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Liquid-liquid Extraction of Black B Dye from Liquid Waste Solution Using Tridodecylamine

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ABSTRACT

Textile batik industry produces wastewater which contributes to water pollution since it utilizes a lot of organic and inorganic chemicals especially dyes. Decolourization of wastewater is very important before discharged. This study explores the liquid-liquid extraction method to recover or to remove Black B dye from batik industry wastewater using tridodecylamine (TDA) in kerosene. The important parameters governing the extraction behaviour of Black B have been investigated such as pH of the source phase, extractant concentration, dye concentration and stripping agent. The experiment was carried out in batch process. Almost 98% of dye was extracted using 0.04 M TDA and pH 4 of source phase. The extraction of dye decreased as the pH of solution increased. The dye loaded in organic phase was back extracted using various types of inorganic acids and bases as stripping agent. The result found that almost 100% of dye was stripped using 0.5 M Thiourea in 1 M sodium hydroxide solution. As a conclusion, Black B dye recovered successfully using TDA in kerosene at favourable condition.

Key words: Liquid-liquid extraction, Black B, textile batik industry, tridodecylamine, sodium hydroxide

INTRODUCTION

Disposal of synthetic dyes in the form of wastewater effluents poses severe hazards to the environment as these effluents contain large amount of surfactants, suspended solids, trace metals, color and have high Chemical Oxygen Demand (COD) (Kim *et al*., 2004). Textile wastewater is coloured effluent and the released of these wastes into receiving waters are contributed to the water pollution. Coloured effluents have been produced, most certainly, since the dyeing technique was invented. Dyes have an adverse aesthetic effect because they are visible pollutants which affect photosynthetic activity in aquatic life due to reduced light penetration (Jusoh *et al*., 2004). Recently, more researchers had concerned on the treatment of dye wastewater as the environmental contamination by dye wastewater has becomes a great environmental problem (Shin *et al*., 2004). The majority of synthetic dyes currently used are the highly water soluble azo-reactive dyes. Azo dyes are characterized by the existence of nitrogen-nitrogen double bonds (-N = N-) and the bright color of their aqueous solutions. The azo-reactive dyes are used extensively in textile industries to their favourable characteristics of bright color, water-fast and simple application techniques with low energy consumption (Asouhidou *et al*., 2009). The main pollution

source of textile wastewater as in batik industry comes from the dyeing processes. Remazol Black B is one of reactive dye that commonly used for dyeing silk in Malaysia.

Remazol Black B was characterized as an azo dyes because of the existing nitrogen to nitrogen double bonds (-N = N-). There are some studies has been done to treat effluent containing Black B. Black B reactive dye has been analyzed using capillary electrophoretic to monitor residual liquors and effluents but also to aid in optimization of dye synthesis, purification, formulation and application (Tapley, 1995). Removal of Black B using biological treatment which is microbial decolorization of black B in a sequential anaerobic-aerobic system was studied (Supaka *et al*., 2004). Degradation of reactive Black B in photo/ferrioxalate system was also reported (Huang *et al*., 2007). This method is also called as a photo Fenton reaction process. A further studied using Fenton process has been carried out by compared the oxidation of Reactive Black B by different advanced oxidation processes which are Fenton, electro-Fenton and photo-Fenton (Huang *et al*., 2008).

There are several types of method have been studied for removal of dye from industrial effluent. Liquid-liquid extraction is one of the methods that used for dye removal. Liquid-liquid extraction defines as purification enrichment separation and analysis of various compounds in mixtures. It is a basic technique in chemical laboratories that 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 (Dong *et al*., 2000). The advantage of solvent extraction includes high through put, ease of automatic operation and of scale up and high purification (Yang *et al*., 2003). 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. Therefore, liquid-liquid extraction is applicable for removal of dye from wastewater. An organic dye removal from water using a predispersed solvent extraction was investigated by Dong *et al*. (2000). Removal of organic dyes from water by liquid-liquid extraction using reverse micelles was reported by Pandit and Basu (2002). Pandit and Basu (2004) are also reported the treatment of ionic dyes from water by liquid-liquid extraction using reverse micelles. Selective extraction and separation of reactive textile anionic dyes by tetra butyl ammonium bromide were studied by Muthuraman and Palanivelu (2005). Recently, this method was used for extraction and recovery of methylene blue from industrial wastewater using benzoic acid as an extractant (Muthuraman and Palanivelu, 2009).

In the present study, the extraction and recovery of Remazol Black B, an azo dye by liquid-liquid extraction using TDA in kerosene as an extractant was studied. The percentage of dye extraction and stripping potential were investigated and operating conditions were optimized.

MATERIALS AND METHODS

This study was conducted at the Department of Chemical Engineering, University of Technology Malaysia, in September 2009.

Materials: The commercial batik dye, Remazol Black B was obtained from Batik industry, Kuala Terengganu. Tridodecylamine was obtained from Merck (M) Sdn. Bhd. as an extractant and kerosene from Acros Organics as diluents. Sulphuric acid, hydrochloric acid, sodium hydroxide and sodium carbonate as stripping agents were obtained from Merck (M) Sdn. Bhd. and Thiourea from GCE Laboratory Chemicals. The extractant, diluent and stripping agent used are industrial grade and used as received. The dye solution was prepared in distilled water. Sulphuric acid and sodium hydroxide were used for pH adjustment.

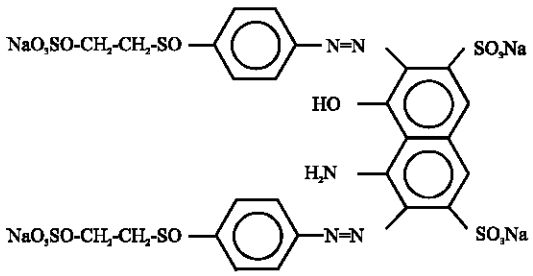

Fig. 1: Chemical structure of Remazol Black B

The apparatus used were shaker IKA KS 130 BASIC for extraction process and spectrophotometer Cole Parmer 1100 RS to measure the absorbance of dye and to establish its maximum wavelength and its concentration. The percentage of extraction (E) and distribution ratio (D) were calculated as the following equations:

$$E = \frac{[day]_{org} - [day]_{aq}}{[day]_{org}} \times 100 \quad (1)$$

$$D = \frac{[day]_{org}}{[day]_{aq}} \times 100 \quad (2)$$

Where:
$[dye]_{org}$ = Concentration of dye in organic phase
$[dye]_{aq}$ = Concentration of dye in aqueous phase

Experimental procedures: For the extraction process, 5 mL of Black B dye solution and 5 mL tridodecylamine in kerosene mixed together in a 25 mL of conical flask and shake for 18 h on a mechanical shaker. After that the sample was poured into separating funnel and let for phase separation for 15 min. The aqueous phase was taken out and analyze their absorbance using spectrophotometer Cole Parmer 1100RS. Same procedure was followed for stripping process. The dye loaded organic phase was mixed with stripping agents. After phase separation, the concentration of the extracted dye and the percentage of extraction determined. The wavelength of maximum absorption (λ_{max}) for Black B was 595 nm. The chemical structure of Black B is shown in Fig. 1.

RESULTS AND DISCUSSION

Effect of pH: Figure 2 shows the effect of pH on dye extraction. The pH was varies from 2 to 12. The experiment was carried out at fixed extractant and dye concentration. The results show that the percentage of dye extraction increased as the pH increase from pH 2 to pH 4 and drastically decreased at pH 6 and further and no extraction at pH 12. The results reveal that the maximum extraction of dye had occurred at pH 4 with 98% extraction. It may be that at low pH the solution become acidic and rich in positively charge, so the anionic Black B dye which is rich in negatively charged can react at maximum rate. Furthermore, at lower pH H^+ ion concentrations is high and allow the anionic dye to forms an ion-pair complex with cationic TDA (Palanivelu *et al.*, 2006). On

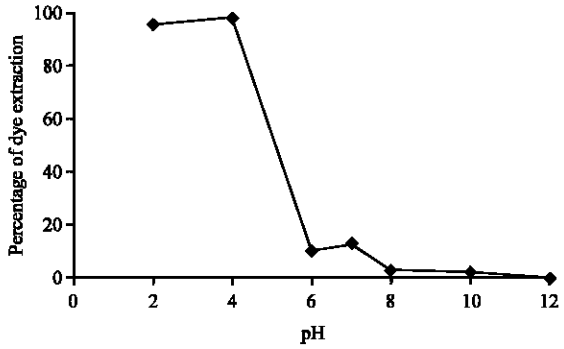

Fig. 2: Effect of pH of source phase on the extraction process (Experimental condition: [Tridodecylamine] = 0.5 M, 5 mL, [Black B] =100 ppm, 5 mL, diluent = kerosene, extraction time = 18 h)

Table 1: Effect of diluents on dye extraction efficiency (Experimental condition: pH = 4, carrier concentration; [TDA] = 0.3 M, [Black B] = 50 ppm, agitation speed = 320 rpm, T = 27±1°C).

Diluents	Dielectric constant (Sekine and hasegawa, 1977)	Percentage of dye extraction (%)
Kerosene	2.0-2.2	93.71
Toluene	2.24	92.48
Xylene	2.26	93.01
Chloroform	4.81	83.73
Methylene chloride	9.08	84.80

the other hand, the extraction of cationic methylene blue dye using benzoic acid is high in basic solution. This indicated that the most efficient liquid-liquid extraction for 100 ppm Black B dye with 0.5 M TDA in kerosene is at pH 4. Thus, for further test, it was decided to maintain the extraction pH at 4±0.1.

Effect of diluents: The extraction was carried out using different diluents such as kerosene, toluene, methylene chloride, xylene and chloroform. Table 1 shows the maximum extraction efficiency of Black B was achieved with all of the diluents. However, kerosene is chosen as diluent because it is less toxic compared to the other diluents. Therefore, succeeding tests were carried out using kerosene as diluents and about 93.71% of dye was extracted into the solvent. The both diluents of methylene chloride and chloroform are not chosen because there are easily evaporated and the percentages of black B extraction are lower compared to other diluents. However, the dichloromethane is a good solvent for other extractant such as Tetrabutyl ammonium Bromide which is using to extract textile anionic dyes (Muthuraman and Palanivelu, 2005). From Table 1 the result is similar to Muthuraman and Tjoon (2009) where high dielectric constant shows lower extraction efficiency.

Effect of extractant concentration: The effect of TDA concentration on distribution ratio (D) of the Black B dye was next investigated in the concentration range of 0.01 M to 0.1 M. Figure 3 shows that the percentage of Black B dye extraction increases as the concentration of TDA increased. The dye extraction increases up to 98% from 0.01 to 0.04 M. Further increases the concentration of extractant the percentages of extraction almost plateau due to excess of extractant. The concentration of extractant used to remove Black B is high compared to the concentration of extractant used to remove basic dyes such as methylene blue. A possible explanation for this might

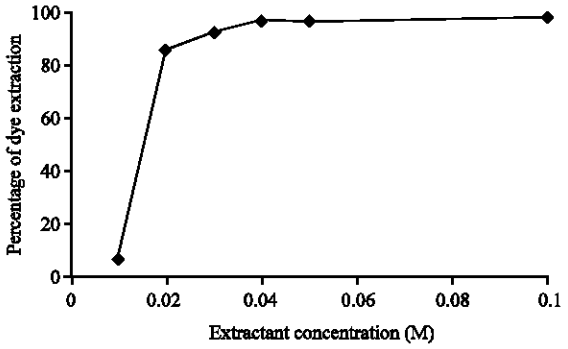

Fig. 3: Effect of extractant concentration on Black B extraction (Experimental condition: [Black B] =100 ppm, 5 mL, pH = 4, diluent = kerosene, extraction time = 18 h)

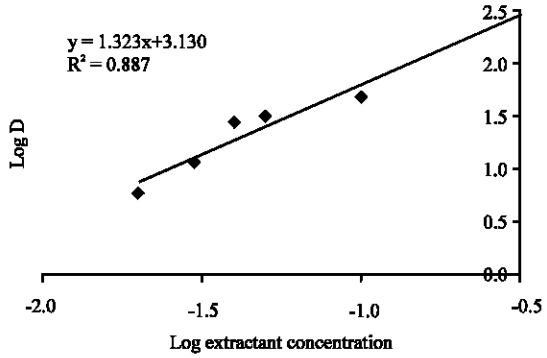

Fig. 4: Distribution ratio of extraction process (Experimental condition: [Black B] =100 ppm, 5 mL, pH = 4, diluent = kerosene, extraction time = 18 h)

be that the structure of azo dye for Black B is complex compared to methylene blue basic dye. The cationic TDA is very strong to cause the cleavage of the azo bond of Black B and leads to the colourization of dye (Tchatchueng *et al.*, 2009). Therefore, the suitable extractant concentration for optimum dye extraction is 0.04 M due to economic factor since the TDA is quite expensive. From the experimental results, there is confirmed that TDA in kerosene is an effective extractant for Black B dye.

To determine the nature of extraction of Black B dye, different concentration of tridodecylamine in organic was studied. The distribution ratio (D) of Black B dye was calculated and the results were presented in Fig. 4 in the form of Log D against Log extractant concentration. Figure 4 plots the distribution ratio of Black B dye increases with increasing initial TDA concentration in the organic phase. It gives a straight line with a slope value of 1.323 indicating that Black B dye to extractant concentration ratio was best at 1: 1 complex. It can then be assumed that 1 mol of TDA can best extract with 1 mol of Black B dye.

Effect of dye concentration: The effect of initial dye concentration on the extraction process was tested at fixed concentration of 0.1 M tridodecylamine in kerosene with the concentration of Black B dye solution in range of 50 to 500 ppm. Figure 5 shows that the percentage of Black B dye extraction decreased with increases in initial dye concentration. At initial dye concentration of 50 ppm, almost 100% of extraction was obtained, while the percentage of extraction is 85% at

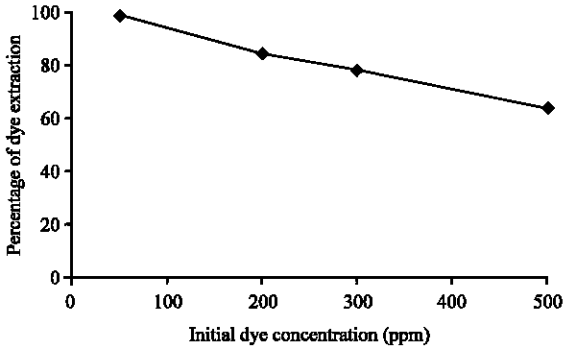

Fig. 5: Effect of dye concentration on extraction process (Experimental condition: [Tridodecylamine] = 0.1 M, 5 mL, volume of Black B = 5 mL, pH = 4 diluent = kerosene, extraction time = 18 h)

Table 2: Effect of stripping agent on extraction process (Experimental condition: [Tridodecylamine] = 0.3 M, 5 mL, [Black B] = 50 ppm, 5 mL, diluent = kerosene, extraction time = 18 h)

Stripping agent (1 M)	Dilution	Abs	Conc.(ppm)	%Stripping
HCl	1	0.1086	4.02	19.18
H_2SO_4	1	0.0140	0.52	2.47
NaOH	1	0.4430	16.41	78.24
Na_2CO_3	1	0.3558	13.18	62.84

Table 3: Effect of stripping agent with thiourea on extraction process (Experimental condition: [Tridodecylamine] = 0.3 M, 5 mL, [Black B] = 50 ppm, 5 mL, diluent = kerosene, extraction time = 18 h)

Stripping agent (1M)+ Thiourea (0.5 M)	Dilution	Abs	Conc. (ppm)	%Stripping
HCl	1	0.0630	2.33	11.13
H_2SO_4	1	0.0164	0.61	2.90
NaOH	1	0.5808	21.51	100.00
Na_2CO_3	1	0.3730	13.81	65.88

200 ppm. It is indicate that 50 ppm dye was saturated when using 0.1 mol TDA. Further increases in dye concentration, the percentage of extraction decreased because of the excess of dye in the solution cannot react with the limited extractant in the solution.

Effect of stripping agent: It is important to back extract the extracted dye from the organic phase and allow recycling of the organic solvent without loss of efficiency in liquid-liquid extraction process. Various inorganic acids and bases were used in this study such as hydrochloric acid, sulphuric acid, sodium hydroxide and sodium carbonate as stripping agent. In this study there were two parts of stripping process.

In the first part of stripping process, various inorganic acids and bases with concentration of 1 M for hydrochloric acid, sulphuric acid, sodium hydroxide and sodium carbonate were used as stripping agent. Second part, all these inorganic acids and bases mixed with 0.5 M of thiourea to enhance the stripping process. This is because of the inorganic acids and bases did not give high percentage of stripping, thus water insoluble thiourea was added to the mixture to form strong acid/base to assist the stripping process.

From Table 2 and 3, the result shows that 1 M of sodium hydroxide with 0.5 M of Thiourea capable to strip the Black B dye very well from the dye loaded organic phase compared to others

inorganic acids or bases. It shows that the presence of 0.5 M thiourea in 1 M of sodium hydroxide solution provide the higher percentage of stripping process which is almost 100% of Black B dye was stripped. The acidic solution give low extraction efficiency for Black B as anionic dyes. However, Sulfuric acid is the best stripping agent for cationic dye such as methylene blue. The result reveal that the 0.5 M thiourea in 1 M of sodium hydroxide solution is the best stripping agent for Black B dye in tridodecylamine. Hence, thiourea in sodium hydroxide with 1: 2 M ratio was chosen for stripping purpose.

CONCLUSION

Based on this study, the developing of liquid-liquid extraction is possible to extract the Black B dye from its solution. From the presented data, the result shows that almost 100% of Black B dye was extracted. The efficiency of extraction is affected by the pH of the source phase. Percentage of extraction decreased at higher pH and the optimum pH for maximum extraction is pH 4. Meanwhile, as the concentration of extractant increase the percentage of extraction was increased. The favourable concentration of TDA for good extraction of 50 ppm Black B dye was 0.04 M. For stripping process, the best stripping agent for Black B dye is 0.5 M thiourea in 1 M of sodium hydroxide solution. These advantages present tremendous method to be promising and might be of interest to use in other textile industries containing dye effluent.

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