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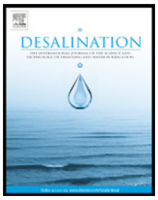

Solvent extraction of methyl violet with salicylic acid from aqueous acidic solutions

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ABSTRACT

The solvent extraction of methyl violet from aqueous acidic solutions by salicylic acid in xylene was studied. Inorganic acids such as hydrochloric acid (HCl), sulphuric acid (H_2SO_4) and nitric acid (HNO_3) were used to adjust the pH of aqueous feed phase. HCl was shown to give higher efficiency of extraction and higher distribution coefficient at $pH = 6.0 \pm 0.1$ than H_2SO_4 and HNO_3. The distribution coefficient increased from 4 to 24 when salicylic acid concentration was increased from 1.4×10^{-2} to 3.6×10^{-2} mol L^{-1}. The presence of salt such as sodium sulphate (Na_2SO_4) in the feed phase decreased the extraction efficiency. The extracted dye was stripped into 9 mol L^{-1} of aqueous acetic acid solution. The loading capacity was found to be 5.1 mg of dye per 3.6×10^{-2} mol L^{-1} of salicylic acid (25 mL of xylene contain 0.0125 g of salicylic acid).

1. Introduction

Textile industry is one of the most important industries in the last few decades. It was broadcasted that more than 60% of the dyes world production was consumed by textiles industries [1]. Among different pollutants of aquatic ecosystem dyes are a large and important group of chemicals. 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 aquatic life and food web. These coloured compounds are not only aesthetically displeasing but also inhibiting sunlight into the stream and affecting the photosynthetic reaction [2]. Conventional treatment methods for the removal of pollutants from aqueous solutions like photochemical degradation, biological degradation, coagulation, flocculation, chemical oxidation and adsorption have been investigated with varying successes [3–5].

Methyl violet is chiefly used in copying papers, in heterograph and printing inks. It imparts deep violet colour in paints and printing inks. It is also used to obtain shades of deep colours that can be applied for the dyeing of cotton, silk, paper, bamboo, weed, straw and leather. It is also widely used in Gram's Stain for the demonstration and primary classification of bacteria, as an anti-allergen and bactericide, the Flemming triple stain with iodine and Newton's crystal violet technique. Methyl violet is metachromatic and is sometimes used to demonstrate amyloid [6].

Adsorption of methyl violet (MV) by granular activated carbon had been studied and the maximum adsorption capacity of 0.095 g/g at equilibrium was achieved [7]. The recovery of MV from wastewater was reported. Various thermodynamic parameters were calculated by applying linear forms of Langmuir and Freundlich isotherm models and the adsorbed dye was recovered by eluting hydrochloric acid of pH 3 through exhausted column [8]. Two kinds of strong-acid cationic exchangers were also used to remove methyl violet and to desorb into 1 mol L^{-1} NaCl in 60% by volume ethanol + water [9]. Magnesium chloride was used as a coagulant in treating dye waste, the colour removal rate was 97.9% and COD reduction was 88.4% [10]. Removal and recovery of various low salt dyes from industrial wastewater was reported [11–14]. Degradation and photo catalytic degradation of cationic dye was investigated [15,16].

Solid membrane separation process plays an increasing role in the reduction and/or recovery of dyestuffs. Fouling of membrane can be a problem [17]. Removal of methyl orange and methylene blue dyes from water using colloidal gas aphrons (CGA) was reported by Basu and Malpani [18]. Roy et al. [19] 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 that are formed when certain water soluble polymers are mixed with one another or with certain inorganic salts in specific concentration [20]. ABS composing of dodecyl trimethyl ammonium hydroxide and sodium dodecyl sulphates was reported to be able to extract methyl orange and porphyry dyes [21]. Solvent extraction or Liquid–liquid extraction (LLE) has been widely used in the recovery of organic and

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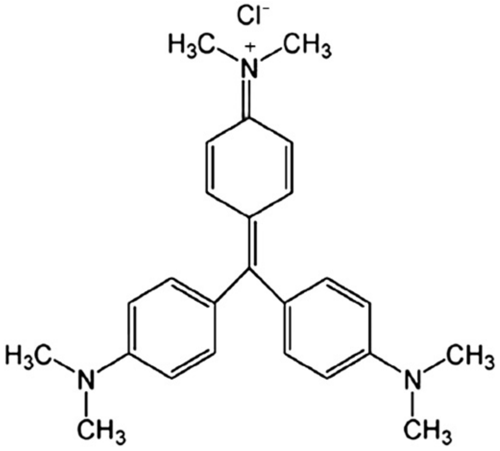

Fig. 1. Structure of methyl violet.

inorganic matters from aqueous solutions. In these processes, ions in the aqueous solution are in contact with a selective solvent; after extraction the process is followed by stripping. LLE has been 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 the extraction process depends on its mass transfer rate [22]. Removal of anionic and cationic organic dyes from water by liquid–liquid extraction (LLE) using reverse micelles was proposed by Pandit and Basu [23]. The advantages of solvent extraction include high through put, ease of automatic operation and of scale up and high purification [24]. In this study, the xylene is used as a diluent, it is non toxic and it can be reused many times as a diluent. This method does not give any disposal problem. The main factors affecting the use of solvent extraction or LLE in dye removal are; organic to aqueous phase ratio, salt concentration, nature of solvent, salting effect and some of the interference mechanisms [25–28].

In the present study, the efficiency of solvent extraction of a cationic dye namely, methyl violet using salicylic acid as extractant prepared in xylene was studied. Dye extraction and stripping of extracted dye were investigated and operating conditions were optimized. Further recovery of dye and stripping reagents were also studied. The structure of methyl violet is given in Fig. 1.

2. Experimental

2.1. Reagents

The following inorganic salts, acids, and organic solvent were used in the experiments without further purification: NaCl (99.8%), NaOH (>96.0%), salicylic acid (99.5%), methyl violet (99.8%) H_2SO_4 (95%), HCl (36%), HNO_3 (65%), H_3PO_4 (>85%), xylene (>98.5%). Chemicals were obtained from Merck and Fisher scientific suppliers. A UV-visible spectrophotometer (Spekol 1200, Analytical Jena, Germany) was used to measure the absorbance of the dye and its concentration, pH of an aqueous solution was measured by a pH meter (WTW, Germany). For agitation of solution a shaker was used (IKD-KS 50, Germany). Deionized water was used for preparing all the aqueous solutions.

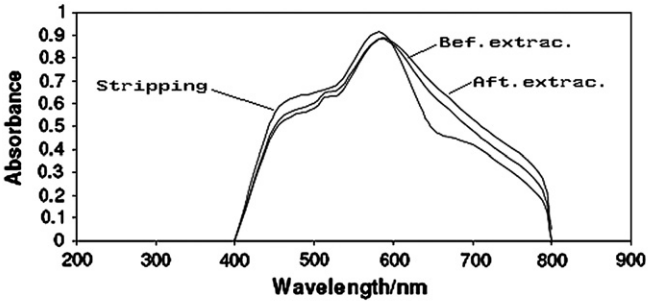

Fig. 2. Visible absorption spectra of methyl violet in various solutions.

2.2. Extraction experiments

The organic solvent [Salicylic acid + xylene] used for extraction was added to the prepared aqueous dye solution in a glass-stoppered bottle. The pH of the aqueous solution was adjusted using three inorganic acids (H_2SO_4, HCl and HNO_3). The glass stoppered bottle was shaken at 100 rpm for 5 min in a shaker. The solution mixture was then transferred into a separating funnel. Sample of aqueous solution at the bottom of the separating funnel was taken for absorbance measurement of the dye to determine dye concentration. The wavelength of maximum absorption (λ_{max}) for methyl violet was 585 nm. The dye concentration in the organic phase was calculated on the basis of mass balance.

2.3. Stripping experiments

In stripping, the loaded extractant and the aqueous strippant were added together into a glass stoppered bottle and shaken at 100 rpm. After 5 min the content was transferred into a separating funnel. The aqueous strippant was taken for dye concentration measurement. 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.

The results are expressed in terms of distribution coefficient D, extraction efficiency E, and recovery efficiency R defined as [29].

$$D = \frac{C_{org,eq}}{C_{f,eq}} \tag{1}$$

The stripped organic solvent was reused many times for MV dye extraction.

$$E = 1 - \frac{C_{f,eq}}{C_{f,ini}} \tag{2}$$

$$R = \frac{C_{s,eq}}{C_{f,ini}} \tag{3}$$

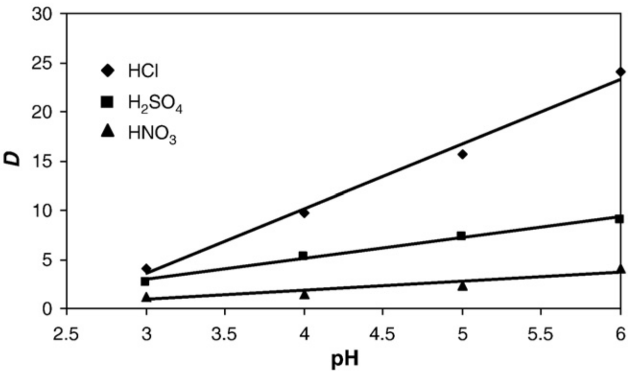

Fig. 3. Effect of inorganic acid used for pH adjustment in feed solution (Experimental conditions: volume of source phase = 25 mL, volume of organic phase = 25 mL, extractant concentration 3.6×10^{-2} mol L^{-1}, equilibration time = 4 min.).