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Characterization and application of a thin-film composite nanofiltration hollow fiber membrane for dye desalination and concentration

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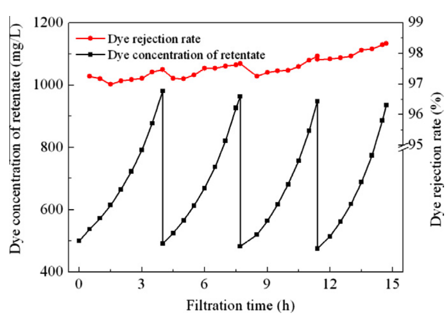
HIGHLIGHTS

- NF membrane could be used desalination and concentration anionic dye solutions.
- NF membrane exhibited retention of 99.99% to Reactive brilliant blue X-BR.
- NF performance was affected by dye and NaCl concentration.
- Dye recovery rate was up to 91.4% and 95.3% NaCl was removed from mixed solution.

GRAPHICAL ABSTRACT

NF hollow fiber membrane was fabricated and was applied to the process of dye desalination and concentration using an X-BR and NaCl mixed aqueous solution as the pollutant. NF hollow fiber membrane possessed a molecular weight cut-off (MWCO) of approximately 520 Da and a pure water flux of 47.5 L/m^2 h at 0.4 MPa. Rejections of different salts followed in the order of $MgSO_4 > Na_2SO_4 > MgCl_2 > NaCl$, with up to 96.20% rejection for $MgSO_4$ and rejections of the anionic dyes reactive brilliant blue X-BR and acid red B were 99.99% and 99.90%, respectively. The dye rejection and permeate flux were affected by the dye concentration as well as the presence of NaCl in the X-BR aqueous solutions. After finishing the process of dye desalination and concentration, the volume of retentate was concentrated 6.25 times, and the dye concentration in the retentate reached 2854.8 mg/L. Moreover, the recovery rate of dye was up to 91.4%, and over 95.3% NaCl was removed from the dye/salt mixtures. The results indicated that NF hollow fiber membrane could be successfully applied to the dye desalination and concentration process.



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ABSTRACT

This study focused on the application of a thin-film composite nanofiltration (NF) hollow fiber membrane formed by interfacial polymerization on a polysulfone/polyethersulfone supporting membrane for dye desalination and concentration. The fabricated NF hollow fiber membrane had a hydrophilic skin layer with an isoelectric point at a pH value of approximately 6.6. Permeation tests revealed that the membrane possessed a molecular weight cut-off (MWCO) of approximately 520 Da and a pure water flux of 47.5 L/m^2 h at 0.4 MPa. Rejections of different salts followed in the order of $MgSO_4 > Na_2SO_4 > MgCl_2 >$ NaCl at a pH value of 6.8, with up to 96.20% rejection for $MgSO_4$. Additionally, due to the negative charge on the membrane surface, rejections of the anionic dyes reactive brilliant blue X-BR and acid red B were 99.99% and 99.90%, respectively. The dye rejection and permeate flux were affected by the dye concentration as well as the presence of NaCl in the X-BR aqueous solutions. Both the dye rejection and permeate flux would decline with the increase of feed dye and salt concentration. The fabricated NF hollow fiber membrane was applied to the process of dye desalination and concentration using an X-BR and NaCl mixed aqueous solution as the pollutant. After finishing the process, the volume of retentate was concen-

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trated 6.25 times, and the dye concentration in the retentate reached 2854.8 mg/L. Moreover, the recovery rate of dye was up to 91.4%, and over 95.3% NaCl was removed from the dye/salt mixtures, which indicated that the fabricated composite NF hollow fiber membrane could be successfully applied to the dye desalination and concentration process.

1. Introduction

Dyes can be defined as soluble colored substances that are applied mainly to textile materials [1]. Presently, synthetic dyes have been widely used in various industries such as textile, rubber, paper, plastic, leather tanning, etc. It is estimated that there are over 10,000 types of commercial dyes, and more than 7×10^5 tons are produced annually worldwide [2–4].

However, the synthesis and use of dyes cause many environmental problems. On the one hand, small molecular weight intermediates, salts and residual compounds are generated, which must be removed as they will affect the purity of the dyes and reduce the product quality standard [5,6]. On the other hand, a large amount of high salinity and high chroma wastewater is discharged into the environment, which can cause considerable environmental pollution and is dangerous to the health of human beings. Additionally, the traditional dye production process cannot meet the requirements of clean production and the reuse of wastewater [7,8]. Accordingly, a new method for dye purification and dye wastewater treatment is highly desirable.

Nanofiltration (NF), possessing separation characteristics between reverse osmosis (RO) and ultrafiltration (UF), has been prevalent since its introduction in the 1980s. NF membranes have two remarkable features that differentiate them from other types of membranes. One is a molecular weight cut-off (MWCO) ranging from 200 to 1000 Da. The other is a high permeability for monovalent ions and a low permeability for divalent ions [9,10]. Therefore, NF membranes are widely utilized in applications such as water softening, municipal and industrial wastewater treatment and separation and concentration in the chemical and pharmaceutical industries [11–16]. In addition to these numerous applications, NF membranes have become increasingly popular in the dye industry to replace the conventional process. The NF process for dye purification can be subdivided into desalination and concentration. The former refers to the process of adding water to the feed that then permeates through the membrane with a certain operating pressure, carrying with salts and impurities while dye is entrapped and cycled back to the feed tank. Concentration refers to the continuous removal of water until the concentration of dyes can satisfy the drying spray requirements [4–6,17]. NF membrane technology is promising and could be the most effective method for dye desalination and concentration.

There are a number of commercially available NF membranes in the current market. The most widely used are the thin-film composite (TFC) NF membranes, which are mainly prepared through interfacial polymerization (IP). Other techniques, for example, chemical cross-linking and UV grafting, have also been used [18–20]. To date, researchers have conducted a large number of studies on dye separations using thin-film composite NF flat-sheet membranes, either for wastewater treatment or dye purification [21–24]. However, research concerning the use of TFC NF hollow fiber membranes for dye wastewater treatment and reuse has rarely been reported. For instance, Akbari [25] fabricated an NF hollow fiber membrane by UV-photografting vinyl monomer sodium p-styrene sulfonate (NaSS) on a UF hollow fiber membrane surface. The fabricated negatively charged hollow fiber membrane with a MWCO of 4500 Da was used to concentrate a saline direct red 80 with a dye rejection of more than 97.0% and a salt rejection lower than 2.0%. He [26] prepared the NF hollow fiber membrane by coating sulfonated poly(ether ether ketone) (SPEEK) on a polyethersulfone (PES) support. The prepared NF membrane showed 97–100% rejection of organic dyes. More recently, Yu [27,28] developed thin-film composite NF hollow fiber membranes by dip-coating sodium carboxymethyl cellulose (CMCNa) on the outside of polypropylene (PP) microporous hollow fiber membranes followed by cross-linking with $AlCl_3$ and $FeCl_3$. The fabricated negatively charged CMCNa/PP TFC hollow fiber membranes yielded a MWCO of approximately 700 Da, and rejections of Congo red and Methyl blue were higher than 99.8% and 99.6%. Moreover, rejection of NaCl with concentrations of 4000 mg/L and 10,000 mg/L was lower than 5.0% and 2.0%, respectively. Sun [29] provided a TFC NF membrane via interfacial polymerization of hyperbranched polyethyleneimine (HPEI) and isophthaloyl chloride (IPC) on a dual-layer hollow fiber membrane surface. Due to the double-repulsion, steric-hindrance, and solute electro-neutrality effects, the developed NF hollow fiber membrane showed superior rejections (over 99%) for both positively and negatively charged dye molecules. Up to now, although dyes or dye/salt mixtures treatment using NF hollow fiber membranes has been studied by some researchers, no systematic study on dye desalination and concentration using a thin-film composite NF hollow fiber membrane has been reported in the literature.

Accordingly, this study focuses on the dye desalination and concentration process using a laboratory fabricated TFC NF hollow fiber membrane. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR), X-ray photoelectron spectroscopy (XPS) and field emission scanning electron microscopy (FE-SEM) were employed to characterize the chemical and morphological structures. Furthermore, the separation properties of the fabricated TFC NF hollow fiber membrane in terms of dye rejection and permeate flux under different operating conditions, including dye type, feed dye concentration and feed NaCl concentration, were also studied.

2. Experimental

2.1. Materials and reagents

Polysulfone/polyethersulfone (PS/PES) hollow fiber UF supporting membranes with a MWCO of approximately 30,000 Da and a pure water flux of approximately 152 L/m^2 h at 0.1 MPa were provided by the Development Center of Water Treatment Technology, State Oceanic Administration, Hangzhou, China. Trimesoyl chloride (TMC, purity >99.0%) was purchased from Qingdao Benzo Chemical Company, China, and used as the active monomer of the organic phase with n-hexane (Shanghai Lingfeng Chemical Reagent Company, China) as the organic solvent. The aqueous phase solution consisted of piperazine (PIP, purity >99.0%, Aladdin Chemistry Company, China) as the active monomer and sodium phosphate (Na_3PO_4, Sigma-Aldrich) as the acid acceptor. Several analytical grade inorganic salts, i.e., Na_2SO_4, $MgSO_4$, $MgCl_2$ and NaCl, were purchased from Shanghai Sihewei Chemical Reagent Company, China. Polyethylene glycol (PEG, chemical grade) with molecular weights of 200, 400, 600, 1000, 2000 and 4000 Da was purchased from Sinopharm Chemical Reagent Company, China. Dyes including reactive brilliant blue X-BR, acid red B and cationic red X-GTL were obtained from a local commercial group without further