Desalination 311 (2013) 31–36

Contents lists available at SciVerse ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

# Gemini micellar enhanced ultrafiltration (GMEUF) process for the treatment of phenol wastewater

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## HIGHLIGHTS

► Gemini surfactant micellar-enhanced ultrafiltration was used to remove phenol.
► The increment of CG concentration and nonionic surfactant improved the performance.
► Electrolyte and temperature had a negative influence on the phenol retention.
► Gemini surfactant had superior performance in solubility for phenol.

## ARTICLE INFO

*Article history:*
Received 30 June 2012
Received in revised form 24 October 2012
Accepted 26 October 2012
Available online 20 December 2012

*Keywords:*
Gemini surfactant
Micellar-enhanced ultrafiltration
Phenol
Retention
Brij35

## ABSTRACT

Comprehensive studies were carried on the micellar-enhanced ultrafiltration of phenol for the treatment of phenol wastewater with the help of cationic Gemini surfactant (CG) and Polyethersulfone (PES) flat sheet membranes of a molecular weight cut-off of 10 kDa. The effects on the retention (phenol and surfactant), permeate flux and secondary resistance of various factors in the practical application of GMEUF were investigated including feed CG concentration, mole fraction of nonionic surfactant, electrolyte concentration and temperature, respectively. The results presented that the retention of phenol kept evidently increasing with the augment of the feed CG concentration and mole fraction of nonionic surfactant. On the contrary, electrolyte concentration and temperature had a negative influence on the phenol retention. Besides, the addition of feed CG concentration and mole fraction of nonionic surfactant led to the decrement of the permeate flux and enhancement of secondary resistance significantly. These results demonstrated that CG surfactant with exceptional structure had brightly application prospect for the treatment of phenol wastewater in micellar-enhanced ultrafiltration.



## 1. Introduction

Phenol wastewater is mainly derived from a variety of industrial sources (e.g., the manufacture of papers, antioxidants, plastics and dyes). It is difficult to be cleaned by natural degradation, leading to serious environmental problems due to severely toxic to most aquatic life and also objectionable odors in drinking water even at very low concentrations [1,2]. At present many conventional technologies such as extraction, adsorption, chemical oxidation, UV oxidation and biological treatment have been applied for treatment of phenol wastewater [2]. However, these methods own significant and intrinsic defects such as their low efficiency, high cost, inferior selection and rigorous running conditions which restrict their widespread application. Besides, they are unfeasible to treat wastewater of low molecular weight solutes due to diseconomy and inefficiency.

Thereafter, a novel and burgeoning technology micellar-enhanced ultrafiltration (MEUF) which combines ultrafiltration (UF) membrane and surfactants appears. It is aimed at ameliorating the performance of UF membranes by capturing small size pollutants into large micelles [3]. In MEUF, surfactant is added into wastewater. Large amphiphilic and transparent micelles will form, when the concentration in the aqueous solution is above a certain concentration level called the Critical Micellar Concentration (CMC), then micelles capturing pollutants are separated subsequently by a UF membrane with pore sizes smaller than the diameter of micelles. In the long run, MEUF has its own advantages such as high removal efficiency, low energy consumption and small space requirement, thus it is regarded as a suitable tool for removing trace amounts and low levels of organic pollutants with respect to conventional techniques [4].

In recent studies, many endeavors have been committed to the selection of proper surfactants to remove relevant pollutants. Xu studied that the interaction between phenol and an anionic surfactant CPC and concluded that phenol was dissolved into the water-micelle interface by the ion interaction between $C_6H_6O^-$ and $C_5H_5N^+$

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http://dx.doi.org/10.1016/j.desal.2012.10.030

[5]; El-Abbassi investigated that the high efficiency of micellar-enhanced ultrafiltration using an anionic surfactant (SDS) for treating polyphenols waste water [6]; Fang et al. reported that cetylpyridinium chloride (CPC) had better performance for removal of phenol in comparing with octadecyl trimethyl ammonium bromide (OTAB) and cetyltrimethylammonium bromide (CTAB) [4]. Generally, the anionic surfactants are apt to remove cationic ions, while the cationic surfactants are suitable to remove anionic metal ions and organic matters [7]. In addition, the structure is the significant factor that affects the removal efficiency of pollutants from wastewater. Therefore, exploring new and effective surfactant systems are significant for improving the efficiency and practical applicability of this potential technique. Beyond the surfactant itself, the concentration of surfactant, ionic strength, pressure difference, temperature and the addition of nonionic surfactant [8,9] are the considerable factors to decrease or avoid the leakage of monomeric surfactant to permeate, which may make the process effluent stream environmentally unacceptable yet [9,10].

Gemini surfactants have the structures and properties that are unique to the world of surfactants. Different from conventional surfactants, Gemini surfactants have two hydrophobic chains and two hydrophilic head groups connected with a spacer [11]. They have unusual characteristics, such as a very low CMC, excellent foaming and wetting properties, a high efficiency in reducing the oil–water interfacial tension and interacting with counterions [12]. Moreover, Gemini surfactants have more charges and can interact with counterions strongly in comparison with conventional ionic surfactants. They have been extensively applied in the fields of protein study, gene therapy, soil remediation, enhanced oil recovery and drug entrapment and release [12]. Nevertheless, the effect of micellar-enhanced ultrafiltration with the help of Gemini surfactant contributing to the removal of organic compounds is not yet clear.

This study aimed at investigating enhanced removal efficiency of phenol by micellar-enhanced ultrafiltration in the presence of cationic Gemini surfactants and developing a new method for phenol wastewater treatment-Gemini surfactant micellar-enhanced ultrafiltration (GMEUF). In addition, the effects of feed CG concentration, mole fraction of nonionic surfactant, electrolyte concentration and temperature on the process performance were analyzed. The performances of micellar-enhanced ultrafiltration experiments were characterized by the retention (phenol and surfactant), permeate flux and secondary resistance. This study is helpful for finding out operational effect and evaluating the viability of GMEUF. Meanwhile, it is significant to provide proof for exploring new and efficient surfactant systems for micellar-enhanced ultrafiltration in waste water treatment.

## 2. Materials and methods

### 2.1. Materials

The cationic Gemini surfactant (CG), N1-dodecyl-N1,N1,N2,N2-tetramethyl-N2-octylethane-1,2-diaminium bromide was supplied by Chengdu Organic Chemicals Co. LTD. Chinese Academy of Science, with a purity of 98%. The nonionic surfactant (Brij35) with purity 98% was obtained from Sigma-Aldrich. The molecular structures and properties of selected surfactants are given in Table 1. Phenol (Log $K_w = 1.46$, $S_w = 8.3$ g $L^{-1}$ (20 °C)) [14] with purity 98% was purchased from Beijing Chemical Reagent Company, China. $Na_2CO_3$ was purchased from Shanghai Pushan Chemical Reagent Company, China. All reagents were used without further purification. Distilled water was used for solution preparation in all experiments.

### 2.2. Methods

#### 2.2.1. Micellar-enhanced ultrafiltration measurements

Micellar-enhanced ultrafiltration was carried out at 20 °C using a flat sheet module supplied by XiaMen Tianquanxin Membrane Technology Co, Ltd, China. PES flat sheet membranes with a molecular weight cut-off of 10 kDa were obtained from Advanced Membrane Corporation, America with total effective areas 0.06 $m^2$. The flow, head and power of the pump were 2 $m^3$ $h^{-1}$, 40 m and 1.1 kW, respectively. A schematic diagram of the UF is presented in Fig. 1. In the preparation of feed, phenol and surfactant solutions were mixed at the required concentrations and stirred adequately to ensure that the solutes were evenly dispersed before feeding to the membrane module. The pressures and retentate flow rates were kept constant at 0.30 MPa and 5 L $min^{-1}$. Then, the solution was fed to the membrane module. Retentate stream was returned to feed tank. Permeate stream was collected into measuring cylinder, and then returned to the feed tank to maintain the feed volume and concentration at almost constant concentrations. Process was stopped when total permeate streams reached 0.5 L. The permeation fluxes ($J_v$) were measured every 5 min. It was found that the permeation fluxes were almost constant after 0.5 h of operation. After that, the retentate and permeate were collected to analyze concentrations. The reported values were the average of three duplicate records for three runs. After each experiment run, tap water was filtered with 0.2 MPa to wash the exterior of membrane within 20 min, and then the distilled water was used to rinse out the membrane at 0.30 MPa for 20 min. At last, the membrane permeability was recovered.

**Table 1**
The physicochemical properties of surfactants in experiment.

| Surfactant | Structure | MW (g $mol^{-1}$) | CMC[a](mM) |
|---|---|---|---|
| $CG_{12}$ | $C_{12}H_{25}N^+(CH_3)_2(CH_2)_2^-$ $N^+(CH_3)_2C_{12}H_{25}\cdot 2Br^-$ | 614.67 | 0.8 [13] |
| Brij35 | $C_{12}H_{25}(OCH_2CH_2)_{23}OH$ | 1200 | 0.065 [13] |

[a] Error limits of CMCs are ±4%.

#### 2.2.2. Analysis

In the synthetic solution of Brij35/CG and phenol, the concentration of Brij35 and phenol was analyzed by Extinction Coefficient method [9] with UV-2102 PCS spectrophotometer. In this study, the detection limit of phenol determination is 2–10 mg/L. The concentration of CG was measured using a titrating method [15]. The viscosities of surfactant solutions were measured by a viscometer (NDJ-5S/8S).

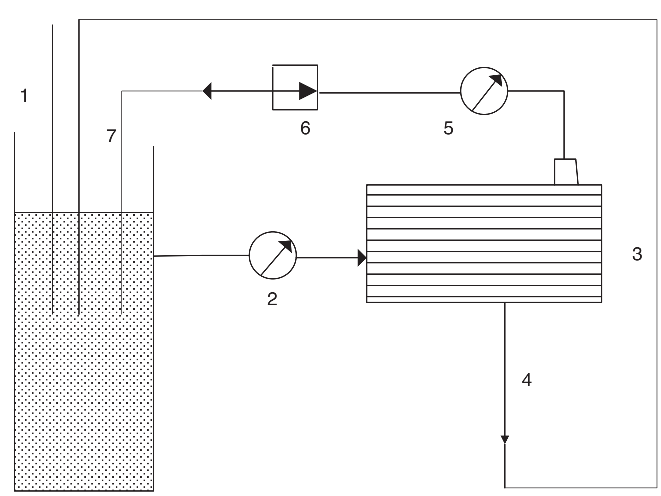


**Fig. 1.** Schematic diagram of the ultrafiltration unit: (1) feed solution, (2) manometer, (3) flat sheet module with PES membrane, (4) permeate stream, (5) manometer, (6) retentate rotameter, (7) retentate stream.