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Recovery of petroleum sulfonate from petrochemical dispersion by modified three-compartment electrodialysis

Dong Wang [a,b], Xueli Gao [a,b,*], Yushan Zhang [c,*], Lili Mao [a,b], Zhen Wang [a,b], Congjie Gao [a,b]

[a] Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, Ocean University of China, Qingdao 266100, China
[b] College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, China
[c] Institute of Tianjin Seawater Desalination and Multipurpose Utilization, State Oceanic Administration, Tianjin 300192, China

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ABSTRACT

Modified three-compartment electrodialysis (MTED), a novel process containing intermediate compartment with fluorinated ion exchange membrane, has been applied to the recovery of petroleum sulfonate from petrochemical dispersion. The fluorinated ion exchange membrane has higher degree of crosslinking than heterogeneous ion exchange membrane. The petroleum sulfonate is separated from the petrochemical dispersion during anion migration by the different steric effect of ion exchange membranes. In order to reduce the membrane fouling and increase the current efficiency, the 50 nm ceramic membrane was utilized as the pretreatment of MTED. The result indicated that in total of 99.4 wt% of petroleum sulfonate in the petrochemical dispersion could be recovered at the applied voltage 25 V, flux rate 30 L/h, temperature 40 °C and initial concentration 7.5 wt% $(NH_4)_2SO_4$. Simultaneously, the $(NH_4)_2SO_4$ solution without petroleum sulfonate was received in concentrate compartment of MTED. The results verified the feasibility of MTED on separating the petroleum sulfonate and inorganic salt in petrochemical dispersion, and provided important technical basis for a large-scale procedure of MTED in petrochemical dispersion treatment.

1. Introduction

The petroleum sulfonate (PS), which has eminent wettability and dispersion, is used worldwide as an oil-displacing agent in tertiary oil recovery [1–3]. PS surfactant is the production of the sulfonation reaction between petroleum fraction and sulfur trioxide or oleum, and then neutralized by ammonium hydroxide [4]. The petrochemical dispersion is generated during the neutral process. The components of petrochemical dispersion include 8.13% PS and 35.18% inorganic salt. Discharging it into natural water directly without appropriate treatment, will not only lead to irreversible liquid and ecological pollution, which will also create a waste of resources.

The superior amphipathy, high micellar and inorganic salt concentration of petrochemical dispersion make it difficult to dispose [5–7]. There are few researches and datum which relate to the petrochemical dispersion treatment. Until now, most of petrochemical dispersion was treated with thermally evaporating process, which needs solid waste management and cannot recycle the PS in petrochemical dispersion.

Recently, Feng et al. [8] separated the PS from the petrochemical dispersion successfully through extracting crystallization. However, the method needs an alcohol processing workshop which may be accident-prone in the amplification of the chemical engineering process. What's more, due to the addition of organic agent, extracting crystallization will easily cause secondary pollution. Therefore, it is urgent to develop an environmental method for treating petrochemical dispersion.

Electrodialysis (ED) technology is one of the membrane separation processes which uses the direct current electric field as driving force [9]. With the aid of the permselectivity of ion exchange membrane, ED could not only lower the concentrations of the targeted pollutant, but also concentrate the useful ingredients in wastewater for further reuse [10–12]. ED was originally used at the desalination of sea water and brackish water [13,14]. As the development of functionalization of the ion-exchange membrane, nowadays ED has been employed in various fields such as the treatment of industrial wastewater, the separation of ions with different valences and the separation of organic and inorganic components [15–21].

* Corresponding authors at: Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, Ocean University of China, No. 238 at Songling Road, Laoshan District, Qingdao 266100, China (X. Gao).
E-mail addresses: gxl_ouc@126.com, wd_charrel@163.com (X. Gao).

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However, petroleum sulfonate has certain particularity comparing with common organic pollutant. The molecule of petroleum sulfonate presents electronegative in aqueous solution and average molecular mass is less than 300. During the early explorative experiment, 20% petroleum sulfonate penetrated to concentrate compartment through anion exchange membrane under the direct current electric field when utilizing traditional heterogeneous membrane electrodialysis. If we choose fluorinated ion-exchange membrane which has a higher degree of crosslinking to separate the petroleum sulfonate from petrochemical dispersion, the membrane would easily be polluted under such petroleum sulfonate concentration [22–27].

To thoroughly separate the petroleum sulfonate from the petrochemical dispersion, the study innovatively invented three-compartment electrodialysis, which contains intermediate compartment with fluorinated anion ion-exchange membrane was elaborately designed on the basis of the conventional electrodialysis stack. The structural schematic diagram of modified electrodialysis stack is shown in Fig. 1.

Based on the results of explorative experiment, we can see that 20% petroleum sulfonate migrated to intermediate compartment. Under such concentration, the fluorinated anion-exchange membrane could separate the petroleum sulfonate from the solution in the intermediate compartment because of the excellent steric effect. The article investigated the effects of pretreatment method, operating parameters and membrane fouling on the modified three-compartment electrodialysis to treat the petrochemical dispersion.

2. Experimental

2.1. Reagents and membranes

The following reagents were used in the modified three-compartment electrodialysis experiment: $(NH_4)_2SO_4$ (Sinopharm Chemical Reagent Co., Ltd), NaOH (Sinopharm Chemical Reagent Co., Ltd), Sodium dodecyl sulfonate (Tianjin Fuyu Fine Chemical Co., Ltd) and de-ionized water (Millipore Milli-Q 18 MΩ). All of the reagents are analytical pure. Cation ion-exchange membrane (CEM) and anion ion-exchange membrane (AEM) are produced by Tianwei membrane technology Co., Ltd, Shandong, China. The fluorinated anion ion-exchange membrane (F-AEM) is obtained from Hangzhou Iontech Environmental Technology Co., Ltd, Zhejiang, China. All three kinds of ion exchange membranes have better electrochemical properties and superior chemical stability. For instance, the three kinds of membranes have higher heat stability than ordinary ion exchange membranes, especially the F-AEM which can tolerate 60 °C during normal running. Also the three kinds of membranes have vast pH applicable scope. All these characteristics will determine whether the three kinds of membrane are suitable in the desalination of the petrochemical dispersion. The specific functional parameter of the three kinds of ion-exchange membranes are presented in Table 1.

2.2. TED apparatus

A lab-scale modified three-compartment electrodialysis apparatus from Tianwei membrane technology Co., Ltd was applied to treat the petrochemical dispersion. The apparatus mainly composed by DC power supply (WYL1702, Hangzhou Siling Electrical Instrument Ltd.), membrane stack and four separated circuits. DC power supply provides direct-current electric field across the membrane stack for migrating the hydrated ion in the solution. The membrane stack composed by two electrodes (titanium plate coated with ruthenium), spacers, and ion-exchange membranes. The structure of MTED membrane stack is shown in Fig. 1. The stack contains ten repeating units. There are three triplet cells in each unit, containing a dilute, an intermediate and a concentrate compartment, so in total ten pieces of AEM, ten pieces of F-AEM, eleven pieces of CEM are used. The ion exchange membranes are separated by the spacers (270 mm × 110 mm, effective surface area 200 cm^2). In consideration of the high viscosity, concentration of inorganic salts of petrochemical dispersion and the membrane fouling, the spacers which have a thickness of 0.9 mm are utilized in the MTED stack. Four separate circuits for dilute, intermediate, concentrate and electrode rinsing solution are circulated by centrifugal pump (CXB-30 Wenzhou Erle Pump Co., Ltd). Each of the circuit contains a 5 L tank, a rotermeter and a gauge. The structure diagram of TED equipment is shown in Fig. 2.

The initial volumes of the solutions in the four separate circuits were all 2 L. A total of 10 wt% ammonium sulfate solution was applied as electrode solution. The petrochemical dispersion after pretreating was fed in dilute compartment. The intermediate compartment and concentrate compartment were fed with 7.5 wt%

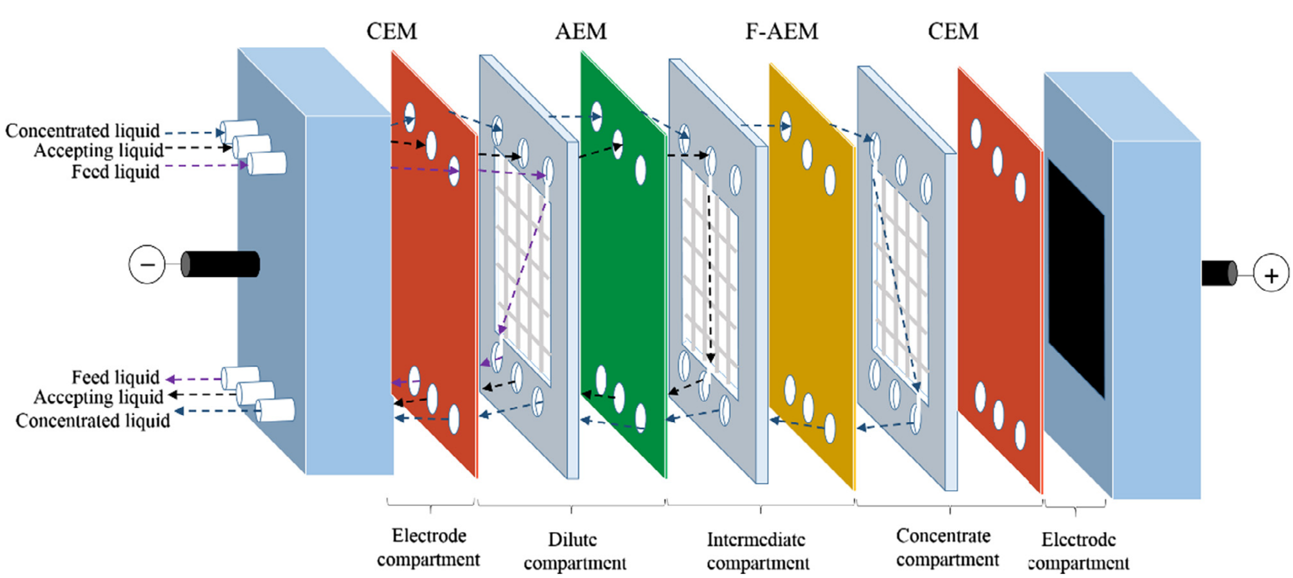

Fig. 1. The schematic of stack in modified electrodialysis.