Journal of Membrane Science 514 (2016) 407–417

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Surface modification of NF membrane with zwitterionic polymer to improve anti-biofouling property

Jing Wang [a,b], Zhi Wang [a,b,*], Yingying Liu [a,b], Jixiao Wang [a,b], Shichang Wang [a,b]

[a] Chemical Engineering Research Center, School of Chemical Engineering and Technology, Tianjin 300072, PR China
[b] Tianjin Key Laboratory of Membrane Science and Desalination Technology, State Key Laboratory of Chemical Engineering, Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin University, Tianjin 300072, PR China

ARTICLE INFO

Article history:
Received 7 January 2016
Received in revised form
4 April 2016
Accepted 8 May 2016
Available online 13 May 2016

Keywords:
Nanofiltration membrane
Anti-biofouling
Easy-cleaning
Zwitterionic polymer

ABSTRACT

The zwitterionic poly-(carboxybetaine methacrylate) (PCBMA) was grafted on two commercial nanofiltration (NF) membranes surfaces to improve the easy-cleaning, anti-adhesive and anti-microbial properties of the membranes. Based on the amine and carboxylic acids groups of NF membranes, the commercial NF membranes (NF90 and NF270) were modified by the redox initiated graft polymerization to obtain the NF90-PCBMA and NF270-PCBMA membranes. The membranes before and after modification were characterized by ATR-FTIR and XPS to analyze the change of the membrane surface chemical structure characterization, and also by contact angle analyzer, zeta potential analyzer, SEM and AFM to analyze the change of the membrane surface physical characterization. The zeta analysis (at pH 7.0) indicated that the NF90-PCBMA and NF270-PCBMA membranes surfaces were near electrically neutral, while the unmodified NF membranes surfaces were negatively charged. The NaCl and $MgSO_4$ solutions were used to analyze the permselectivity of the membranes, which changed little after modification. The aqueous solutions containing positively charged lysozyme and negatively charged bovine serum albumin were used to analyze the anti-adhesive property of the membranes, and the water fluxes of the modified membranes were all decreased less than those of the unmodified membranes. After the membranes being cleaned, the water flux recovery rates of the modified membranes were all above 90% and much higher than those of the unmodified membranes. The anti-microbial property of the membranes was analyzed by being contacted with Escherichia coli and bacillus subtilis, the mortality of which could reach to 99%. The PCBMA modification method had improved the anti-adhesive, anti-microbial and easy-cleaning properties of two aromatic polyamide NF membranes without sacrificing the permselectivity of the membranes. What's more, this method may be suitable for all aromatic polyamide membranes to increase the anti-biofouling property.

1. Introduction

Nanofiltration (NF) can either be used to treat all kinds of water including ground, surface, wastewater or being used as a pretreatment for desalination [1]. However, fouling is still a prevalent issue that may hinder successful application of NF membranes [2]. The most prevalent and problematic type of fouling in NF systems is biofouling, which is inherently more complicated than other membrane fouling phenomena because microorganisms can grow, multiply and relocate on the membrane surface [3,4]. Biofouling cannot be completely eradicated, as it only requires a few initial colonies on the membrane surface to form a mature biofilm. What's more, biofouling has been found to occur extensively on NF membrane even after significant pretreatment of the influent stream [3,5].

Currently, many studies have been focused on NF membrane surface modification to obtain the anti-adhesive membrane. The bacterial initial attachment can be largely controlled by the anti-adhesive membrane surface, most of which is hydrophilic, neutral and smooth [4]. Shao et al. [6] synthesized the NF membrane through interfacial polymerization (IP) of the high hydrophilicity polyethylene glycol (PEG) and trimesoyl chloride (TMC). The hydrophilicity PEG can bind the water molecules through hydrogen bonding and enhance the anti-fouling property of NF membrane. Gao et al. [7,8] modified the surface of the NF membrane with the zwitterionic materials, which improved the membrane flux and the resistance of bacteria and protein fouling remarkably. The low fouling behavior of zwitterionic materials is attributed to their ability to bind a significant number of water molecules through

* Correspondence to: Tianjin University, School of Chemical Engineering and Technology, Chemical Engineering Research Center, Weijin Road 92#, Nankai District, Tianjin 300072, PR China.
E-mail address: wangzhi@tju.edu.cn (Z. Wang).

http://dx.doi.org/10.1016/j.memsci.2016.05.014
0376-7388/

both electrostatic and hydrogen bonding interactions, and the water molecules bond with the zwitterionic materials will form the strong hydration layer and effectively prevent the adhesion of proteins [9–14]. However, most of these modification methods to obtain the anti-adhesive NF membranes were difficult to realize industrialization amplification now, and these anti-adhesive NF membranes were not anti-microbial and could not prevent the membrane biofouling exhaustively.

A low adhesion rate might delay biofilm formation, but could not prevent it [15]. There is an increasing body of evidence suggesting that the rate of bacterial adhesion is not predictive to the extent of biofilm formation [16,17]. Therefore, the ideal functionalized membranes should prevent the settlement of bacteria during NF process with both anti-microbial and anti-adhesive properties. Zhang et al. [18] modified the NF membrane with the biogenic silver nanoparticles, which made the modified membrane surface with the antimicrobial property and more hydrophilic. However, the release based antibacterial mechanism of the silver nanoparticles made them unstable. Therefore, it is still extremely challenging to modify the NF membrane to make it have both "anti-adhesive" and "anti-microbial" properties, which would be benefit to completely prevent the biofouling of the NF membrane.

Recently we had modified reverse osmosis (RO) membrane by zwitterionic polymer poly-(carboxybetaine methacrylate) (PCBMA) containing quaternary ammonium cation and improved the permselectivity, easy-cleaning, "anti-adhesive" and "anti-microbial" properties of RO membrane at the same time [19]. We had speculated that the zwitterionic PCBMA may also be applied to modify the other aromatic polyamide membranes and increase their anti-biofouling property, such as nanofiltration membrane, forward osmosis membrane, etc. In our previous work, to avoid decreasing the RO membrane permselectivity, the graft degree of PCBMA on RO membrane was controlled to be not too high, which led that the anti-adhesive property of the RO membrane was not improved significantly. What's more, the surface properties of RO and NF membranes are different in terms of their physicochemistry (i.e. surface hydrophobicity, charge and chemical composition) as well as their physical attributes (i.e. surface topology and morphology) [16]. Therefore, we would use the zwitterionic PCBMA to modified two aromatic polyamide nanofiltration membranes, which would help to proof this method may be universally suitable for all aromatic polyamide membranes; and considering the differences of RO and NF membranes, we will adjust the parameters of the grafting solutions and increase the anti-adhesive property of the membrane significantly.

In this work, we modified the commercial NF membranes with the zwitterionic polymer PCBMA containing quaternary ammonium (N^+) group to improve the easy-cleaning, anti-adhesive and anti-microbial properties of them. We chose two typical commercial NF membranes: NF90 and NF270 to modify. The active layers of NF270 and NF90 membranes are different, therefore, the surface chemical structure, physicochemistry and permselectivity of the two membranes are also different. The zwitterionic polymer PCBMA, which has a cationic quaternary ammonium (N^+) group and an anionic carboxylate (COO^-) group on its backbone, has good resistance to protein adsorption and bacterial attachment, and will improve the easy-cleaning and anti-adhesive properties of the NF membranes. The zwitterionic polymer containing the cationic quaternary ammonium (N^+) will also improve the antimicrobial property of the NF membrane. The NF membranes were analyzed by attenuated total reflectance-Fourier transform infrared (ATR-FTIR), scanning electron microscopy (FE-SEM), atomic force microscopy (AFM) and Electrokinetic Analyzer. The effects of the modification on the membrane permselectivity, easy-cleaning, anti-adhesive and anti-microbial properties were experimentally evaluated.

2. Experimental

2.1. Materials

Two commercial available nanofiltration membranes (NF90 and NF270, FilmTec™ membranes of Dow Chem. Company, USA) were used as the base matrix for grafting. N,N′-dimethylamino ethyl methacrylater (DMAEMA), potassium persulfate and sodium sulfate were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). 3-bromopropionic acid (3-BPA, purity 98%) was purchased from J&K Scientific Co., Ltd. (Beijing, China). Yeast extract, peptone, agar and lysozyme were purchased from Ding guo chang sheng biotech Co., Ltd. (Beijing, China). Bovine Serum Albumin (BSA) was purchased from Tian qin yi he biotech Co., Ltd. (Beijing, China). NaCl and sodium hydrogen sulfite were purchased from Jiang tian Chemical Technology Co., Ltd. (Tianjin, China). All reagents were of analytical grade and used without further purification. Deionized water with conductivity less than 15 μs/cm was produced by a two-stage reverse osmosis system in the laboratory.

2.2. Membrane modification

The NF90 or NF270 membrane piece (15.5 cm × 12.5 cm) kept in sodium bisulfite solution (0.5 wt%) was thoroughly rinsed with pure water, and then was fixed in polyfluortetraethylene frame. The NF-90 or NF-270 membrane was covered by 50 mL DMAEMA grafting solution, containing the DMAEMA (0.2 mol/L), the redox initiators $K_2S_2O_8$ (1×10^{-3} mol/L) and $Na_2S_2O_5$ (1×10^{-3} mol/L), for 60 min at 30 °C in the oven.

After being dried thoroughly, the DMAEMA-polymer chains modified membrane was covered by 100 mL solution containing excessive 3-BPA for 48 h at 30 °C in the oven. The resulting membrane was the PCBMA modified NF90 or NF270 membrane, which was respectively named as NF90-PCBMA or NF270-PCBMA membrane and should be thoroughly washed before being stored in pure water.

2.3. Characterizations

The NF membrane surface functional groups were characterized by ATR-FTIR spectroscopy (FTS-6000, Bio-Rad Inc., America) with a hundred scanning times, providing a solution of 4 cm^{-1}.

The elementary composition of membrane functional separation layers was analyzed by an X-ray photoelectron spectroscopy (XPS, PHI1600, USA) using MgKα as the radiation source, with the voltage of 15 kV, vacuum for 2×10^{-7} Pa and a resolution of 0.7 eV, and the area of analysis was 0.8 mm^2. The membrane samples were completely dried under vacuum at 40 °C for 4 h before the XPS and ATR-FTIR characterization.

The static contact angles were measured by a contact angle goniometer (OCA15EC, Dataphysics, Germany) equipped with a video camera. The water droplet morphologies and contact angles were analyzed by the SCA 202 software (Dataphysics, Germany). At least six water contact angles at different locations on one membrane surface were averaged to get a reliable value.

Membrane surface streaming potential was measured by SurPASS solid surface Zeta potential analyzer (Anton Paar GmbH, Austria). The measurements were conducted in a background electrolyte solution containing 1 M KCl at pH 7 and 25 °C. The zeta potential of the membrane was computed from the Helmholtz–Smoluchowski equation.

Scanning electron microscope (SEM) (Nova NanoSEM430, FEI, USA) was used to analyze the surface morphologies of the membranes and the surface roughness analysis was performed by atomic force microscopy (AFM) (Bruker Optics, Germany) using tapping mode in air. The scanning area was 10 mm^2. The