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Polysulfone/sulfonated polysulfone alloy membranes with an improved performance in processing mariculture wastewater

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HIGHLIGHTS

- Hydrophilic SPSf was synthesized and blended into PSf membranes.
- Improved hydrophilicity, porosity, charged property.
- Improved separation performance in the fouling test (compared the pure PSf membrane).
- Much higher permeation flux and stability in real mariculture wastewater treatment.

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ABSTRACT

In this study, hydrophilic sulfonated polysulfone (SPSf) was synthesized via direct sulfonation of polysulfone (PSf) and efficiently implemented as a hydrophilic additive to prepare the polysulfone/sulfonated polysulfone alloy membranes. On a basis of a high compatibility of PSf and SPSf, the effect of SPSf content in the casting solution on the structure and separation performance of the membranes was investigated. It was demonstrated that the SPSf incorporation could significantly change the hydrophilicity, porosity, morphology and the charge characteristic of the resulting membranes. Compared the pure PSf membrane, the membrane with SPSf 15% yielded an improved hydrophilicity (contact angle was lowered by 23%), more porous structure and more negatively charged surface. It exhibited a high pure water permeability of 2521.6 L/m^{2}h MPa, excellent steady-state flux of 118.0 L/m^{2}h and HA rejection of 86.8% when filtrating 10 mg/L humic acid (HA) solution in dead-end mode under an operating pressure of 0.08 MPa. In a real treatment of mariculture wastewater for 8 h, this membrane exhibited a significant improved steady-state permeation flux of 175.7 L/m^{2}h, which was increased by 144% and 26% compared to those of the homemade and commercial PSf membranes, without any deterioration of the permeate quality. The current investigation indicated that the PSf/SPSf alloy membranes held a promise for the real application.

1. Introduction

With increasing demand for seafood and the continuous reduction of its annual yield, mariculture industry consistently develop in a more sustainable and more efficient way. Generation of large quantities of solid waste and wastewater remains a challenge of the commercial mariculture industry [1]. Because feed and additive chemicals are added into seawater as a nutrition and disinfectant for the growth of aquaculture during the cultivation process, wastewater contains mainly organic contaminants in soluble, colloidal and particulate forms, which has to be treated properly before discharge to avoid the deterioration of marine ecological environment such as eutrophication and water pollution in the coastal areas. The purified wastewater can also be reused as recirculated seawater in a large-scale marine aquaculture plant to achieve zero-liquid-discharge and can efficiently prevent the breakout of infectious disease.

Nowadays, the wastewater treatment for mariculture industries has attracted many interests whether from academic or practical points of view [2,3]. The existing major obstacles involve the complexity of process and operation management, large footprint, low retention efficiency and high operating cost. In particular, biochemical methods such as conventional activated sludge (CAS),

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which is considered to be an efficient way for the wastewater treatment, often fails to treat mariculture wastewater due to the poor growth of activated sludge at a high salinity (seawater), leading to poor removal efficiencies of COD and NH_3-N [4–6].

To overcome these challenges, membrane separation has been proposed as a useful method for the mariculture wastewater treatment to avoid the negative influence of the salinity effect of seawater [7]. A mineral tubular ultrafiltration (UF) membrane with molecular weight cut-off (MWCO) of 15 kDa exhibited a flux of 97.7 L/m^{2}h and a protein rejection of 26.0% at 0.4 MPa in processing seafood wastewater [8]. Mameri et al. [9] also investigated the UF performances of a ZrO_2 membrane and a polysulfone (PSf) membrane in treating seafood wastewater, exhibiting the high protein rejections more than 70.2%, respectively. However, the steady-fluxes decreased with the operating time, even lowered to 58 L/m^{2}h after operation of 2 h [9]. It indicated that the membranes suffered a severe membrane fouling due to the contaminant accumulation on the membrane surface in processing mariculture wastewater, resulting in a significant decline in the separation performance. Therefore, the membranes with an improved separation performance and anti-fouling property are urgently required.

Polysulfone (PSf) with high thermal, mechanical and chemical stabilities [10,11] is now one of the commonly commercial ultrafiltration (UF) membrane materials. However, the hydrophobic nature of PSf makes membrane surface easily suffer from an undesirable membrane fouling, especially organic fouling and bio-fouling [12]. Consequently, a great deal of studies has focused on the hydrophilic modification of membrane surface to improve the anti-fouling property and separation performance, including mainly surface grafting [13], surface coating [14] and blending [15]. Compared to other techniques, blending method was advantageous on the process simplification, easy industrialization and no damage impact on the substrate.

Recently, membranes with high performance have been prepared by incorporating a certain amount of hydrophilic sulfonated polymers into the membrane matrix via blending-phase inversion, involving PSf /sulfonated polysulfone (SPSf) [16], polyethersulfone (PES)/ SPSf [17,18], PSf/sulfonated poly(ether ketone) (SPEK) [19] and PSf/sulfonated polyphenylenesulfone (sPPSU) [20]. These alloyed sulfonated polymers were proved that they not only adjust the surface hydrophilicity and membrane morphology, but also significantly enhance the separation performance [21,22] as well as anti-fouling property [23]. Among the various sulfonated polymers, SPSf is one of the most important hydrophilic sulfonated aromatic polymers, which exhibits the unique chemical and physical properties involving high thermal and oxidation stabilities, adjustable hydrophilicity and excellent mechanical property [24,25], which was usually blended into PSf or PES casting solution to fabricate NF membranes [16,18] and serve as substrate of thin film composite membranes [26]. Water transport and salt rejection can be enhanced by the introduction of the hydrophilic SPSf into the hydrophobic PSf substrates [16,26]. More important, on a basis of similar dissolve mutually theory, SPSf is characteristic of high compatibility with PSf due to the quite similar molecular chains between them, which would facilitate the long-term stability and durability of membranes. Therefore, we believe that the incorporation of SPSf in the PSf membrane can adjust the membrane structure, enhance the membrane hydrophilicity, and thus improve the UF performance as well as the membrane durability in a real application such as mariculture wastewater treatment.

In this work, a homemade water-soluble SPSf was synthesized via direct sulfonation method using chlorosulfonic acid (CSA) as sulfonating agent and used as part of membrane materials to fabricate the hydrophilic PSf/SPSf UF membranes via phase inversion method. The objectives of this study are (1) to investigate the effects of SPSf content on the membrane formation, structure and separation performance of the resulting PSf/SPSf membranes; (2) to evaluate the separation performance in treating a model organic-foulant solution as well as a real mariculture wastewater, which holds promise for the treatment of mariculture wastewater through an ultrafiltration process. As a benchmark, a homemade non-sulfonated PSf membrane and a commercial PSf membrane were also tested for comparison.

2. Experimental

2.1. Materials

Polysulfone (PSf, Udel P-1700, USA) was dried at 100 °C for 24 h prior to use. Chlorosulfonic acid (HSO_3Cl, CSA, 99%) from Xiya Reagent Research Center and chloroform ($CHCl_3$) from the Iron Pagoda Reagent were employed to synthesize SPS powders. N-methyl-2-pyrrolidone (NMP) and polyethylene glycol 400 (PEG-400) purchased from Sinopharm Chemical Reagent Co. Ltd were used as the solvent and pore-former in the casting solution, respectively. HA purchased from Sigma (St. Louis, USA) was applied as the simulated organic foulant. Mariculture wastewater from offshore fishing grounds was supplied by Huanghai Fisheries Research Institute (Qingdao, China). The commercial PSf membranes purchased from Lanjing Membrane Co. Ltd. were used for comparison. Deionized (DI) water used in all experiments was purified using a Millipore water purification system to maintain a minimum resistivity of 18.0 MΩ cm.

2.2. SPSf synthesis and characterization

SPSf was synthesized by direct sulfonation method using CSA as the sulfonating agent similar to that described by Smitha and Tang et al. [27,28]. Typically, the dried PSf was completely dissolved in $CHCl_3$ for 14 h at 50 °C in a three-neck reaction flask. A certain amount of CSA in $CHCl_3$ was transferred into a dropper and then added dropwise to the cooled polymer solution while stirring the solution vigorously at 0 °C. This reaction continued to form a slimy mixture. Finally, the reaction mixture was poured into a large amount of frozen ice water to precipitate in the acidic form of SPSf. The product was filtered and washed with DI water repeatedly until a neutral pH level and then the resulting SPSf powders were finally obtained. The chemical structures of PSf and SPSf are illustrated in Fig. 1.

Degree of sulfonation (DS) is the average number of sulfonic acid groups (-SO_3H) in per repeating unit of SPSf polymer chain, and it is often used to calculate the ion exchange capacity (IEC, meq/g) which is defined as the number of moles of proton per gram of dry powders [26]. DS and IEC were calculated by the following Eqs. (1) and (2), respectively [25]. The measurement procedure was presented in Supporting Information.

$$DS = \frac{0.442MV}{W - 0.08MV} \times 100\% \quad (1)$$

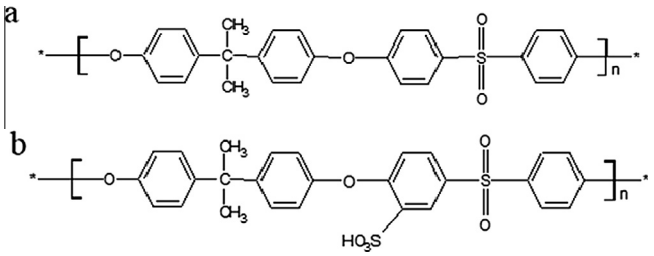

Fig. 1. Chemical structures of PSf (a) and SPSf (b).