Journal of Membrane Science 516 (2016) 1–12

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Understanding ultrafiltration fouling of ceramic and polymeric membranes caused by oxidized iron and manganese in water treatment

Seyedeh Laleh Dashtban Kenari *, Benoit Barbeau

Polytechnique Montreal, Department of Civil, Geological and Mining Engineering, NSERC-Industrial Chair on Drinking Water, Environment, C.P. 6079, Succursale Centre-Ville, Montreal, QC, Canada H3C 3A7

ARTICLE INFO

Article history:
Received 24 March 2016
Received in revised form
2 June 2016
Accepted 3 June 2016
Available online 6 June 2016

Keywords:
Water treatment
Iron/manganese control
Constant flux dead-end ultrafiltration
Ceramic/polymeric membrane
Fouling resistance

ABSTRACT

Ultrafiltration (UF) with ceramic membrane has attracted growing attention in drinking water treatment. In this regard, a ceramic and a polymeric UF membrane process with in-line preoxidation has been applied for iron and manganese control in water. The effect of water chemistry including pH, ionic strength and hardness on the characteristics of oxidized iron and manganese aggregates, and subsequent UF fouling behavior were evaluated. The fouling of constant flux dead-end UF membranes was assessed using blocking low and resistance-in-series model analyses. Results suggest that the water chemistry has not possessed notable impact on the overall iron and manganese removal efficiencies but did contribute to the extent of fouling caused by manganese dioxide aggregates. The resistance of the cake layer and its compressibility could be explained by the manganese dioxide aggregate properties, such as size, ζ-potential and fractal dimension, which were controlled by the water chemistry. However, the cake formed by ferric hydroxide aggregates induced very low and comparable resistance to the membranes under all conditions, in line with the similar aggregate properties. The fouling behavior of ceramic membrane was generally similar to that of polymeric one, however, the reversibility of the fouling differed from one another. Overall, this work provides further insight on the fouling of ferric hydroxide and manganese dioxide in water treatment.

1. Introduction

Iron and manganese commonly occur in groundwater and some sources of surface water from weathering of metal-bearing minerals and rocks, leaching from soils rich in organic matter, contamination by industrial effluents and thermal stratification in lakes. Among different water sources, groundwater frequently contains high levels of dissolved iron and manganese arising from more reduced redox conditions. The presence of these metals in finished water creates aesthetic issues, such as colored water formation, increased turbidity, metallic taste, odor, and staining of laundry and plumbing fixture [1]. In this regard, the United States Environmental Protection Agency [2] and Guidelines for Canadian Drinking Water Quality [3] have recommended an aesthetic objective limit of 0.3 and 0.05 mg/L for the concentrations of iron and manganese in drinking water, respectively. However, iron and manganese concentrations as low as 0.05 [4] and 0.02 mg/L [5], respectively, may still cause aesthetic problems. In addition, manganese control in drinking water is receiving an increased attention due to its potential neurotoxicity [6,7]. Manganese intake from water ingestion has been associated with intellectual impairment in children, even at low concentrations (<0.25 mg/L) [8]. Thus, it is crucial to effectively control the concentration of manganese in drinking water.

A common treatment strategy for iron and manganese control in drinking water includes oxidation of dissolved iron and manganese followed by separation of oxidized particles from water. Traditional processes to remove particulate and colloidal matter from water are coagulation, flocculation, sedimentation and granular media filtration, which have drawbacks of operating in successive steps heterogeneous reactions that require significant contact time and, therefore, process footprint. Furthermore, oxidized manganese is not always effectively removed by such treatment technologies [9] due to its propensity to form small colloids [10,11]. Alternatively, compact membrane processes, such as microfiltration (MF) and ultrafiltration (UF), are increasingly used in water treatment facilities for filtration of dilute suspensions containing fine particles and colloids based on size exclusion [12]. Management of membrane fouling is an important limitation of this technology. As opposed to surface water systems where organic fouling is dominant, management of inorganic fouling caused by iron/manganese is of importance for many UF/MF

---

* Corresponding author.
E-mail addresses: laleh.dashtban@polymtl.ca (S.L. Dashtban Kenari), benoit.barbeau@polymtl.ca (B. Barbeau).

http://dx.doi.org/10.1016/j.memsci.2016.06.003
0376-7388/

Table 1
Specifications of ceramic and polymeric membranes utilized in this study.

Manufacturer	Material	Surface area (cm^2)	MWCO[a] (kDa)	Permeability (LMH/bar) at 20 °C	pH stability[b]	Temp. stability[b] (°C)	Pressure stability[b] (kPa)
Norit (polymeric)	PES/PVP[c]	700	200	840	2–12	40	300
Atech (ceramic)	ZrO_2/Al_2O_3[d]	95	150	780	0–14	N.A.	1000

N.A.: Not available

[a] Molecular weight cut off.

[b] Reported by manufacturer.

[c] Polyethersulfone/polyvinylpyrrolidone.

[d] Zirconium dioxide/α-aluminum oxide.

groundwater systems.

Several factors impact membrane fouling including membrane types and material properties, operating conditions, process configuration, cleaning strategies and feed solution characteristics [12,13]. In recent years, application of ceramic membranes has been receiving growing attention due to their inherent advantages over conventional polymeric membranes. Namely, ceramic membranes offer superior chemical, thermal and mechanical stability allowing much more aggressive physical and chemical cleaning approaches which can prolong their life expectancy. In addition, the higher integrity and reliability of ceramic membranes would reduce the repetitive testing, repair and replacement of membrane modules leading to savings in operation cost [14]. In spite of the high potential of ceramic membrane application for iron/manganese removal, their fundamental fouling behavior caused by ferric hydroxide and manganese dioxide particles has not yet been documented.

Regarding feed water characteristics, it is expected that membrane performance during filtration of metal oxide colloids and particles will be considerably impacted by pH, ionic strength and salt valency as these parameters are known to have an impact on particle-particle and particle-membrane interactions [15,16]. Moreover, changes in pH, ionic strength and salt valency may alter water permeability of MF/UF membranes, even though salt rejection is negligible in these systems [17–20]. Consequently, understanding the behavior and characteristics of ferric hydroxide and manganese dioxide particles deposition on UF/MF membranes is of interest for their application for iron and manganese control in drinking water.

This study aimed to investigate the removal of iron/manganese oxides and the associated fouling during the operation of preoxidized dead-end UF ceramic or polymeric membranes. Characteristics (such as size, ζ-potential and fractal dimension) of ferric hydroxide and manganese dioxide aggregates achieved under various water chemistry conditions, were assessed against the fouling behaviors that they produced on UF membranes. The performance of ceramic versus polymeric UF membrane with respect to the extent of fouling and iron/manganese removal were then compared. Constant flux blocking law model was applied to determine the specific resistance and the compressibility of the filter cake. Finally, the resistance-in-series model was applied to quantitatively analyze the advantage of ceramic membrane with respect to the cleaning processes effectiveness and reversibility of fouling.

2. Materials and methods

2.1. UF membranes

Although the majority of membranes that have been using in industries are hollow fiber polymeric membranes and tubular ceramic membranes, most of the publications focused on the fouling behavior of a simple disc-type membrane. These results could not well predict the rate and extent of fouling in full-scale plant [21]. In this study, two types of UF membranes, which are relevant for industrial applications, were selected. A hollow fiber polymeric membrane, UFC M5, composed of a blend of polyvinylpyrrolidone and polyethersulfone with a nominal molecular weight cut off (MWCO) of 200 kDa was used (Norit X-Flow, Enschede, The Netherlands). The membrane contains 93 fibers with an inner diameter of 0.8 mm, a length of 300 mm and an effective filtration area of 700 cm^2. This membrane is resistant to temperature up to 40 °C and pressure up to 300 kPa and its tolerance to pH ranges from 2 to 12. A single-channel tubular ceramic UF membrane with an outer diameter of 10 mm, an inner diameter of 6 mm, a length of 500 mm and a filtration area of 95 cm^2 was purchased from Atech Innovations GmbH (Gladbeck, Germany). This asymmetric membrane is made of zirconium dioxide and a support of α-aluminum oxide with open pores which provides maximum permeability and high mechanical stability. According to the manufacturer, the nominal MWCO of the membrane is 150 kDa. The membrane is resistant to a pressure up to 1 MP, and pH of 0–14. The initial permeability of the ceramic and the polymeric membranes were measured as 780 and 840 LMH/bar, respectively, using demineralized (DM) water at pH 6 and 20 °C. The specifications of the ceramic and polymeric membranes are summarized in Table 1.

The pore size of the membranes was estimated from the Stokes-Einstein equation [22]. Accordingly, the pore size of 150-kDa ceramic membrane and 200-kDa polymeric membrane are approximately 17 nm and 19 nm, respectively.

2.2. Preparation of synthetic feedwater (SFW)

A fresh SFW was prepared prior to each experiment via addition of appropriate amount of sodium chloride, calcium chloride dihydrate and sodium bicarbonate stock solutions to demineralized (DM) water to achieve the final desired ionic strengths (0.5, 1.0 and 10 mM), pHs (6, 7 and 8) and hardness values (0, 100 and 317 mg $CaCO_3$/L). The pH of the SFW was then adjusted by bubbling CO_2 and/or N_2 gas into the water. The stock solutions were prepared using Milli-Q water. Dissolved manganese stock solution (100 mg Mn^{2+}/L) was prepared by dissolution of manganese (II) sulfate monohydrate into Milli-Q water while Milli-Q water was first acidified to a pH of 3 and N_2 gas was bubbled into the water for 15 min prior to the dissolution of iron (II) sulfate heptahydrate (100 mg Fe^{2+}/L). All chemicals were analytical grade reagents.

Although iron and manganese are commonly co-occurring in natural waters, they have been studied separately to better assess the fouling characteristics of each mineral. Table 2 summarizes the SFW conditions applied in this study, relevant to typical natural water conditions.

2.3. Experimental procedure

The experimental setup consisted of two steps, as shown schematically in Fig. 1: oxidation and membrane filtration. In the