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Studies on the solubilization of aqueous methylene blue in surfactant using MEUF

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ABSTRACT

The solubilization of methylene blue (MB) in sodium dodecyl sulfate (SDS) using hollow fiber membrane was studied. In MEUF, the effects of important factors (MB and SDS concentrations, temperature and electrolyte concentration) on the permeate and retentate concentrations of MB and SDS, equilibrium distribution constant (K_d) and micelle loading (L_m) were investigated. It was found that MB molecules could be solubilized fully within micelles of SDS. The increase of feed SDS concentration promoted retentate MB concentration. Temperature could change the SDS micellization effect. The addition of NaCl could improve the retentate MB and SDS concentrations and reduce significantly the permeate SDS concentration.

1. Introduction

The effluents containing methylene blue (MB) may lead to serious problems, which has a harmful influence on human health and environment. Many methods have been applied to remove dyes from wastewater in the current literatures, such as chemical oxidation, adsorption, precipitation, biodegradation, flotation, ion exchange, nanofiltration and reverse osmosis. However, there are inherent deficiencies in these technologies, such as high cost, low efficiency and inconvenient operation [1,2]. Accordingly, micellar-enhanced ultrafiltration (MEUF) is recognized in the disposal of trace amounts and low concentration of organic matters and/or heavy metal ions. This technology has a series of advantages of high efficiency, low energy consumption, small space demand, no phase change, low operative pressure and high permeate flux [3–5]. Furthermore, it is feasible to be inserted into the entire treatment process. For example, reactive dyes were removed from an aqueous solution by coagulation and MEUF combined processes [6]; electrolysis and MEUF processes were combined for heavy metal removal [7].

In MEUF process, the surfactant containing hydrophobic and hydrophilic groups is added into the solution containing organic matters or heavy metal ions. The surfactant aggregates to form large amphiphilic micelles that bind the solutes. The micelle is made up of the inner core (constituted by hydrophobic groups), palisade layer (constituted by CH_2 groups) and outer layer (constituted by hydrophilic groups). The organic matters get embedded in the micelles via "like dissolves like" principle while heavy metal ions are adsorbed on the opposite-charged micelles via electrostatic interaction [8,9]. The micelles along with the solutes are rejected into the retentate stream by ultrafiltration membrane. Due to different solubilization principles, organic and inorganic contaminants could be retained simultaneously by MEUF [10,11]. The solubilization system of organic matters or heavy metal ions with surfactant is a dynamic balance system, namely, the location of solutes in micelles changes with time. It spends only 10^6–10^{10} s on solutes within micelles [12]. If solubilization effect is seen as the distribution of solutes between micelles and water, the equilibrium distribution constant (K_d) and micelle loading (L_m) could be estimated [3,13,14].

Large ionic dyes, such as MB and eriochrome blue black, can be solubilized into the hydrophobic and hydrophilic medias in micelles, or dissociate to ions which are adsorbed on the surfactant micelles [15,16]. Therefore, opposite-charged surfactant should be utilized to retain these organics in order to obtain the high rejection in MEUF, which was proved by the literatures [17,18]. The type of surfactant is the dominant factor affecting the solubilization capability. In this study, anionic surfactant sodium dodecyl sulfate (SDS) was chosen to solubilize cationic MB molecules.

MEUF method aims to discharge the permeate solutions containing water, small amounts of solutes and free surfactants into streams and recycle the organic matters, heavy metal ions

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Table 1
Properties of MB.

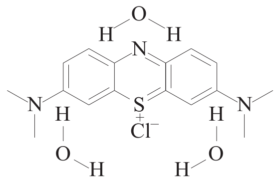
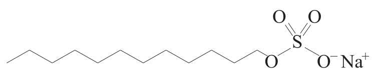
Formula	Molecular structure	Molecular weight	Type
$C_{16}H_{18}ClN_3S{\cdot}3H_2O$		373.90 g/mol	Cationic dye

Table 2
Properties of SDS.

Formula	Molecular structure	Molecular weight	Type	CMC
$C_{12}H_{25}NaO_4S$		288.38 g/mol	Anionic surfactant	8.0 mM

and surfactants enriched in the retentate. These make the MEUF technology more economical. For instance, the chelation and acidification methods were used to recover SDS from a MEUF retentate containing Cd^{2+} or Zn^{2+} by ultrafiltration [19]; the surfactant hexadecyl pyridinium chloride (CPC) from retentate and permeate solutions was recovered by a two-step chemical treatment process [8].

In the present work, the effects of feed MB and SDS concentrations, temperature and NaCl concentration on permeate and retentate concentrations of MB and SDS were studied. In addition, the equilibrium distribution constant (K_d) and micelle loading (L_m) values, of MB between SDS micelles and water were also estimated. As is well known, the addition of surfactant causes the secondary pollution. Nonionic surfactant is often utilized to reduce the permeate surfactant concentration. It was found in this work that the NaCl which is economical and nontoxic could improve retentate MB and SDS concentrations and decrease significantly the permeate SDS concentration.

2. Materials and methods

2.1. Specimen preparation

MB offered from Shanghai SSS reagent Co., Ltd., China, was selected as a kind of dye. SDS offered from Tianjin Kermel Chemical Reagent Co., Ltd., China, was selected as a kind of surfactant. The properties of MB and SDS are listed in Tables 1 and 2 respectively. NaCl and HCl were purchased by Sinopharm Chemical Reagent Co., Ltd., China. NaOH with a purity of 96% was offered from Tianjin No. 3 Chemical Reagent Factory. In addition, the distilled water was used in all experiments.

2.2. Ultrafiltration

Ultrafiltration was performed in an experimental setup (ZM50-1) with the hollow fiber membrane (ZU503-22), procured from Yidong Membrane Engineering Equipment, Ltd., Dalian, China. The membrane was made of polysulfone. The pore size of the membrane was 10,000 Da and the effective membrane area was 0.8 m^2. The feed tank was initially filled with 2 L solution. The retentate stream was recycled to the feed tank. When the feed solution was left over 0.5 L, permeate and retentate solutions were collected to be determined. After each run, the membrane had to be washed with distilled water to ensure that the permeability remain almost constant.

2.3. Measurement and analysis

UV spectroscopy analysis on MB and SDS was performed with Shimadzu UV-2550 (P/N206-55501-93) spectrophotometer from Japan. The SDS concentration was analyzed by the methylene blue spectrophotometric method (ISO-7875-1-1996) [20]. The concentration of MB was analyzed at the wavelength of 663 nm. Blank samples of distilled water were used for MB measurement in permeate and blank samples of 1 CMC SDS for that in retentate.

2.4. Calculations

Ultrafiltration of micellar solutions could be considered as a research method helpful in estimating the equilibrium distribution constant (K_d) and micelle loading (L_m) [13,21,22].

According to the law of mass action, one definition of K_d is defined as:

$$K_d = \frac{D_m}{S_m - D_w} \tag{1}$$

The L_m is defined as:

$$L_m = \frac{D_m - D_w}{S_m - S_w} \tag{2}$$

where S_m and D_m are the concentrations of surfactant and dye pollutant in retentate, S_w and D_w are the concentrations of surfactant and dye pollutant in permeate.

3. Results and discussion

3.1. Variation of MB concentration

The feed MB concentration varied from 2 to 24 mg/L, the SDS concentration was fixed at 8.0 mM (one CMC). The experiments were conducted at 0.03 MPa and 25 °C. As shown in Fig. 1, as the initial MB concentration increased, the permeate MB concentration increased from 0.019 to 0.140 mg/L, and retentate MB concentration ascended from 6.44 to 36.45 mg/L linearly. It was obvious that with the increase of the amount of MB molecules in feed solution, MB molecules distributed between the water and micelles increased accordingly [23]. However, the SDS concentrations in permeate and retentate kept about 3.0 mM and 13.0 mM respec-