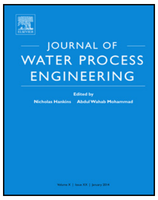
Journal of Water Process Engineering 7 (2015) 1–10

Contents lists available at ScienceDirect

Journal of Water Process Engineering

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



NOM fouling behavior during ultrafiltration: Effect of membrane hydrophilicity

Xiangrong Chen, Jianquan Luo, Benkun Qi, Weifeng Cao, Yinhua Wan*

State Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

ARTICLE INFO

Article history:
Received 9 March 2015
Received in revised form 16 April 2015
Accepted 18 April 2015
Available online 16 May 2015

Keywords:
Organic fouling
Fouling resistance
Polyethylene oxide
Ultrafiltration
Hydrophilicity

ABSTRACT

Polyethylene oxide (PEO)-modified ultrafiltration (UF) membranes were prepared using polyacrylonitrile-graft-polyethylene oxide (PAN-g-PEO) copolymers through immersion precipitation phase inversion method. Compared to PAN membrane, the PEO-modified UF membranes possessed extraordinary hydrophilic surface owing to the enrichment of PEO segments, which was confirmed by X-ray photoelectronic spectroscopy (XPS). The effects of membrane hydrophilicity on the organic fouling resistance were investigated by means of the resistance-in-series model. The results showed that the hydrophilic modification of UF membrane contributed to the fouling control in bovine serum albumin (BSA) and *Escherichia coli* (*E. coli*) bacteria filtration. The antifouling ability of the membranes increased with increasing PEO content. The pure water flux could recover completely after filtering BSA and bacteria, respectively, for the membranes with 25.2% and 8.5% PEO content. In contract, the increase of membrane hydrophilicity had a negative effect on the humic acid (HA) and sodium alginate (SA) filtration. The membrane permeability of the PAN membrane unexpectedly increased after HA or SA filtration, while the flux recovery ratio of PEO-modified membranes decreased with increasing PEO content. The differences in fouling behavior of the various organic foulants on hydrophobic or hydrophilic membrane were attributed to the nature of organic foulants and their interaction with membranes.

1. Introduction

Recently, ultrafiltration (UF) has been used extensively in water treatment, concentration and clarification of feed, as well as purification and fractionation of mixture due to its advantages of low energy requirements, continuous flow operation, and ability to be easily scaled-up. However, the flux decline over time caused by concentration polarization and membrane fouling is a main challenge for UF process, which to some extent impedes the large-scale commercial application of UF. In general, naturally occurring organic matter (NOM), such as humic substances, proteins and polysaccharides are recognized as the major foulants that block the membrane pore and reduce permeate flux [1]. Therefore, considerable effort has been expanded to investigate the effects of NOM on the membrane performance and subsequently to understand the fouling mechanisms, especially in water treatment process. There are three key factors responsible for membrane fouling, including solution chemistry (ionic strength, pH) [2,3], NOM characteristics (molecular weight distribution, hydrophilic–hydrophobic character) [4–6], and membrane properties (hydrophilicity, pore size) [7].

To alleviate membrane fouling, many strategies have been developed, such as optimization of hydrodynamic conditions [8,9] and preparation of novel antifouling membrane [10–36]. It is generally accepted that improving the intrinsic hydrophobic character of membranes is the most common method to avoid the non-specific adsorption between membrane and solute. Several hydrophilic materials were used to enhance antifouling ability of the conventional hydrophobic membranes, including PEO-like polymers [10–22], zwitterionic polymer [23–25], phospholipid polymer [26,27], heparin [28,29], zirconium oxide [30], titanium oxide [31], zeolite [32], silica [33], carbon nanotubes [34], graphene oxide [35], and their mixture [36]. Among these materials, PEO-like polymers have attracted much attention due to their superior antifouling ability [37]. Although the kinetic and thermodynamic reasons for the protein resistance of PEO are still controversial, many researchers have attempted to mix the various PEO-containing amphiphilic copolymers with the usually used membrane materials to prepare the antifouling membranes [10–21]. The results confirmed that PEO chain had a trend to enrich on the membrane surface, which imparted good hydrophilicity to the hydrophobic membranes. Consequently, the blend membranes exhibited an

---

* Corresponding author. Tel.: +86 10 82544991; fax: +86 10 62650673.
E-mail address: yhwan@ipe.ac.cn (Y. Wan).

http://dx.doi.org/10.1016/j.jwpe.2015.04.009
2214-7144/

Nomenclature

A	Membrane effective area (m^2)
C_p	Foulant concentrations in permeate ($g L^{-1}$)
C_f	Foulant concentrations in feed solutions ($g L^{-1}$)
FRR	Flux recovery ratio
J_1	Pure water flux for new membrane($L m^{-2} h^{-1}$)
J_2	Final flux for the feed solution($L m^{-2} h^{-1}$)
J_3	Pure water flux of cleaned membranes ($L m^{-2} h^{-1}$)
ΔP	Transmembrane pressure (MPa)
R	Rejection of model foulant
R_t	Total filtration resistance (m^{-1})
R_m	Intrinsic membrane resistance (m^{-1})
R_{rev}	Reversible resistance (m^{-1})
R_{irr}	Irreversible resistance (m^{-1})
Δt	Permeation time(h)
μ	Dynamic viscosity of water at room temperature (Pa s)
V	Volume of permeated water (L)

improved fouling resistance property. The effects of the copolymer composition and PEO chain length on the membrane properties have been investigated in details [17]. Meanwhile, the other researchers obtained the low fouling membranes by coating or grafting PEO chain on membrane surface [22], and generally there was a trade-off between membrane permeability and antifouling performance.

In the above studies, however, the antifouling property of the PEO-modified membranes was measured usually using protein solution as the testing feed. It is very difficult to understand completely the antifouling behavior of the PEO-modified membranes in complex actual feed. Therefore, in the present work, our goal was to assess the antifouling ability of the PEO-modified membranes in various potential organic foulants, including humic substances, protein, polysaccharide, and bacteria. A series of polyacrylonitrile-graft-polyethylene oxide (PAN-g-PEO) copolymer membranes with different hydrophilic compositions were prepared firstly. The structure composition and molecular weight distribution of the synthesized copolymers were determined by ^{1}H nuclear magnetic resonance spectroscopy (^{1}H NMR) and gel permeation chromatography (GPC), respectively. Meanwhile, the surface chemical composition, hydrophilicity, and permeability of the membranes were characterized by X-ray photoelectron spectroscopy (XPS), contact angle measurement, and filtration test, respectively. In order to provide guides for different fouling control in terms of membrane materials, the effect of membrane hydrophilicity on organic fouling behavior was investigated, and the resistance-in-series model was applied to analyze the fouling mechanism.

2. Experimental

2.1. Materials and reagents

Acrylonitrile (AN, Tianjin Kremel Chemical Reagents Development Center, China) was purified by distillation under reduced pressure, and stored at 4 °C for use. Poly(ethylene glycol) methyl ether methacrylate (PEGM, Mn 475 Da) was purchased from Sigma–Aldrich, USA for grafting preparation of copolymer. A stock solution of 0.1 M ceric ammonium nitrate (Ce(IV), Tianjin Jinke Fine Chemical Engineering Institute, China) in 1 N HNO_3 was prepared and stored at 4 °C for use. PAN ultrafiltration membrane with the molecular weight cutoff of 30,000 Da, was purchased from Sepro Membrane Inc. used as a control. Bovine serum albumin (BSA), sodium alginate (SA), humic acid (HA) and *Escherichia coli* (*E. coli*) bacteria were chosen as the model organic foulants and the characteristic properties of the model foulants are listed in Table 1. The model solutions with concentrations of 1.0 g/L were prepared freshly. The BSA stock solution (pH 7.0) was prepared by dissolving 1 g BSA (Sigma–Aldrich, USA) into 1 L 0.1 M phosphate buffer solution (PBS, pH 7.0). The SA stock solution was prepared by dissolving 1 g SA (Sigma–Aldrich, USA) into 1 L deionized water. The HA stock solution (pH 12) was prepared by dissolving 1 g HA (Shanghai Aladdin Reagent Co. Ltd., China) into 1 L 0.01 M NaOH solution. The *E. coli* bacteria were cultured in Luria–Bertani broth at 37 °C. The cells were harvested by centrifugation, washing, and finally resuspending in sodium chloride solution (154 mM, pH 7.0). The cell concentration in feed solution was approximately 10^6 cell/L. All other reagents were of analytical grade and were used as received.

2.2. Synthesis of PAN-g-PEO

A series of different composition copolymers were prepared via the redox polymerization. A typical procedure was as follows: In a 250 mL three-necked flask equipped with a dropping funnel, nitrogen inlet and stirrer, 1 mL anhydrous ethanol, 7.05–9.20 mL AN, 0.20–2.35 mL PEGM and 138 mL deionized water were charged, and then stirred for 30 min under a N_2 atmosphere at 40 °C. Then 14 mL Ce (IV) stock solution was added dropwise in 10 min. The vessel was sealed and the stirring was continued further for 5 h. The copolymers obtained were filtered, washed several times with deionized water and then with acetone, and finally dried under vacuum. The block copolymers thus obtained were dissolved in *N*,*N*-dimethylformamide (DMF) and reprecipitated with water for purification.

The graft copolymers are denoted as PAN_x-g-PEO, where x stands for the mole composition ratio of AN and PEO in the copolymers. The structure and composition of the copolymers were characterized by ^{1}H NMR spectroscopy with Bruker Avance 400 spectrometer using deuterated DMF as a solvent, and the spectra is shown in Fig. 1. The molecular weight and the molecular weight distribution of the copolymers were determined by gel permeation chromatography in DMF. The resulting copolymer details are listed in Table 2.

2.3. Membrane preparation

Membranes were prepared by means of the classical immersion precipitation phase inversion method. The copolymers with various compositions were dissolved in 1-methyl-2-pyrrolidinone (NMP) at 10 wt% concentration. After completely dissolved, the copolymer solutions were filtrated by vacuum, and casted onto the glassplate (~200 μm in thickness), then immersed into a

Table 1
Characteristic properties of the model foulants.

Model foulant	Molecular weight	Comment
Bovine serum albumin	66.5 kDa	583 amino acids
Humic acid	10^2–10^4 Da	COOH—, OH—, aromatic structure, anionic polyelectrolytes
Sodium alginate	32–250 kDa	A linear copolymer with homopolymeric blocks of (1–4)-linked β-D-mannuronate (M) and its C-5 epimer α-L-guluronate (G) residues