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Extraction and recovery of methylene blue from industrial wastewater using benzoic acid as an extractant

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ABSTRACT

Liquid–liquid extraction (LLE) of methylene blue (MB) from industrial wastewater using benzoic acid (extractant) in xylene has been studied at 27 °C. The extraction of the dye increased with increasing extractant concentration. The extraction abilities have been studied on benzoic acid concentration in the range of 0.36–5.8 × 10^{-2} M. The distribution ratio of the dye is reasonably high (D = 49.5) even in the presence of inorganic salts. Irrespective of the concentration of dye, extraction under optimal conditions was 90–99% after 15 min of phase separation. The extracted dye in the organic phase can be back extracted into sulphuric acid solution. The resultant recovered organic phase can be reused in succeeding extraction of dye with the yield ranging from 99 to 87% after 15 times reused, depending on the concentration of the initial feed solution. Experimental parameters examined were benzoic acid concentration, effect of diluent, effect of pH, effect of initial dye concentration, effect of equilibration time, various stripping agents, aqueous to organic phase ratio in extraction, organic to aqueous phase ratio in stripping and reusability of solvent.

1. Introduction

Among different pollutants of aquatic ecosystem dyes are a large and important group of chemicals. They are widely used in industries such as textile, paper, rubber, plastic, cosmetic, etc., to colour the products. These dyes are invariably left in the industrial waste and consequently discharged mostly to surface water resources. Dyes even in low concentration are visually detected and affect the aquatic life and food web. These coloured compounds are not only aesthetically displeasing but also inhibiting sunlight into streams and affecting photosynthetic reaction [1]. It is estimated that more than 100,000 commercially available dyes with over 7 × 10^5 tons of dyestuff are produced annually [2]. Methylene blue (MB) is one of the most commonly used substances for dyeing cotton, wood and silk. Though MB is not strongly hazardous, it can cause some harmful effects where acute exposure to MB will cause increased heart rate, vomiting, shock, cyanosis, jaundice, and quadriplegia and tissue necrosis in humans [3]. The advantages and disadvantages of some methods of dye removal from wastewater are given in Table 1 [4].

Removal of MB by carbon derived from peach stones by H_3PO_4 activation was studied [5]. Adsorption of MB by algal biomass based materials was also reported [6]. Kavitha and Namasivayam [7] also used coir pith activated carbon. The adsorption capacity was found to be 5.87 mg/g by Langmuir isotherm for the particle size of 250–500 μm. In these cases disposal of spent activated carbon is a problem. Micellar enhanced ultra filtration (MEUF) is one possible method to remove organic dyes from water. Even though MEUF method is not yet applied on an industrial scale, many studies have shown that it is a suitable method for the retention of metal ions [8,9], anions [10], and organic pollutants [11,12]. Separation of MB from aqueous solution by micellar enhanced ultra filtration was also reported [13].

Electrochemical degradation of MB was studied by Panizza et al. [14]. Photo catalytic degradation of MB was also investigated [15,16]. Removal and recovery of dye stuffs (DSs) using ion exchange method was proposed by MonaNaim and Yehia [17]. Electrochemical oxidation of dye wastewater was studied by various researchers [18,19]. Sundrarajan et al. [20] reported that ozonation is efficient in decolorization of exhausted dye bath effluent containing conventional reactive dyes. Ozone treatment was used on acid red 18, acid orange 7, acid orange 10 and acid red 73 by Muthukumar et al. [21]. For all the dyes two successive recycling processes were carried out. Ozonation method does not remove total dissolved solids (TDS), but it reduces chemical oxygen demand (COD) of the effluent.

Membrane separation process plays an increasing role in the reduction and/or recovery of DSs. Fouling of membrane is a problem in this case [22]. Removal of anionic and cationic organic dyes

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Table 1
Advantages and disadvantages of the current methods of dye removal from industrial effluent [4]

Physical/chemical methods	Advantages	Disadvantages
Fenton's reagent	Effective decolourization of both soluble and insoluble dyes	Sludge generation due to Fe^{2+} used
Ozonation	Applied in gaseous state no alternative of volume	Short half life (20 min) of ozone
Photochemical	No sludge production	Formation of by products
NaOCl	Initiate and accelerates azo bond cleavage	Release of aromatic amines and adsorption of organic halides
Electrochemical destruction	Breakdown compounds are non hazards	High cost
Activated carbon	Good adsorbent due to cellular structure	Very expensive and disposal of spent
Peat	Good adsorbent due to cellular structure	Specific surface areas of adsorbent are lower than activated carbon
Wood chips	Good sorption capacity for acid dyes	Requires long retention time
Silica gel	Effective removal for basic dyes	Prevent commercial application
Ion exchange	Regeneration, no adsorbent loss	Not effective all types of dyes

from water by liquid–liquid extraction (LLE) using reverse micelles was proposed by Pandit and Basu [23]. Removal of methyl orange and methylene blue dyes from water using colloidal gas aphrons (CGA) was reported by Basu and Malpani [24]. Roy et al. [25] studied the separation of organic dyes such as methyl orange, methylene blue, cibacrome 4G, cibacrome 6B from wastewater using CGA. Hexa tetramethyl ammonium bromide and sodium dodecyl benzene sulphonate were used as surfactants for the generation of CGA.

Aqueous bibasic system (ABS) consists of two immiscible phases formed when certain water soluble polymers are mixed with one another or with certain inorganic salts in specific concentration [26]. ABS composing of dodecyl trimethyl ammonium hydroxide and sodium dodecyl sulphates was reported to be able to extract methyl orange and porphyry dyes [27].

Liquid–liquid extraction method is used for the purification enrichment separation and analysis of various compounds in mixtures. It is 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 [28]. The advantage of solvent extraction includes high through put, ease of automatic operation and of scale up and high purification [29]. 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.

In the present study, the efficiency of liquid–liquid extraction of a cationic dye namely, methylene blue using benzoic acid prepared in xylene as extractant was studied. The dye extraction and stripping extracted dye were investigated and operating conditions were optimized. Further recovery of dye and stripping reagents were also studied.

2. Experimental

2.1. Materials

Benzoic acid, xylene, methylene blue, sulphuric acid, sodium hydroxide, sodium chloride, nitric acid and hydrochloric acid, were obtained from Merck. All chemicals used in this study were of AR grade.

A UV–visible spectrophotometer (Spekol 1200, Analytical Jena, Germany) was used to measure the absorbance of the dye and to establish its λ_{max} and its concentration. pH of an aqueous solution was measured by a pH meter (WTW, Germany). For agitation of solutions a mechanical stirrer was used (IKD-KS 50, Germany).

Benzoic acid was used as extractant and dissolved in xylene. The dye solution was prepared in distilled water. Sulphuric acid was used as stripping agent and sodium hydroxide was used to adjust pH.

2.2. Procedure

2.2.1. Liquid–liquid extraction of dye

The organic solvent [(benzoic acid + xylene) (V_o mL)] used for extraction was added to the prepared aqueous dye solution (V_a mL) in a glass-stoppered bottle and the glass-stoppered bottle was shaken for known time in a shaker at 100 rpm. The solution was then transferred into a separating funnel. Sample of aqueous solution at the bottom of the separating funnel was taken for absorbance measurement of dye. The wavelength of maximum absorption (λ_{max}) for methylene blue was 650 nm. The experimental setup is shown in Fig. 1. The distribution ratio (D) and percentage of extraction (E) were calculated as per the following equations

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

$$E = 100 \times \frac{[\text{dye}]_{aq0} - [\text{dye}]_{aq}}{[\text{dye}]_{aq0}} \quad (2)$$

where $[\text{dye}]_{org}$ is the dye concentration in the organic phase (mg/L), $[\text{dye}]_{aq0}$ is the initial dye concentration of aqueous phase (mg/L), $[\text{dye}]_{aq}$ is the dye concentration of aqueous phase after extraction (mg/L).

In stripping, the loaded extractant (V_o mL) and the aqueous strippant (acid solution) were added together into a glass-stoppered bottle and shaken at 100 rpm. The content was then transferred into a separating funnel. The aqueous strippant was taken for dye concentration measurements. All the experiments were run in duplicate and analytical parameters were performed in triplicate for each run. Confidence limit of 95% was taken for reliable results.

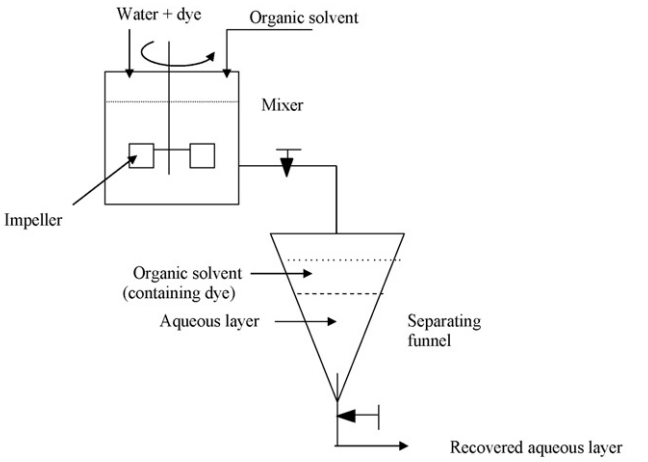

Fig. 1. Schematic experimental setup for liquid–liquid extraction for removal of dye from aqueous solution.