Journal of Membrane Science 455 (2014) 15–23

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Surface fluorination of polyamide nanofiltration membrane for enhanced antifouling property

Yafei Li [a], Yanlei Su [a,b], Xueting Zhao [a], Runnan Zhang [a], Jiaojiao Zhao [a], Xiaochen Fan [a], Zhongyi Jiang [a,b,*]

[a] *Key Laboratory for Green Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China*
[b] *Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China*

ARTICLE INFO

Article history:
Received 21 August 2013
Received in revised form
15 November 2013
Accepted 24 December 2013
Available online 2 January 2014

Keywords:
Fluorinated polyamine
Surface grafting
Polyamide nanofiltration membrane
Low surface free energy
Antifouling

ABSTRACT

A new kind of fluorinated polyamine was successfully synthesized and grafted onto the polyamide membrane surface to fabricate an antifouling nanofiltration membrane with low surface free energy. The surface composition of the fluorinated polyamide nanofiltration membrane was confirmed by Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). The membrane cross-section morphology was observed by a field emission scanning electron microscopy (FESEM). The presence of perfluoroalkyl groups on the membrane surface significantly lowered the surface free energy from 60.0 to 44.4 mJ/m^2. The filtration experiment results indicated that the surface fluorination did not lower the separation performance of the polyamide nanofiltration membrane significantly. The antifouling experiment results demonstrated that the fluorinated polyamide nanofiltration membranes exhibited superior antifouling property, that is, high flux recovery ratio (~98.5%) and low total flux decline ratio (~11%) during protein aqueous solution and humic acid aqueous solution filtration.

1. Introduction

Membrane fouling is a major hindrance to the effective application of nanofiltration (NF) technology in water treatment, pharmaceuticals, and biochemical industries [1–8]. Fouling leads to a decrease in membrane performance, which, in turn, increases the overall energy requirement of the separation process and decreases membrane life [9]. Thus, fouling control is one of the most pressing challenges faced by the membrane science community. Pretreatment of feed solution and/or chemical cleaning are popular approaches to cope with membrane fouling [10]. However, these approaches would dramatically increase the operation and maintenance costs of the membrane process. Therefore, there is significant interest in enhancing membrane fouling resistance and fouling release property to reduce the burden of feed pretreatment and lower the cleaning cost.

Most state-of-the-art nanofiltration membranes are currently the thin-film composite (TFC) membranes, comprising a thin selective active layer on a porous support. As the benchmark material for the active layer, polyamide shows unrivaled permeability and selectivity performance and a high degree of tenability in the membrane process [11]. The active layer surface properties including hydrophilicity, roughness and charge are reported to influence fouling [12]. For better antifouling performance, efforts toward membrane active layer modification have focused on rendering the surface more hydrophilic, smooth, and less charged [13]. Examples include the production of novel polyamide-based materials with tailored chemistry and morphology achieved by the addition of monomers or variation of conditions during interfacial polymerization [14–16]. However, the unsurpassed separation properties of polyamide limit the range of improvements that can be made following this pathway. Other studies have investigated modifications of the thin film surface by postfabrication procedures [12,17]. So far, majority efforts are devoted to enhancing the fouling resistant property of the membrane, that is to say, effectively preventing foulants from arriving at membrane surface via the nonspecific adsorption. Probably, weakening the interfacial interaction between membrane and foulants, so that attached foulants are more easily removed, may be another strategy to tailor membrane antifouling characteristics.

The surface free energy of a solid surface gives a direct indication of intermolecular or interfacial attractive forces [18]. A number of studies demonstrated that bacterial and organism are less prone to adhere or attach to low energy surfaces and easier to clean because of weaker binding force [19,20]. Silicone elastomers and fluoropolymers, as the two major polymeric materials with low free energy, have been wildly used in many antifouling fields

---

[*] Corresponding author at: Key Laboratory for Green Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China. Tel.: +86 22 27406646; fax: +86 22 23500086.
E-mail address: zhyjiang@tju.edu.cn (Z. Jiang).

0376-7388/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.memsci.2013.12.060

including marine coatings and membrane separation fields. Fouling release coatings as toxin-free alternatives have gained many attention after the prohibition of tributyitin (TBT) contamination by the International Maritime Organization (IMO) [21]. Currently, several surface active block copolymers with fluoroalkyl side chains [22,23], semifluorinated block copolymers [24,25] and perfluoropolyether/poly(ethylene glycol) networks [26,27] have been explored as fouling release coatings. Ober and coworkers have also developed amphiphilic coatings with silicone segments as fouling release moieties and heightened their importance in reducing potential environmental impact [28–30]. Recently, fluorine-containing copolymers and silicone-containing copolymers are also used as additives in non-solvent-induced phase separation (NIPS) process to fabricate the ultrafiltration (UF) membrane, and the membrane displayed the excellent ability to resist and release various foulants [31–34]. Grafting perfluoroalkyl groups onto UF membrane surface has also been reported to improve the fouling release property of the membrane [35]. However, to the best of knowledge, no report has been found for improving the antifouling property of nanofiltration membranes by minimizing the interaction forces between nanofiltration membrane and foulants via low surface free energy strategy.

In this study, to prepare an antifouling NF membrane with low surface free energy, a new kind of fluorinated polyamine was synthesized by perfluorooctanoic acid (PFOA) and triethylenetetramine (TETA) via condensation reaction. The fluorinated polyamine was then grafted onto polyamide NF membrane surface through the acylation reaction between the amine groups of fluorinated polyamine and the carbonyl groups on polyamide NF membrane. The membranes were characterized by contact angle, surface free energy, SEM, FTIR and XPS. The permeation and rejection properties, the antifouling behavior of fluorinated polyamide NF membrane in filtration of protein and humic acid were explored.

2. Experimental section

2.1. Materials

Polyethersulfone (PES, 6020 P) was purchased from BASF Co. (Germany) and dried at 110 °C for 12 h before use. Poly (ethylene glycol) (PEG, *Mw*=2000), N, N-dimethylformamide (DMF), n-heptane, xylene, ethanol, Na_2SO_4, $MgSO_4$ and $MgCl_2$ were purchased from Kewei Chemical Reagent Co. (Tianjin, China). Trimesoyl chloride (TMC) was purchased from Alfa Co. (USA). Piperazidine (PIP), triethylenetetramine (TETA) and humic acid (HA) were received from Guangfu Fine Chemical Research Institute (Tianjin, China). Perfluorooctanoic acid (PFOA) was purchased from Boman Chemical CO. LTD. (Zhangjiagang, China). Bovine serum albumin (BSA) was purchased from Institute of Hematology, Chinese Academy of Medical Science (Tianjin, China). Orange GII was purchased from Dingguo Bio-Technology Co. (Beijing, China). The water used was deionized water at pH 6.0.

2.2. Synthesis of a new kind of fluorinated polyamine

Fluorinated polyamine was synthesized by condensation reaction in the xylene solutions. PFOA (4.64 g, 10 mmol), xylene (50 mL) and TETA (1.61 g, 11 mmol) were put into a three-necked round bottom flask provided with a reflux condenser and a mechanical stirrer. The reaction flask was placed in an oil bath and the mixture was refluxed with rapid mechanical stirring at 130 °C for 4 h. After reacting for 4 h, the obtained polyamine solution was then placed on the rotary evaporator to remove solvent and by-product water. The fluorinated polyamine was then oven-dried to a constant weight.

To confirm the successful synthesis of the fluorinated polyamine, the product was analyzed by Fourier transform infrared spectroscopy (FT-IR). The sample was dissolved in ethanol and sprayed on a KBr plate. Transmittance spectra were obtained in the region of 4000–400 cm^{-1} with resolution 4 cm^{-1} for 64 scans.

2.3. Preparation and surface fluorination of the polyamide NF membrane

PES ultrafiltration membranes were used as the porous support. The detailed fabrication process had been described in our previous works [36]. The PES support was first wetted in PIP aqueous solution with PIP concentration of 0.30 wt%. After 30 min, the residual water on the surface was drained off using filter papers. Second, the PIP-saturated support membrane was immersed for 120 s in a 0.15 wt% TMC in n-hexane to form the ultrathin polyamide layer by interfacial polymerization. Third, the membrane was taken from organic phase and air dried at room temperature for 30 min to allow the n-heptane to evaporate and subsequently post-treated for attaining the desired stability of the formed structure.

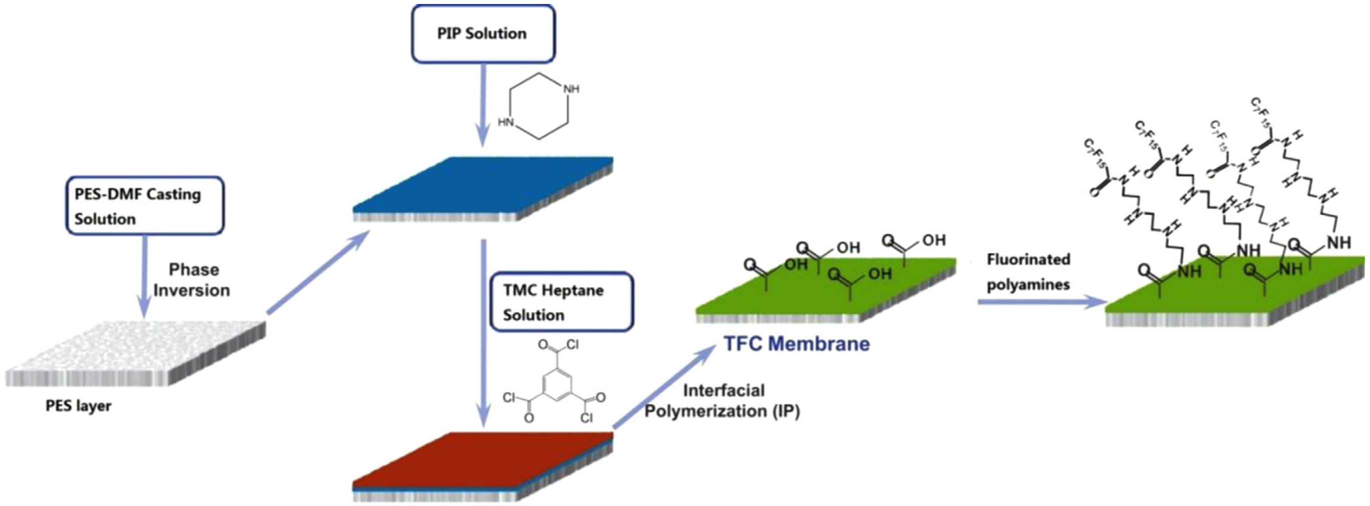

Fig. 1. Schematic diagram of fabricating polyamide NF membrane (TFC membrane) and grafting fluorinated polyamine onto the surface of polyamide NF membrane.