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RESEARCH ARTICLE

Kinetic extraction of basic dye using vegetable oil as a solvent

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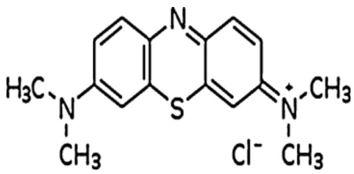
Graphical abstract



Abstract

Vegetable oil such as palm oil and corn oil are more environmentally friendly and economic compared to petroleum based solvent. In this study, liquid-liquid extraction (LLE) of basic dye methylene blue (MB) from simulated textile wastewater using di(2-ethylhexyl) phosphoric acid (D2EHPA) in vegetable oil was investigated. The parameter of extraction studied included types of solvent, D2EHPA concentration, types and concentrations of stripping agent and initial pH of aqueous waste solution. D2EHPA concentration was varied in the range of 0.005 - 0.50M. The results showed that palm oil provided good potential as a solvent in the MB extraction. Almost 100% of MB was extracted at 0.1M D2EHPA in palm oil with distribution ratio of 38 which is reasonably high. The extracted MB in loaded organic phase are capable to re-extracted back for dye recovery using 0.6M of sodium bicarbonate ($NaHCO_3$) as a stripping solution.

***Keywords*:** Palm oil, methylene blue, textile wastewater, removal, liquid-liquid extraction

INTRODUCTION

Dye is the most obvious indicator of water pollution. It was used widely in various industries such as, cosmetic, rubber, paper, textile in order to become colouring agents to the products [1]. Normally, basic dyes are commonly applied to polyester fibers, wool, silk, and acrylic fibers due to increasing development in production of synthetic fiber lately [2]. Every year, an enormous volume of coloring agents were made. Also, there are more than 10,000 dyes that are commercially available with variety chemical and physical properties [3]. The existence of lower concentration of dyes in wastewater which is less than 1 ppm for some dyes is highly detectable and harmful [4]. The dyes upset the biological activity in water bodies. They also pose a problem because they may be mutagenic and carcinogenic and can cause severe damage to human beings, such as the dysfunction of kidney, reproductive system, liver, brain and central nervous system [5-6].

Therefore, before discharged into the environment, industrial effluents containing dyes must be treated. The treatment methods include membrane filtration, photodegradation, adsorption, coagulation-flocculation, ion exchange, advanced oxidation, flotation, chemical reduction, ozonation, electrochemical, solvent extraction and biological treatment but meet some limitations [7-10]. Currently, the most widely used combination of techniques for dye removal from dye-containing industrial effluents is by physio-chemical means. Adsorption of dye stuffs on cotton fabric wastewater using semi-activated carbon has been proposed by Ozoh [11]. The problem regarding to this method is disposal approach of the spent activated carbon after removing of dye stuffs. Besides, removal and recovery of acid dyes from wastewater using ion exchange were investigated by many researchers [12]. Ahmad *et al.* reported that membrane separation process offered the method for increasing the removal of dyes [13]. However, fouling membrane is the main problem for this technique. Solvent extraction or liquid-liquid extraction (LLE) has been successfully studied for both anionic and cationic dyes from wastewater [14, 15]. They found that almost 100% of dyes were extracted. The principle of this methods is solute can distribute itself in a certain ratio between two immiscible diluents/solvents. It will affect the equilibrium of the system that was rely on the selected of both diluent and carrier. The advantage of liquid-liquid extraction includes high purification, ease of automatic operation and scale up and high through put. The importance parameter affecting liquid-liquid extraction process is carrier concentration, stripping agent concentration and pH of feed solution.

In this research study, the efficiency of LLE of MB using D2EHPA in palm oil as organic phase/solvent was studied. The palm oil is produced from harvested fruits bunches of oil palm trees which is abundant in Malaysia. It is harmless to health and environment compared to petroleum based solvent in terms of toxicity and biodegradability. Thus, the objective of this study is to determine the feasibility of using vegetables oil as a solvent in extraction of MB from simulated wastewater. Investigation on the dye extraction and stripping performance were study. Also, operating conditions were optimized.

EXPERIMENTAL

Chemicals and reagents

The following reagents were used: methylene blue (minimum assay of 82%) from QRec, di(2-ethylhexyl) phosphoric acid (D2EHPA) (assay of 95%) from MERCK, SPAN 80 (assay of 99%) from Sigma, kerosene (assay of 78%) from Sigma, palm oil and corn oils from Lam Soon Edible Oils Sdn. Bhd. Malaysia. For stripping agent; sodium hydroxide (NaOH) (98% assay) and NaCl (99% assay) were obtained from J.T. Baker. $NaHCO_3$(99.5% assay) was obtained from GCE laborotary chemical and Na_2CO_3 obtained from EmSure®(99% assay). All the chemicals were of analytical grade and used without further purification.

Experimental procedures
Preparation of MB solution

Methylene blue (MB) IUPAC name is 3,7- bis(dimethylamino)-phenothiazin-5-ium chloride. It is a cationic dye. It is classified as CI Basic blue 9, CI solvent blue 8, CI 52015. It has a molecular formula $C_{16}H_{18}N_3ClS$ and molecular weight of 319.85 g/mol. The MB used was of analytical grade so it was used without further purification. A stock solution of 1000 mg/L 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.

Extraction and stripping process

Equilibrium solvent extraction were divided onto two reaction which is forward and backward extraction. Equal volumes (10ml) of organic solution which contain 0.1M of D2EHPA in palm oil and 25ppm of simulated methylene blue solution were mixed using mechanical shaker at 320rpm for 18 hours. After forward extraction completed, the mixture was carefully poured into the separating funnel for phase separation (15 min). The bottom part of treated aqueous solution was carefully separated from the organic solution. The concentration of methylene blue in the aqueous solution was measured by UV spectrophotometer. The wavelength of maximum absorption (λmax) for methylene blue was 650 nm. Meanwhile, the extracted methylene blue in organic solution was calculated based on mass balance. The procedures were repeated for other parameters including different concentration of carrier and pH of aqueous solution. The optimum condition was obtained.

Backward extraction so called stripping extraction was carried out by mixing equal volume of methylene blue loaded organic solution and stripping agent ($NaHCO_3$) using same setting as forward extraction. After 15 min of phase separation, the bottom part of stripping aqueous phase was carefully segregated. UV spectrophotometer was used to measure the concentration of stripping methylene blue. The procedures were repeated with different stripping agent concentration. All the experiments were run in duplicate and analytical parameters were performed in triplicate for each run.

Determination and calculation

The distribution ratio (D), percentage of extraction (E), and stripping (S), were calculated as per the following equations:

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

$$E(\%) = 100\,x\,\frac{[dye]_{aq0} - [dye]_{aq}}{[dye]_{aq0}} \quad (2)$$

$$S(\%) = 100\,x\,\frac{[dye]_{int}}{[dye]_{org}} \quad (3)$$

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

RESULTS AND DISCUSSION

Effect of vegetable oil types

Liquid membrane can be modified to "green liquid membrane" by using environmentally friendly diluent. The effect of vegetables oil such as palm oil and corn oil as a solvent in the extraction of MB was investigated. The results as shown in Figure 1 indicate that both vegetables oil had potential to use as a LLE of MB using D2EHPA as a carrier. Almost 100% of MB was extracted from the solution. Mean that the oils can act as a perfect solvent/diluent in the process. Because -of palm oil is cheaper and easy to get compared to corn oil, it was used as a solvent for further the studies. In addition, palm oil has been found to work well for extraction of phenol using supported liquid membranes (SLM) [16].

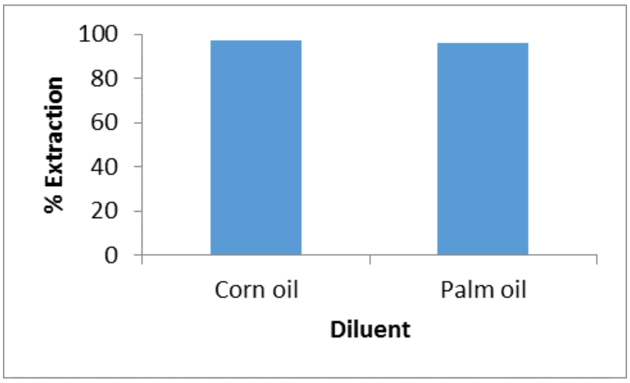


Figure 1 Extraction performance on difference types of vegetable oils (Experiment conditions: [dye] = 25ppm, agitation speed= 320rpm, duration = 18 hrs, pH 6±0.1, feed:organic ratio =1:1)

Effect of carrier concentration

The effect of D2EHPA concentration on the extraction of cationic dye range from 0.005-0.5M was shown in Figure 2. The experimental data plotted illustrate the extraction percentage increase dramatically with increase in carrier concentration from 0.005 to 0.01M. Then, it increase gradually and reached maximum 96% at 0.1M of carrier. Further increase the concentration of carrier the extraction percentage became plateau. The trend confirms that even though using palm oil as diluent, D2EHPA is effective in extracting cationic dyes. During extraction, carriers were reacted with dye and form complex. More carriers provided enhance the extraction efficiency. The saturation capacity of the organic phase for the complex reached at optimum 0.1M D2EHPA. The equilibrium of reaction was achieved when all carriers get associated with dye ion and form complex [17]. D2EHPA is anionic carrier with negative charges showed attractive force to cationic dyes and its good performance on cationic dyes was evaluated using kerosene as diluent [13]. The extraction efficiency of using kerosene was comparable to this study which was using palm oil as diluent. Palm oil has a density of 887.5 kg/m^3 and a viscosity of 130 mPa·s at 20 ˚C. Meanwhile, kerosene has a density of 790 kg/m^3 and a viscosity of 1.78mPa.s at 20 ˚C. Although palm oil has higher viscosity than kerosene, its efficiency was comparable.

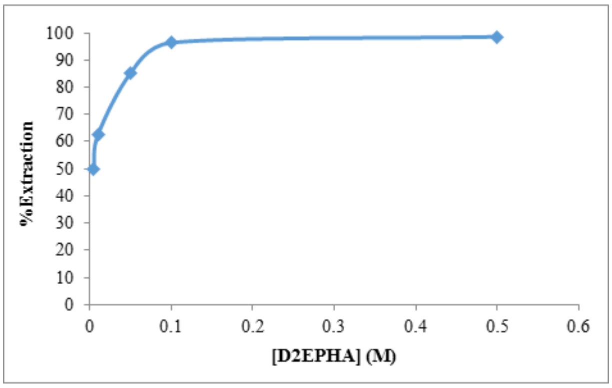


Figure 2 Effect of carrier concentration in liquid-liquid extraction. (Experiment conditions: [dye] = 25ppm, agitation speed= 320rpm, duration = 18 hrs, diluents = palm oil, pH 7±0.1, feed:organic ratio =1:1)

For determination the nature of extraction of methylene blue dye, Table 1 shows the distribution ratio (D) of dye. The results show that the distribution ratio of methylene blue dye increased with increases the carrier concentration in the organic phase. The Figure 3 in the form of Log D against log carrier concentration was plotted. The slope value of 1.006 indicating that dye to carrier concentration ratio was best at 1:1 complex. It can then be assumed that 1 mol of D2EHPA extract 1 mol of methylene blue dye to form complex.

Table 1 Distribution ratio of MB in organic solvent

Carrier concentration [M]	Distribution ratio (D)
0.001	0.98
0.005	1.00
0.01	1.70
0.05	6.14
0.1	38.06

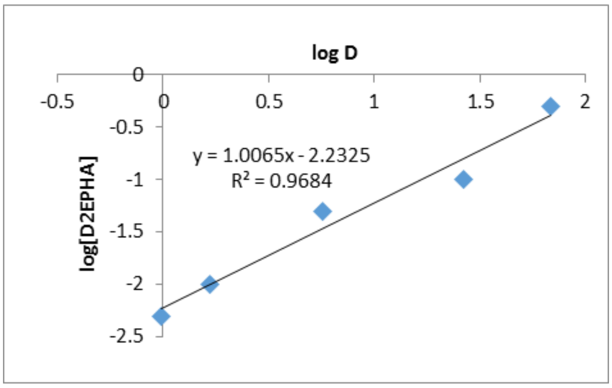


Figure 3 Stoichmetric plot for the equilibrium extraction of methylene blue using D2EHPA as carrier and palm oil as solvent.

$$C_{16}H_{18}N_3S^+(\text{Dye}) + HR(\text{carrier}) \rightarrow C_{16}H_{18}N_3SR + H^+ \quad (4)$$

Where HR is the D2EHPA in the palm oil solvent.

Effect of stripping agent type

For the purpose of recovery methylene blue process, it is desired to extract back the methylene blue from the organic phase. Various types of stripping agents were tested such as Sodium carbonate (Na_2CO_3), sodium bicarbonate ($NaHCO_3$), sodium hydroxide (NaOH) and sodium chloride (NaCl). The extraction performance is shown in Table 2. The highest extraction percentage is 1.0M $NaHCO_3$ which is 88%, followed by 73% for 1.0M NaCl, 3% for 1.0M Na_2CO_3 and no extraction for 1.0M NaOH. It indicate that inorganic base are strong acid compared to organic acids, Therefore, stripping performance of the dye become less effectively from organic to aqueous phase [9]. On the other hand, the results also showed an ineffectiveness of strong base in extracting dye from dye loaded organic phase. From the observation an emulsion is formed during the stripping process when using NaOH due to hydrolysis process of dyes and ion OH^-. An emulsion is a mixture of immiscible solvents which refuses to separate into two distinct phases [18]. Therefore, next experiments were carried out using stripping agent of $NaHCO_3$

Table 2 Effect of stripping agents type in stripping process. (Experimental conditions: [dye] = 25ppm, [D2EHPA] = 0.1M, stripping agent concentration =1.0M, agitation speed=320rpm, duration = 18 hrs, feed:organic ratio 1:1).

Stripping agent	Stripping percentage (%)
NaCl	73
$NaHCO_3$	88
Na_2CO_3	3
NaOH	0

Effect of stripping agent concentration

Figure 4 present the effect of $NaHCO_3$ concentration on the extraction of dye from methylene blue loaded organic phase to stripping phase. Various $NaHCO_3$ concentrations were tested which is 0.1M, 0.3M, 0.5M, 0.6M, 0.8M and 1.0M. It inferred that the increase in stripping agent concentrations, the stripping percentage was increased. This same with previous study [19] indicates that the extraction driving force significantly increases with the different sodium ions concentration in the stripping and organic phase. This is owing to the fact that with the increase in stripping concentration, number of $NaHCO_3$ molecules available for reaction with MB-D2EHPA complex also increased. Thus, more dye ions to be stripped out from organic phase. It was found that maximum stripped occurred at 0.6M $NaHCO_3$ concentration. Further increase of $NaHCO_3$ concentration to 1.0M showed no significant effect on the stripping performance. Therefore, 0.6M was chosen for the next experiment.

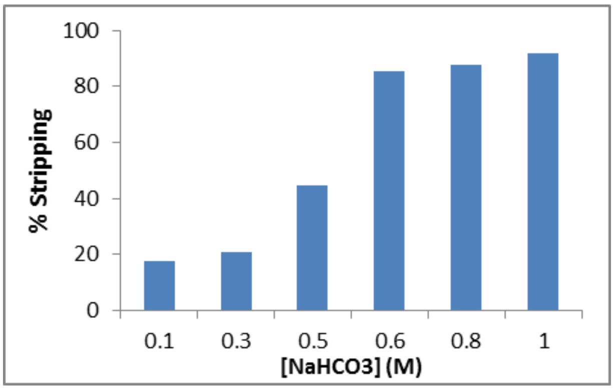


Figure 4 Effect of stripping agent concentrations in stripping process. (Experimental conditions: [dye] = 25ppm, [D2EHPA] = 0.1M, stripping agent =$NaHCO_3$, agitation speed=320rpm, duration = 18 hrs, feed:organic ratio 1:1).

Figure 5 in the form of Log D against log stripping agent concentration was plotted. The slope value of 3.6412 indicating that dye to stripping agent concentration ratio was best at 1:3 complex. It can then be assumed that 3 mol of $NaHCO_3$ was needed to strip 1 mol of methylene blue dye from dye loaded organic phase.

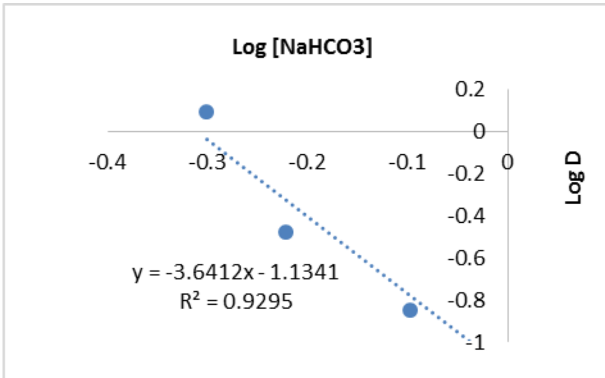


Figure 5 Stoichiometric plots for the equilibrium stripping of methylene blue by using $NaHCO_3$ as stripping agent

The $NaHCO_3$ existed are assumed to be fully reacted with loaded methylene blue-D2EHPA complexes and the nature of the stripped solute can be evaluated as in Equation 5. Therefore, the stripping reaction of methylene blue-D2EHPA with $NaHCO_3$ is:

$$C_{16}H_{18}N_3SR + H^+ \rightarrow C_{16}H_{18}N_3S^+ + HR \quad (5)$$

The $C_{16}H_{18}N_3S^+$ will dissolve in stripping phase and insoluble complexes of D2EHPA (HR) were formed in the organic phase.

Mechanism of basic dye (methylene blue) extraction

In the extraction process, the D2EHPA as a carrier reacts chemically with cationic methylene blue to form complex of $C_{16}H_{18}N_3SR$ at the organic-feed interface as represented in Equation 4. Then, stripping process occurred when the $C_{16}H_{18}N_3SR$ complexes react with $NaHCO_3$ as shown in Equation 5. It is concise the liquid-liquid extraction of MB dye with D2EHPA in palm oil as carrier and $NaHCO_3$ as the stripping agent. The slope analysis study of log D versus log [D2EHPA] and log D versus log [$NaHCO_3$] as shown in Figure 3 and Figure 5 respectively indicates that one mole of D2EHPA extracts 1 mole of methylene blue dye to form complex and one mole of the complex is needed to reacts with three mole of $NaHCO_3$ to strip the dye into the stripping phase. The extraction and stripping mechanisms are shown in Equations 1 and 2 respectively.

Furthermore, the percentage of extraction and stripping in 5 minutes time are illustrated in Figure 6 and Figure 7. The results show that the extraction rate is high. Almost 80% of the MB dyes was extracted. It is due to the fact that throughout the extraction process, there are potential of anionic dye to form complexes with the D2EHPA. Meanwhile, the rate of stripping process relies on the strength of $NaHCO_3$ to strip out the dye from the complexes into the strip solution.

Effect of feed solution pH

The impact of feed pH is one of the crucial parameter to study on removal of MB dye because wastewater containing MB dyes are always discharge at different pH. Figure 8 present the feed phase pH effect on the MB extraction performance. The difference of pH between organic phase and the feed phase could affect the extraction efficiency. The range of pH in this study is from 1 to 5 and 9 to11 for acidic and basic condition respectively. The pH of the sample has been adjusted by using 0.1 M H_2SO_4 and 0.1 M NaOH. At pH 1, the efficiency of MB dyes extracted was lower at 47%. This is due to present of H^+ ion in feed solution that competes effectively with the MB dye cation to react with the carrier. By increased the pH up to pH 9, it shown that the percentage of MB dyes extraction was increased. This is because the MB solution tends to promote the D2EHPA to become negatively charged that enhanced the extraction of positively charged dye cation through electrostatic force of attraction [20]. However, after pH 9, the percentage of extraction is declined because at alkaline pH, D2EHPA become negatively charged and the dye is negatively charged that contribute to repulsive force of extraction. It justified that increasing the pH in feed solution might alter the dye molecule from its original structure. In overall, it can be seen that percentage of extraction at pH 9 is higher and can be considered as optimum pH for MB dye extraction.

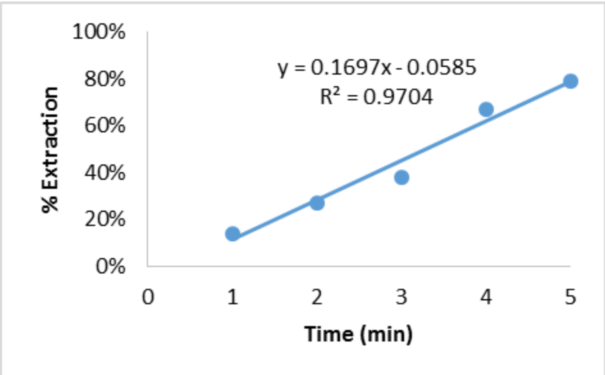


Figure 6 Extraction performance in 5 minutes equilibrium times (Experimental conditions: [dye] = 25ppm, [D2EHPA] = 0.1M, stripping agent =$NaHCO_3$, agitation speed=320rpm, duration = 18 hrs, feed:organic ratio 1:1).

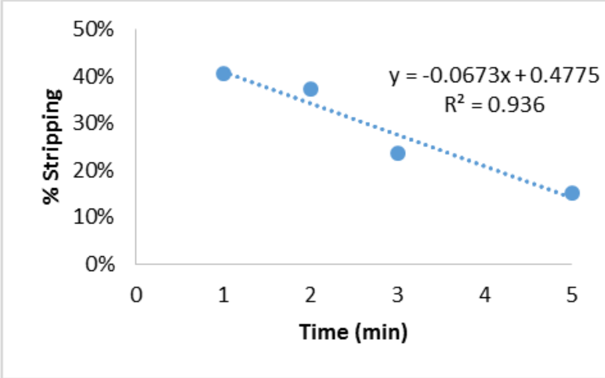


Figure 7 Stripping performance in 5 minutes equilibrium times (Experimental conditions: [dye] = 25ppm, [D2EHPA] = 0.1M, stripping agent =$NaHCO_3$, agitation speed=320rpm, duration = 18 hrs, feed:organic ratio 1:1).

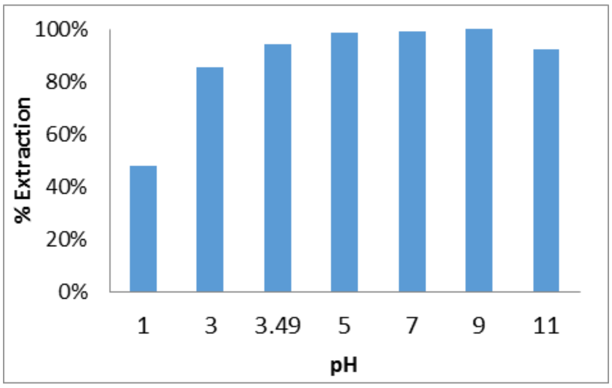


Figure 8: Effect of pH on extraction performance. (Experimental conditions: [dye] = 25ppm, [D2EHPA] = 0.1M, stripping agent=$NaHCO_3$, agitation speed=320rpm, duration = 18 hrs, feed: organic ratio 1:1, pH 1 - 11).

CONCLUSION

The liquid-liquid extraction method used offers a simple approach for selective extraction of MB for extraction and recovery. The results showed that LLE is an effective method for removal of MB from aqueous solution. The optimal process conditions are 0.1M D2EHPA in palm oil as a diluent, and 0.6M of $NaHCO_3$ as a stripping agent. D2EHPA in palm oil is able to extract 100% of MB from aqueous solution. However, the recovery of dye was yet to be success. Further study on different type of stripping agent will be investigated.

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