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Comparative study between liquid–liquid extraction and bulk liquid membrane for the removal and recovery of methylene blue from wastewater

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ABSTRACT

In this research liquid–liquid extraction and bulk liquid membrane methods are used to study on the removal and recovery of methylene blue dye from textile wastewater by using salicylic acid in benzene. First, the liquid–liquid extraction of methylene blue dye was investigated. The parameters examined in this research were the effect of diluents, effect of pH, effect of extractant concentration, effect of dye concentration and the suitable stripping agent. Second, taking into consideration the obtained results, the transport of methylene blue dye across a bulk liquid membrane was studied. All the mentioned parameters applied in BLM technique and results are discussed.

Introduction

Dyes or dyestuffs are essentially colored substances capable of imparting their color to other substances. Today, the majority of dyes are synthetically produced [1]. Various industries use dyes extensively such as textile, plastics, leather, paper, cosmetics and food industries. Approximately 15% of the dyes produced throughout the world are lost during the dyeing process [2]. Textile wastewater possess a high COD concentration, large amount of suspended solids, broadly fluctuating pH, strong color, high temperature and low biodegradability caused by varying contaminates discharged into the environment, particularly aquatic environment [3]. Synthetic dyes usually have complex aromatic molecular structures which make them more stable and these compounds have recalcitrant nature and their release in to the environmental poses serious environmental, esthetical and health problem and various hazards such as mutagen and carcinogenic problem for living organism and reduces the photosynthesis by decrease in oxygen penetration to water [4]. Thus, the removal of dyes from wastewater before they are mixed up with unpolluted natural water bodies is important [5].

Methylene blue (MB) has been selected for the present study. It is a cationic dye and has a lot of applications like in coloring paper, dyeing clothes and wool, hair colorant, photosensitizer and as a redox indicator in analytical chemistry. It is a heterocyclic aromatic compound which is heavily used in the textile industry. However, MB is not very much hazardous but its higher concentrations can cause hypertension, precordial pain, fever, and mental confusion, staining of skin, decolouration of urine, cyanosis and anemia [6].

The acute exposure to methylene blue dye may cause some harmful effects such as increased heart rate, shock, vomiting, jaundice and tissue necrosis in humans [7,8]. The removal of MB from wastewaters is an environmental issue and has launched the extensive research efforts in this regard. Aerobic granulation for methylene blue biodegradation in a sequencing batch reactor was investigated [9]. Removal of methylene blue from aqueous solution using cotton stalk, cotton waste and cotton dust was also reported [10].

Various methods have been used to remove dyes from aqueous solutions. The treatments for dye containing wastewater can be classified into three groups of physical, chemical and biological treatments. Biological treatment requires a large land area, toxicity of some chemicals, less flexibility in design, operation and their application is often restricted because of technical constraints [11]. Besides, chemical methods include coagulation or flocculation combined with filtration, precipitation–flocculation etc., were

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investigated [12,13]. However, the chemical methods are often expensive and although the dyes are removed, accumulation of concentrated sludge creates a disposal problem and a secondary pollution problem will arise because of excessive chemical use [14]. Physical method such as adsorption has been investigated [15–20]. However, the adsorption treatment using activated carbon as adsorbent is quite expensive.

The above mentioned methods are only removing the colors and not recovering the dyes from wastewater. In recent years, much attention has been focused on a separation technique such as solvent extraction or liquid–liquid extraction (LLE) and liquid membrane. LLE is based on the principle that a solute can distribute itself in a certain ratio between immiscible solvents, and the extraction process depends on its mass transfer rate [21]. Muthuraman et al. [22] reported the extraction and recovery of methylene blue from industrial wastewater by LLE, using benzoic acid as the extractant. Similarly, golden yellow low salt anionic–type dye was extracted and recovered from aqueous solutions by the solvent extraction method was reported [23]. Recovery of methylene blue from aqueous solution by liquid–liquid extraction was also reported [24].

Ultimately, a simple, cost effective and safe alternative for color removal and recovery of dyes from textile effluent is required and membrane technology may provide this alternative to the solvent extraction processes for selective separation of dyes. Liquid membranes have acquired a prominent role for their use in separation, purification or analytical application in various areas, such as biomedicine, ion selective electrodes, effluent treatment and hydrometallurgy [25]. It has been given considerable attention by researchers due to its outstanding characteristics such as simultaneous pollutants removal and materials recovery in a single unit, non-equilibrium mass transfer, high selectivity, high fluxes, reusability and low energy consumption [26]. In recent years, remarkable increases of the applications of liquid membranes techniques in separation processes have been observed [27–34]. LMs can be designed as bulk liquid membranes (BLM), supported liquid membranes (SLM), emulsion liquid membranes (ELM), polymer inclusion membranes (PIMs) and activated composite membranes (ACM) [35].

Among membrane technologies, the bulk liquid membrane (BLM) is one of the simple, lowest and efficient types of liquid membranes [36,37]. BLM constitute the cheapest separation techniques because of their relatively small inventory and low capital cost. In a BLM, a relatively thick layer of immiscible fluid is used to separate the donor and acceptor phase. There is no means of support for the membrane phase and it is kept apart from the external phases only by means of its immiscibility.

Bulk liquid membranes consist of three phases: two aqueous phases as a donor or an acceptor and one organic phase in which a carrier is dissolved. The dye transport from an aqueous donor phase through an organic membrane phase to an aqueous acceptor phase occurs. In its simplest form, this technique can be carried out in either H-type or a U-type configuration depending on the density of the solvent used.

In the presence study, we selected the methylene blue dye for comparative study of solvent/liquid–liquid extraction and bulk liquid membrane separation techniques. Methylene blue is the cationic dye, so it requires an anionic carrier for extraction purpose. Salicylic acid acts as an anionic carrier in this study. Salicylic acid is a diprotic acid with p*K*a value 2.97 and 13.4 in aqueous medium. The extraction of a cationic dye (MB) while it makes an ion-pair with salicylic acid in a sequence of non-polar solvent benzene as an extractant. The liquid–liquid extraction studies were carried out varying different parameters such as effect of pH, effect of carrier concentration, effect of dye concentration and effect of stripping agent. In bulk liquid membrane the effect of various process such as, stirring speed, pH of feed solution, effect of dye concentration in the feed phase and effect of receiving phase were also thoroughly studied and reported here.

Materials and methods

Materials

Benzene, salicylic acid, methylene blue were obtained from Merck and used without further purification. The following inorganic acids and organic solvents such as salicylic acid (≥99.8%), methylene blue (98%), oxalic acid (99%), sulphuric acid (98%), nitric acid (70%), hydrochloric acid (35.4%), benzene (≥99%), toluene (98%), hexane (99%), xylene (99%) were used without further purification.

All chemicals used were analytical reagents grade and aqueous solutions were prepared in double distilled water.

Apparatus and measurements

A UV visible spectrophotometer (Elico Sl 159, India) was used to find out λ_{max} and measure dye concentration in the raffinate phase and strip solution. pH meter (Elico Li 120, India) was used to measure pH of aqueous solutions. For agitation of solution a shaker and stirrer was used (IKD-KS 50, India). Systronics Electrophoresis 606 was used to find out whether the dye is cationic or anionic.

Preparation of MB solution

Methylene blue is a cationic dye. Its IUPAC name is 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride. 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 properties and structure of methylene blue dye (MB) presented in Table 1.

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.

Table 1
Properties of MB dye.

Properties	
Suggested name	Methylene blue
IUPAC name	3,7-Bis(dimethylamino)-phenothiazin-5-ium chloride
CI name	Basic blue 9
CI number	52015
Molecular formula	C16H18N3SCl
Molecular weight (g/mol)	319.85
λ_{max} (nm)	662 (Measured value)
Chemical structure