Extraction of Methylene Blue from Aqueous Solutions by Waste Cooking Oil and its Back-Extraction

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Abstract. This work aimed to use waste cooking oil as a greener replacement for the petroleum-based solvents in removing methylene blue (MB) from aqueous solutions by solvent extraction. The effects of different extraction parameters such as equilibrium pH, aqueous to organic phase ratio, and initial MB concentration on the extraction of MB from aqueous solutions by waste cooking oil were investigated. The back-extraction of MB from MB-loaded waste cooking oil was also explored. The maximum extraction (~90%) and back-extraction (>90%) of MB were attained at equilibrium pH of 8, aqueous to organic phase ratio of 1:1, initial MB concentration of 20 mg/L, and with 1 M of sodium bicarbonate as the back-extraction agent.

1. Introduction

Dyestuffs are organic or inorganic materials that could absorb and reflect light to show colors. They are categorized into acid, basic, reactive, direct, vat, mordant, disperse, metal complex, and sulfur dyestuffs and are widely used as colorants in textile, leather, paper printing, food, cosmetics, and pharmaceutical industries. However, the release of a large number of dyestuffs into the environment during dyeing processes from numerous industries (textiles, dyeing, paper and pulp, tannery and paint, and dye manufacturing) is of global concern due to their toxicity, carcinogenicity, mutagenicity, and non-biodegradability [1].

With the rise in demand for dyestuffs following the rapid population growth, industrialization, and urbanization, an assortment of dyestuffs has been synthesized. Methylene Blue (MB) is one of the dyestuffs that has been synthesized and used extensively in various industries. Despite the fact that MB shows superior stability than its natural counterparts, its complex aromatic molecular structure has resulted in its recalcitrant nature which poses severe environmental, esthetical and medical issues when it is released into the environment [2]. Hence, the removal of MB from wastewater prior to discharge is indispensable.

Today, a number of physicochemical and biological technologies have been used to remove dyestuffs from wastewater which encompass adsorption, coagulation-flocculation, activated sludge, membrane bioreactor, advanced oxidation, and electrochemical processes [1]. Among the various treatment technologies, solvent extraction appears as one of the promising technologies for treating wastewater containing dyestuffs owing to its ability to remove and recover dyestuffs from wastewater through the extraction and back-extraction processes, respectively [3]. However, the conventional solvents used in solvent extraction are mostly petroleum-based which are harmful, non-biodegradable, and non-renewable [4]. Hence, this work attempted to use eco-friendly and renewable biomass,
namely, waste cooking oil, as a greener replacement for the petroleum-based solvents in removing MB from aqueous solutions by solvent extraction. The effects of different extraction parameters such as equilibrium pH (pHeq), solvent type, aqueous to organic (A:O) phase ratio, and initial MB concentration on the extraction of MB from aqueous solutions by waste cooking oil were investigated. The back-extraction of MB from MB-loaded waste cooking oil was also explored.

2. Materials and Method

2.1. Materials
The waste cooking oil was collected from a local restaurant which was filtered with a cheesecloth before use, while the fresh cooking oil was bought from a local supermarket which was used as received. MB (Merck, > 82% purity), sodium hydroxide (NaOH) (Merck, > 97% purity), hydrochloric acid (HCl) (Qrec, 37% purity), tributylphosphate (TBP) (Sigma-Aldrich, > 99% purity) and sodium bicarbonate (NaHCO\textsubscript{3}) (Sigma-Aldrich, > 99% purity) were used as received.

2.2 Method
The extraction of MB from aqueous solutions was carried out based on the procedure reported in our previous work [4]. Firstly, an organic solvent made up of waste or fresh cooking oil and 80 mM of TBP (phase modifier) was added to an aqueous solution containing a specific amount of MB (20, 40 or 60 mg/L) in a conical flask at an A:O phase ratio (1:1, 2:1 or 1:2). An orbital shaker (Lab Companion, SK-300) was then used to agitate the mixture at 150 rpm for 7 minutes after which it was allowed to stand to separate for about 5 min. Next, some aqueous sample was taken from the flask with a syringe and its pH\textsubscript{eq} was measured with a pH meter (Eutech, pH 700). If the pH\textsubscript{eq} measured varied from the desired pH\textsubscript{eq}, the sample was returned to the flask and its pH\textsubscript{eq} was adjusted with 1 M NaOH or 1 M HCl. The mixture was allowed to separate and the pH\textsubscript{eq} was measured and adjusted again. This continued until the desired pH\textsubscript{eq} was obtained. Next, the mixture was moved to a separating funnel for phase separation and some aqueous sample was collected for MB concentration analysis by using a UV-visible spectrophotometer (PerkinElmer, LAMBDA 365) at a wavelength of 662 nm [5]. The percentage of extraction (%E) of MB is calculated by [5]:

\[
\%E = \left(1 - \frac{[MB]_{f, aq}}{[MB]_{o, aq}}\right) \times 100\%
\]

where \([MB]_{o, aq}\) and \([MB]_{f, aq}\) are the initial and final concentrations of MB in the aqueous feed phase.

Lastly, MB was back-extracted from the MB-loaded waste cooking oil by using a NaHCO\textsubscript{3} solution (0.2-1.0 M) following the same procedure as that of MB extraction but without the pH\textsubscript{eq} adjustment step. The % of back-extraction (BE) of MB is given by [5]:

\[
\%BE = \left(\frac{[MB]_f}{[MB]_{o, aq}}\right) \times 100\%
\]

where \([MB]_f\) is the final dye concentration in the NaHCO\textsubscript{3} solution.

3. Result and Discussion

3.1. Effect of pH\textsubscript{eq} on MB extraction
Figure 1 shows the effect of pH\textsubscript{eq} on the %E of MB by using waste and fresh cooking oils. Other parameters like A:O phase ratio and initial MB concentration were fixed at 1:1 and 20 mg/L, respectively. As can be seen in figure 1, the highest %E of MB by both waste (93.4%) and fresh (73%)
cooking oil were achieved at pH\textsubscript{eq} of about 8 but decreased with pH\textsubscript{eq} below and above 8. The latter may be attributed to the increasing competition between H\textsuperscript{+} ions and MB cations to bind with the active components in the cooking oil as pH\textsubscript{eq} decreased below 8 [6] and the increasing negative charge surrounding MB cations which repelled them from the active components in the cooking oil as pH\textsubscript{eq} increased above 8 [7]. Meanwhile, the greater performance of waste cooking oil in MB extraction than its fresh counterpart could be explained from its larger amount of acidic proton-bearing active components such as free fatty acids that could react with MB cations through a cation exchange process [3, 5]. Since pH\textsubscript{eq} of 8 achieved the highest %E of MB, it was selected for further studies.

![Figure 1. Effect of pH\textsubscript{eq} on %E of MB by using waste (Δ) and fresh (○) cooking oils.](image)

3.2. Effect of A:O phase ratio on MB extraction

Figure 2 shows the effect of A:O phase ratio on %E of MB by using waste cooking oil. Other parameters like pH\textsubscript{eq} and initial MB concentration were fixed at 8 and 20 mg/L, respectively. It was found that A:O of 1:2 attained the highest %E (91%), followed closely by A:O of 1:1 (89%), and the lowest %E (66%) was achieved by A:O of 2:1. This was because a higher amount of organic phase than that of aqueous phase implied a greater amount of active components available for MB extraction, and thus favored the MB extraction, while the opposite disfavored it due to the lack of active components for MB extraction [5]. Since there was no significant difference in the %E of MB attained between A:O of 1:1 and 1:2, the A:O of 1:1 was selected for further studies.

![Figure 2. Effect of A:O phase ratio on %E of MB.](image)
3.3. Effects of initial MB concentration on MB extraction

Figure 3 shows the effect of initial MB concentration on %E of MB by using waste cooking oil. Other parameters like pH\textsubscript{eq} and A:O phase ratio were fixed at 8 and 1:1, respectively. As shown in figure 3, the %E of MB decreased gradually from 87 to 80% with the initial MB concentration. This could be ascribed to the insufficient active components for MB extraction at high initial MB concentrations and this finding is consistent with other similar previous works [3, 5]. Since the maximum %E of MB was achieved at an initial MB concentration of 20 mg/L, it was selected for further studies.

Figure 3. Effect of initial MB concentration on %E of MB.

3.4. Effect of NaHCO\textsubscript{3} concentration on MB back-extraction

Figure 4 shows the effect of NaHCO\textsubscript{3} concentration on %BE of MB from MB-loaded waste cooking oil which was obtained from the extraction experiments conducted under the optimum conditions (pH\textsubscript{eq} of 8 (figure 1), A:O of 1:1 (figure 2), and initial MB concentration of 20 mg/L (figure 3)). As can be seen in figure 4, %BE of MB increased with NaHCO\textsubscript{3} concentration and the maximum %BE was accomplished with 1 M NaHCO\textsubscript{3}. The was due to the increasing amount of NaHCO\textsubscript{3} molecules available for reaction with MB as the concentration of NaHCO\textsubscript{3} increased. This is in good agreement with similar previous works [6].

Figure 4. Effect of NaHCO\textsubscript{3} concentration on %BE of MB.
4. Conclusions

All extraction parameters studied were found to affect MB extraction significantly. The maximum extraction (~90%) and back-extraction (>90%) of MB were attained at equilibrium pH of 8, aqueous to organic phase ratio of 1:1, initial MB concentration of 20 mg/L, and with 1 M of sodium bicarbonate as the back-extraction agent. Hence, waste cooking oil is a potential greener replacement for petroleum-based solvents in MB removal by solvent extraction.

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