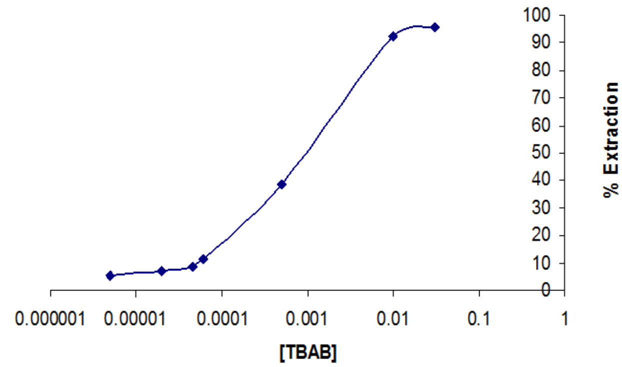

Figure 6 Effect of TBAB concentrations on the extraction of dye in the low TBAB concentration region (Experimental conditions: dye concentration-100ppm; volume of aqueous-10mL; volume of organic-10mL; diluent used-dichloromethane)

From Both Figures 3 and 6, it can be seen that the extraction efficiency is keep increasing until 0.05M concentration of TBAB. Further excess of TBAB for a given concentration has no considerable effects on the extraction efficiency since the graph is maintained after 0.05M of TBAB. It is happened because all dye had been used and no more dyes left to react with TBAB. Further studies were carried out using 0.07M of TBAB in CH_2Cl_2.

3.4 Effect of Initial Dye Concentration

The effect of initial dye concentration on the extraction process had been tested at 0.07M of TBAB in dichloromethane as shown in Figure 7. It can be seen that the percentage of dye extraction decreased with the increase of initial dye concentration. The results revealed that the highest percentage of 99% of the extraction is obtained at the dye concentration of 50ppm and the percentage is being decreased with further increased of dye concentration. This is because the capacity of TBAB is not enough for extracting the dye for a given TBAB concentration since TBAB concentration is being fixed during this study. Thus, the percentage of extraction is decreased with the increasing of initial dye concentration.

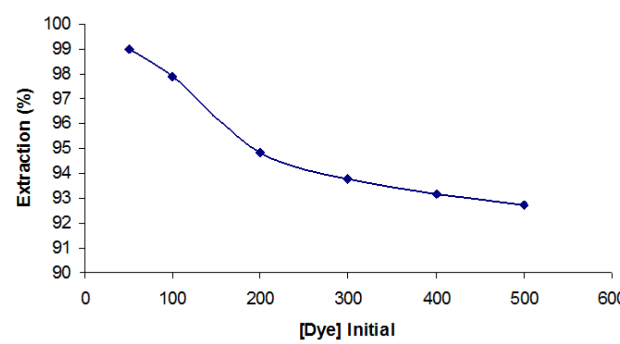

Figure 7 Effect of initial dye concentration on the extraction of dye (Experimental conditions: extractant concentration-0.07M; volume of aqueous-10mL; volume of organic-10mL)

3.5 Effect of Stripping Agents

In any of the extraction process, it is imperative to back extract the extracted species from organic phase and allow recycling of the organic phase without loss of the efficiency. Various inorganic and organic anions were investigated for the dyes recovery. The effect of stripping agents on the extraction of dye is shown in Table 1.

Table 1 Effect of stripping agent on extraction of dye

Stripping Agent (1M)	% Stripping
H_2SO_4	2.736
HCl	0.36
NaOH	0.176
HNO_3	1.4
Na_2CO_3	0.248
$NaHCO_3$	1.032

It can be seen that inorganic anions like SO_4^{2-}, Cl^-, OH^-, NO_3^-, CO_3^{2-} and HCO_3^- were ineffective in stripping the dye as the results revealed <10% of stripping percentage when stripped with sulphuric acid, hydrochloric acid, sodium hydroxide, nitric acid, sodium bicarbonate and sodium carbonate. This is because there were no salting agents that can activate them to strip the dye from organic solvent.

Further studies were carried out in the presence of water insoluble salicylic acid that dissolved in those stripping reagents. Sulphuric acid, hydrochloric acid, and nitric acid still give the percentages lower than 10% because they were not reacted with salicylic acid to form sodium salicylate to strip the dye. However, the existing of salicylic acid in Na_2CO_3 solution provides good extraction (72%). The result indicates that salicylic acid in Na_2CO_3 have a potential to strip the dye. The reaction of stripping the dye is shown in Figure 8.

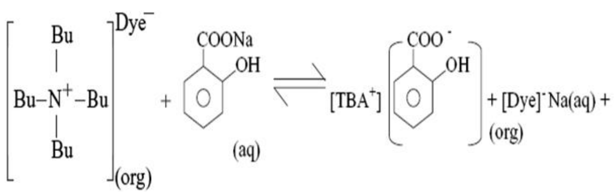

Figure 8 The reaction mechanism of stripping process of dye

The study was continued by varying the concentration of salicylic acid and Na_2CO_3 in the range of 1M – 2M to determine the Na_2CO_3 to salicylic acid ratio. Based on the result, dye stripping was maximum (98%) with 2:1 Na_2CO_3 to salicylic acid ratio. Hence, Na_2CO_3 with the presence of salicylic acid (2:1) was chosen for the stripping purpose.

4.0 CONCLUSION

The laboratory-based analysis method presented seems to be promising and offers a simple approach for liquid-liquid extraction of anionic remazol brilliant Red 3bs dye for removal and recovery. Tetrabutyl ammonium bromide (TBAB) in dichloromethane is able to extract more than 98% of anionic remazol red 3bs dye from aqueous solution. The percentage of dye extraction is high and acceptable enough (90%) at its natural pH of 7 ± 0.1 and 98% of dye loaded can stripped using 1:2 ratio of salicylic acid in Na_2CO_3.

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