Journal of Membrane Science 497 (2016) 450–457

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Ultrasonic cleaning of polytetrafluoroethylene membrane fouled by natural organic matter

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ARTICLE INFO

Article history:
Received 24 July 2014
Received in revised form
29 June 2015
Accepted 12 August 2015
Available online 3 September 2015

Keywords:
Membrane fouling
Natural organic matter
PTFE membrane
Coagulation
Ultrasonic cleaning

ABSTRACT

Chemical cleaning of membranes fouled by natural organic matter (NOM) generates secondary pollution. In this study, the effect of ultrasonic cleaning of polytetrafluoroethylene (PTFE) membrane fouled by pre-coagulated humic acid-bentonite mixture was investigated. Results show that chemical coagulation prior to microfiltration improved turbidity and TSS removals by 9.5% and 11.4%, respectively. Experimental data fitted to constant pressure filtration models determined the sequence of dominant fouling mechanism as follows: (i) membrane resistance-limited, (ii) pore blocking resistance-limited, and (iii) cake formation resistance-limited. Relative membrane permeability of 53 and flux recovery of 45% were achieved when continuous ultrasonic cleaning was done at a 2.0 cm probe distance, 25 min total cleaning time, 15 mg/L coagulant dose, and 15 W ultrasonic power. Ultrasonic cleaning was found to be more effective than hydraulic cleaning in terms of flux recovery. Compared to chemical cleaning, it is a competitive and safer alternative in mitigating NOM-induced fouling.

1. Introduction

Natural organic matter is a product of microbiological, chemical, and photochemical transformations of plant and animal residues. In surface waters, the concentration of NOM ranges from 0.1–20 mg/L, the dominant fraction of which comprise humic substances such as humin, fulvic acid, and humic acid [1–3]. Humic acid (HA) accounts for almost 50–90% of the total organic matter in surface water and is one of the most difficult NOM fraction to remove [4, 5].

The deterioration of the quality of water resources partly due to NOM contamination has led to stricter water quality regulations and a growing need for effective water treatment technologies [6]. One such technology is membrane filtration, a pressure-driven, size-exclusion based separation process classified according to minimum allowable particle size (*i.e.* microfiltration (MF), ~0.1 μm) [7]. It may completely remove hardness, particulate and microbial contaminants, and disinfection by-product precursors (*i.e.* NOM) from aqueous media [8,9]. Based on cost, polymeric membranes such as PTFE are preferred to ceramic membranes [10].

Modern membrane filtration systems boast of compact installation, high efficiency, and low capital and operation cost requirements but the technology remains limited by fouling [11–13]. Fouling occurs when particles adhere onto the membrane surface causing a decline in the effective filtration area of the membrane and reduction in liquid throughput, membrane productivity and lifetime [14–19]. It is usually affected by feed water chemistry, membrane characteristics, filtration mode, and hydrodynamic conditions [19]. The fundamental mechanisms of fouling such as pore constriction, complete and intermediate pore blocking, and cake filtration have been described by various mathematical models [12,20].

Several strategies have been implemented to minimize membrane fouling and to maintain the economic viability of the filtration operation: (i) pretreatment of the feed solution [21–24], (ii) modification of the properties of the membrane material [25–28], (iii) membrane cleaning [29–32], and (iv) improvement of operating conditions during filtration [25,26]. The pretreatment of NOM-contaminated water prior to MF by coagulation causes particle aggregation which improves NOM filterability [4,33,34]. The formation of insoluble aggregates during the coagulation–flocculation of colloidal organic matter suspensions is attributed to a combination of charge neutralization, adsorption, complexation and colloid entrapment [35]. While aluminum- and iron-based

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http://dx.doi.org/10.1016/j.memsci.2015.08.031
0376-7388/

coagulants are widely used, the latter is more effective at lower dosage, has a wider operating pH range, forms heavier flocs, and poses less health risks [5]. At high coagulant dosage, NOM-metal complexes are formed which enmesh colloidal particles as the complexes settle [36]. The addition of bentonite clay, a key component of surface waters, may enhance the formation of flocs and thereby reduce fouling [22,37].

Fouling due to NOM could be removed through various membrane cleaning strategies, including hydraulic cleaning [16,20] and chemical cleaning [19,31,38]. Hydraulic cleaning requires relatively high cross-flow velocities and frequent cleaning interruptions [31,39], and it is only effective in removing surface fouling but not those of pore blocking and NOM adsorption [11]. Chemical cleaning, on the other hand, may reduce both surface fouling and internal pore clogging and even yield high flux recoveries [31,40]. However, this approach is likely to cause severe membrane damage, generate secondary pollution, and incur additional expenses due to chemical requirement, membrane replacement, and chemical waste disposal [41]. Kim and Dempsey [42] compared the performance of hydraulic and chemical cleaning in removing humic acid fouling, and they found that chemical cleaning is required to return the membrane close to its initial permeability. Grelot et al. [43] also investigated the use of hydrogen peroxide for the intensive cleaning of a fouled polyvinylidene difluoride (PVDF) membrane and showed that a cake layer remained on the fouled membrane surface even after cleaning.

Ultrasonic cleaning has attracted attention as a potential alternative or a supplementary technique to hydraulic and/or chemical cleaning. This technology uses high frequency sound (>18 kHz) to produce acoustic streaming and cavitation that can promote membrane vibration, disturb pollutant–to–membrane attachment, and possibly prolong membrane life [38,44–46]. Several operating parameters affect the effectiveness of ultrasonic cleaning. Cai et al. [47] evaluated the performance of the ultrasonic cleaning of a dead-end ultrafiltration (UF) membrane fouled by dextran aqueous solutions by varying the ultrasonic frequencies. Muthukuraman et al. [48] also investigated the application of ultrasonic cleaning in dairy membrane processes by varying the frequency and duration. They also compared the cleaning performance of continuous and intermittent operations. The intermittent application of ultrasound or pulsed cleaning may be used in lieu of continuous ultrasound irradiation because the latter suffers from higher energy consumption and may readily cause irreversible membrane damage [49]. Chen et al. [50] investigated the effect of the ultrasonic probe distance from the membrane and the length of the pulse interval in intermittent operations in the fouling removal due to colloidal silica particles. Combination of cleaning strategies was also done in previous studies. The study of Li et al. [51] showed a significant improvement in flux recovery when intermittent hydraulic cleaning was done simultaneously with ultrasonic cleaning for the removal of membrane fouling.

This study aims to investigate the effectiveness of ultrasound irradiation in cleaning PTFE membrane fouled by NOM (humic acid) and inorganic particles (bentonite). In this study, the effect of pre-coagulation of the feed solution on humic acid microfiltration was evaluated. The fouling mechanism of the PTFE membrane by NOM was analyzed using constant pressure filtration models. In addition, the effects of (a) vertical distance from the tip of the ultrasonic horn to the membrane surface, (b) ultrasonic power, (c) coagulant dose, and (d) cleaning time on ultrasound-assisted membrane cleaning in terms of relative permeability were evaluated. Moreover, the performances of continuous and pulsed ultrasonic cleaning were compared. Finally, the performance of ultrasonic cleaning with multiple filtration cycles was investigated.

2. Materials and methods

2.1. Synthetic feed solution and PTFE membrane pretreatment

Separate stock solutions, both with a concentration of 1000 mg/L, were prepared by dissolving humic acid ($C_9H_8Na_2O_4$, 50-60%, ACROS Organics) and bentonite ($H_2Al_2O_6Si$, 99%, Sigma-Aldrich) in deionized water. The suspensions were agitated at 200 rpm for 15 min using a magnetic stirrer (PC-420D, Corning) to ensure even distribution of particles, and were left to settle for 24 h. The supernatant was decanted and further stirred at 200 rpm for another 15 min.

The variation in groundwater characteristics was simulated by mixing predetermined volumes of bentonite and HA solutions and diluting the mixtures with aerated tap water (Table 1) to the desired composition prior to agitation at 200 rpm for 5 min. Aeration was carried out to mitigate residual chlorine concentration in the tap water.

The hydrophobic PTFE membrane purchased from GE Infrastructure Water and Process Technologies had a nominal pore size and effective filtration area of 0.60 μm and 19.6 cm^2, respectively. The PTFE membrane was first soaked in methanol (CH_3OH, 99%, Merck) for 5 min and thoroughly washed with deionized water prior to use in filtration experiments.

2.2. Analytical methods

The pH and turbidity of the solution were determined using a portable pH meter (pH 6011, EZ Do) and a turbidimeter (2100Q, Hach), respectively. The total suspended solids, total dissolved solids, and water hardness (Mg^{2+} and Ca^{2+} concentrations) were analyzed using a UV–vis spectrophotometer (DR 3900, Hach) while the concentrations of free and total chlorine were measured using the Hach Pocket Colorimeter II. The particle size distribution and zeta potential values of the pre-coagulated NOM wastewater were determined by a particle size analyzer (N5 Sub Micron, Beckman Coulter) and a zeta potential analyzer (ZetaPlus, Brookaven), respectively.

2.3. Coagulation–flocculation and dead-end microfiltration

A schematic diagram of the dead-end microfiltration set-up and the horn-type sonicator used in the experiment is shown in Fig. 1. The initial pH of the synthetic feed water was adjusted to 7.0 ± 0.1 using 10% nitric acid (HNO_3, Merck) and complete mixing was done at 200 rpm for 5 min. A known amount of ferric chloride ($FeCl_3$, 99% Merck) coagulant was then added. Coagulation proceeded at 200 rpm for 5 min then at 60 rpm for 25 min. Membrane fouling was carried out by allowing the pre-coagulated feed water to pass through the PTFE membrane for 30 min at a constant pressure of 50 kPa. Based on preliminary fouling experiments, the value of the permeate flux dropped to less than 4% of the initial permeate flux within 20 min of filtration. Hence, a filtration time

Table 1
Characteristics of tap water.

Parameter	Value
pH	8.3 ± 0.1
Turbidity (NTU)	4.69 ± 0.01
Total suspended solids (mg/L)	5 ± 1
Total dissolved solids (mg/L)	245 ± 1
Magnesium, Mg^{2+} (mg/L)	1.89 ± 0.01
Calcium, Ca^{2+} (mg/L)	0.69 ± 0.01
Free chlorine (mg/L)	0.01 ± 0.01
Total chlorine (mg/L)	0.15 ± 0.01