Removal of methylene blue from aqueous solution using sodium bis (2-ethylhexyl) sulfosuccinate-hexanol reverse micellar system

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Abstract. Textile manufacturing is one of the core industries which discharges a heavy load of chemicals during the dying process. As a result, the release of large contents of dyes through aqueous effluents leads to both environmental and economic concerns. The present study investigates the removal of a model cationic dye, i.e., methylene blue using a reverse micelles system of 1-hexanol as an organic solvent and sodium bis(2-ethylhexyl)sulfosuccinate (AOT) as an anionic surfactant. The influence of different parameters including surfactant concentration, reaction time and dye concentration on extraction performance, was studied. Extraction efficiency was increased with increasing time and surfactant concentration, while it was decreased with the increase in dye concentration. For this system, the optimum extraction condition correspond to surfactant concentration around 0.05M, equilibrium time 20min and dye concentration around 500 ppm, resulting in extraction efficiencies around 99%. The microdomains of water within the reverse micelle system are the driving force for the clarification of methylene blue dye from aqueous solution.

1. Introduction

The technological development and world quest for improved materials have increased the usage of color imparting agents called dye. Dye unique adhesion properties made it a suitable candidate to be used in various industries such as textile, food, carpet manufacturing, dyeing, pulp, and paper industries. It is alarming to know that around 10% of dyes used in industries are discharged into the environment of which textile industries alone cause the dispose of 280,000 tons of dye effluent [1, 2]. The dye effluents in aqueous ecosystems reduce the water quality, photosynthetic activity, and dissolved oxygen concentration. Moreover, it had severe effects on aquatic flora and fauna, which leads to environmental problems worldwide [3].

Several studies have been conducted for the removal of dye from wastewater as nowadays it is the major environmental concern and challenge. Typical dye effluent treatment methods are membrane filtration, coagulation-flocculation, electrochemical treatment, adsorption, chemical oxidation and biological [4-7]. However, most of these methods display some major drawbacks such as low removal
efficiency, high running and regeneration cost, the toxicity of chemicals, short half-life time and lengthy processes [8]. Liquid-liquid extraction (LLE) is an alternative and cost-effective method for the treatment of dye-containing wastewater as it has been a preferred choice for the separation processes [9].

Liquid-liquid extraction with reverse micelles has got much attention for the removal of dyes from aqueous solutions. For example, Ana C. Ueda studied the extraction of three basic dyes from aqueous solution by reverse micelles using isopentanol as solvent and sodium dodecyl sulfate (SDS) as an anionic surfactant. The percentage of extraction achieved in these experiments was 98% [10]. Moreover, Adina Roxana Petcua reported the 90% removal of ionic dyes by non-ionic Water/Brij 30/Ethyl Acetate microemulsions [11]. Furthermore, an anionic surfactant AOT is commonly used for reverse micellar extraction. With reference to the ability of AOT surfactant for extraction of cationic dyes [12], 1-hexanol as an organic solvent for reverse micellar extraction has been investigated here.

In the present study, we have evaluated the extraction of methylene blue by the RM system using 1-hexanol as an organic solvent and AOT as an anionic surfactant. In RM extraction, the hydrophobic and electrostatic interaction is the main driving force for the transfer of dye from aqueous solution to the reverse micellar core. The main factors which affect reverse micelle extraction such as reaction time, the concentration of surfactant and dye were studied.

2. Materials and Methods

Organic Solvent 1-hexanol, methylene blue (3,7-bis(dimethylamino)-phenothiazin-5-iium chloride), (MB, dye ≥82%) and sodium bis(2-ethylhexyl)sulfosuccinate (AOT, >99% purity) was supplied by Sigma-Aldrich (USA). The water employed for aqueous solutions was Milli-Q grade distilled water.

2.1. Methods

The scheme of the whole extraction procedure is shown in Figure 1. Initially, AOT was weighted under vacuum to prepare a reverse micelle solution in hexanol. A clear solution was obtained after vortex mixing. RM solution was added to aqueous MB dye solution at a fixed volume ratio of 1:2. Both the aqueous and solvent phase was mixed at 100rpm for 20 min to achieve complete equilibrium, and phase separation occurred after cessation of stirring with the reappearance of two immiscible layers[13].

The mixture was then left for gravity settling for 24 hours to ensure complete phase separation. The aqueous phase was then analyzed by UV-vis spectrophotometer to determine the remaining concentration of methylene blue. Dye extraction efficiency (E %) was calculated as follows Equation. (1):

\[ E\% = \left( \frac{C_i - C_f}{C_i} \right) \times 100 \]  

(1)

Where \( C_i \) and \( C_f \) are the dye concentrations (ppm) before and after removal, respectively.
3. Results and Discussions

3.1. Reverse Micelle Process Optimization
In this study, methylene blue was extracted using liquid-liquid extraction through the reverse micellar system. As mentioned in the literature, the reverse micellar extraction is driven by electrostatic and hydrophobic interaction between the dye and reverse micelles for the diffusion of MB dye into the micellar core [14]. The main variables which affect the reverse micelle process were optimized by performing several experiments under different conditions. When a variable was optimized, the next variable was studied at that optimum value.

3.2. Effect of Equilibrium Time
The influence of reaction time is pertinent as the contact time between the two phases directly affects the extraction efficiency. The effect of equilibrium time was studied by varying the extraction time from 1 to 20 min under constant dye concentration (300 ppm) and surfactant concentration (0.005 M). The results presented in Figure 2 verified that the extraction of methylene blue increased gradually as the equilibrium time increases from 1-18 min and to ensure complete equilibrium, 20 min was selected as the optimum equilibrium time.

![Figure 2. Effect of time (t) on extraction efficiency.](image)

3.3. Effect of Surfactant Concentration
The effect of initial AOT concentration Figure 3 on percentage removal of cationic dye from aqueous solution was investigated in the range of 0.01-0.05 M while keeping the dye concentration as constant at 500 ppm. Figure 3 shows that the percentage removal of methylene blue was enhanced with the increase of AOT concentration [15]. The pronounced increase in extraction efficiency can be co-related to the enhanced micellar formation with an increase of AOT amount in the organic solvent which in result increases the solubility of methylene blue into the organic phase while clearing aqueous phase. According to results, the surfactant concentration of 0.05 M was found to be optimum because after that there is no significant change in extraction efficiency. The aqueous phase was clarified while the organic phase was dyed with methylene blue (MB+). Therefore, the dye is transferred from the aqueous layer to the organic layer [16].
3.4. Effect of Dye Concentration

The influence of initial dye concentration Figure 4 was studied with a fixed AOT concentration of 0.05M. Figure 4 shows the change in extraction efficiency with respect to initial dye concentration. The result verified that the extraction yield tends to drop by increasing the dye concentration from 300-1000 ppm. This can be explained by saturation of the organic phase with dye results in the reduction of its capacity to solubilize more dye from aqueous phase as the aqueous phase dye concentration rises. The best extraction efficiency was observed at 500 ppm.
It was verified that with constant surfactant concentration, an increase in initial dye concentration simulates amount of dye contaminants in aqueous phase causes decrease in extraction efficiency, which point out saturation of organic phase as stated above.

3.5. Effect of Organic Solvent
In this section hexanol over isooctane, organic solvent combination with surfactant AOT was studied under identical experimental conditions (Surfactant concentration 0.05M, 500ppm MB aqueous dye solution in its natural pH and room temperature with a stirring speed of 100rpm for 20min mixing). The influence of the type of organic solvent on extraction efficiency is shown in Figure 5. As shown in Figure 5, 1-hexanol provided a higher capability for dye extraction over isooctane in combination with AOT surfactant.

![Figure 5. Effect of solvent type on extraction efficiency.](image)

The MB extraction efficiency obtained by 1-hexanol-AOT reverse micelle system was high enough as compared to literature values[12, 17].

4. Conclusions
In this work, the use of AOT and 1-hexanol reverse micelle system for the removal of methylene blue from aqueous media has been reported. Besides the organic solvent type effect, the influence of mixing time, surfactant concentration and dye concentration on extraction efficiency was also significantly observed. In conclusion, complete removal of methylene blue dye from aqueous solution was obtained by optimum selection of time, surfactant concentration and dye concentration.

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