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Formation and performance of Kaolin/MnO_2 bi-layer composite dynamic membrane for oily wastewater treatment: Effect of solution conditions

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ABSTRACT

To develop an efficient dynamic membrane for application in oily wastewater treatment, there is a need to explore an appropriate coating technique and to advance its separation performance. The formation and separation performance of the dynamic membrane from Kaolin and MnO_2 were investigated with particular objectives on the choice of an appropriate membrane-coating technique and the discussion of the effect of solution conditions. The microstructures of the dynamic membrane were examined using the scanning electron microscope. The results showed that the deposition of MnO_2 particles onto the surface of Kaolin dynamic layer forming a Kaolin/MnO_2 bi-layer composite dynamic membrane is an effective coating technique. The optimum concentrations of the Kaolin solution and $KMnO_4$ solution should be 0.4 g L^{-1} and 0.1 g L^{-1} respectively. With the rise of oil concentration, the steady permeate flux decreased and oil retention ratio increased. In the low oil concentration range from 0.1 g L^{-1} to 1.0 g L^{-1}, the variation characteristics were more obvious. In neutral or alkaline environments, the dynamic membrane was stable with high permeate flux and oil retention ratio of over 99%. As the temperature rose from 283 K to 313 K, the steady retention ratio decreased from 99.9% to 98.2% and the steady permeate fluxes increased from 120.1 L $m^{-2}h^{-1}$ to 153.2 L $m^{-2}h^{-1}$.

1. Introduction

Dynamic membrane (DM), also called secondary membrane, can be formed on the surface of porous supports, such as the ceramic tube, stainless steel tube, polymeric membrane and so on, by in situ deposition of fine particles from a coating solution [1–3]. The main advantages of dynamic membrane lie in the good antifouling property and the possibility of forming them by a simple way from inexpensive coating materials, such as the hydrated oxide, or natural and synthetic polyelectrolyte. During the separation process of the dynamic membrane, some contaminants would be hindered from entering into the inner pores of the support because of the isolating effect of the deposited layer [4–6]. The support pollution would be greatly reduced. In other words, the deposited layer would more easily get polluted than the support. After long time separation, the seriously fouled deposited layer could be removed in a simple way. The same support could be used again to prepare a new dynamic membrane in the same method. Moreover, its high permeate flux and high retention ratio also aroused much interest in many researchers [7–10]. Dynamic membrane was even regarded as a very promising separation membrane for application in many fields [11–13].

According to its formation process, the dynamic membrane could be classified into three types: self-forming dynamic membrane, pre-coated dynamic membrane and composite dynamic membrane [6,14]. Among them, the composite dynamic membrane made from two or more kinds of coating materials seemed to exhibit different or better separation performances in comparison to the dynamic membrane from single coating material for the different chemical compositions of the deposited layers. For example, Juh-Yaun Wang [14] found that the dextran-Zr composite dynamic membrane was able to reject hemoglobin completely, simply at the expense of a smaller permeate flux. Li Na [6] proved that a series of PVA composite dynamic membranes with broad molecular weight cut-off and good antifouling property could be readily obtained by suitable controlling and combination of various preparative conditions. F.G.Neytzell-de Wilde[15] successfully prepared the hydrous zirconium (IV) oxide/polyacrylic composite dynamic membrane with high permeate flux and good retention ratio at formation pressure. The separation performance of the composite dynamic membrane seemed superior to the dynamic membrane from single coating material [16,17].

For the oily wastewater treatment, only a few studies were reported using such coating materials as $Mg(OH)_2$, MnO_2 or $Fe(OH)_3$ to prepare the dynamic membrane, mainly concerning the effects of operating parameters and pH values of coating solution on its separation performance [18–20]. However, there were few reports on treating oily wastewater with composite dynamic membrane. It

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may be a good way for the composite dynamic membrane to treat the oily wastewater. As usual, the properties of the dynamic layer and wastewater were very important aspects for the separation performance of the dynamic membrane. For the properties of the dynamic layer, the coating materials and membrane-coating techniques play a very important role.

Therefore, the present work is to study the formation and performance of Kaolin/MnO_2 composite dynamic membrane for the oily wastewater treatment with particular objectives on the choice for an appropriate membrane-coating technique and the discussion of effect of concentrations of coating materials on its formation and separation performance. In addition, the effects of properties of oily wastewater including the oil concentration, temperature and pH value on its separation performance were discussed in detail, and the microstructures of the dynamic layers were examined using the SEM.

2. Experimental

2.1. Apparatus

The experimental apparatus is schematically shown in Fig. 1, which mainly consists of two 30 l feed tanks, a purpose-built membrane module, a vortex pump, a flow meter, pressure gauges and regulation valves. The feed tanks, membrane module and piping were all made of stainless steel. One feed tank was used to contain the solution of coating materials, the other was used to contain the oily wastewater. A ceramic tube was fitted into the membrane module. The heat exchanger tubes with cooling circuits were placed in the feed tanks to ensure that the suspensions were kept at constant temperature. The applied transmembrane pressure and crossflow velocity were regulated by manually operated valves. A graduated cylinder was used to collect the permeate samples to measure the permeate flux.

2.2. Materials

The support used in the test was Al_2O_3 porous ceramic tube (Jiangsu Tianya Membrane Separation Ltd.Co., P.R.China). The general characteristics of the ceramic tube are: inner diameter 9 mm, outer diameter13mm, length 400 mm and nominal pore size about 1.0 μm. The outside surface photograph of the support was observed using a scanning electron microscope (SEM, QUANTA200, and FEI, USA). The result is showed in Fig. 2.

The Kaolin clay (Shanghai Yuejiang Titanium Chemical Manufacture Ltd.Co., P.R.China) and synthesized MnO_2 were used as potential coating materials. The MnO_2 was prepared by dissolving a predetermined quantity of Manganese Sulfate and polyvinyl alcohol as a disperser with a known volume of tap water in a container and then slowly adding into it potassium permanganate in a power form, during which a blender quickly stirred the mixture.

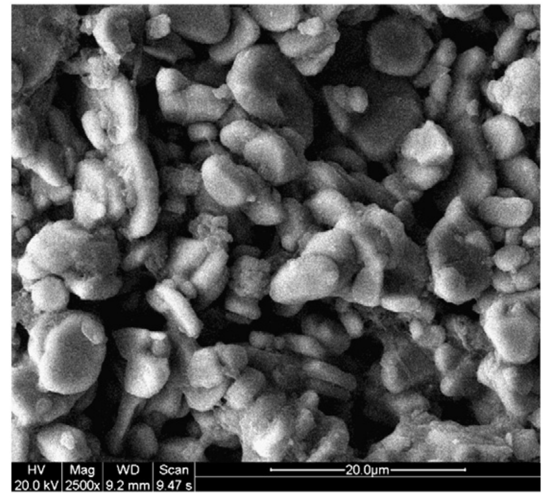

Fig. 2. SEM photograph of outside surface of support.

The oily water emulsion was prepared with a kerosene, 50 ppm surfactant (op-10) and tap water. A high-shearing dispersing emulsifier (FLUKO, Shanghai, China) was used to mix the mixture at a speed of 15,000 rpm for 8 min, by which a stable and reproducible oily water emulsion was formed. The solution pH was adjusted by dilute HCl and NaOH solutions.

The size distributions of the oil droplets, Kaolin and MnO_2 particles were all determined by a particle size analyzer (Mastersizer Microplus, Malvern 2000). The result in Fig. 3 shows that the oil droplets, Kaolin and MnO_2 particles nearly had the same range of sizes, and the MnO_2 particles showed some intermediate sizes obviously missing. The average diameter of the oil droplets and Kaolin particles were about 1.2 μm and 2.0 μm, respectively, and most of the MnO_2 particle sizes ranged from 0.3 μm to 1.0 μm.

2.3. Experimental procedure

2.3.1. Preparation of dynamic membrane

Before the experiment, the ceramic tube was thoroughly cleaned to make sure that the pure water flux of the support was completely recovered. Two types of dynamic membrane were prepared. One type was the monolayer dynamic membranes which were formed by

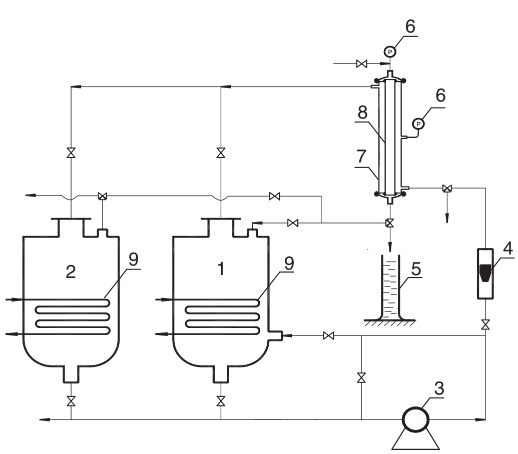

Fig. 1. Schematic diagram of experimental apparatus. 1 Coating solution tank, 2 oily wastewater tank, 3 vortex pump, 4 flow meter, 5 graduated cylinder 6 pressure gauge, 7 membrane module, 8 dynamic membrane, 9 heat exchanger.

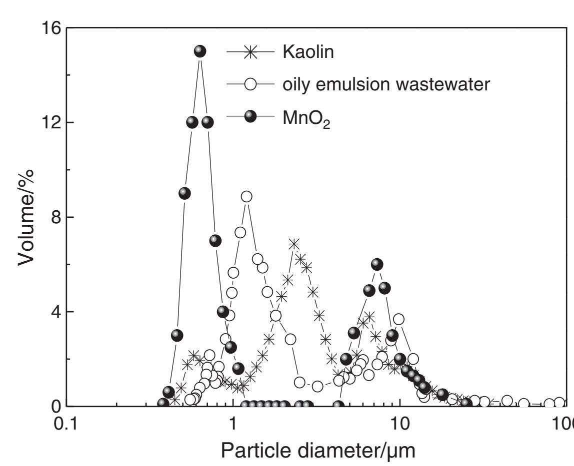

Fig. 3. Diameter size distributions of Kaolin particles, MnO_2 particles and oil droplets.