



ELSEVIER

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Engineered iron/iron oxide functionalized membranes for selenium and other toxic metal removal from power plant scrubber water



Minghui Gui^a, Joseph K. Papp^a, Andrew S. Colburn^a, Noah D. Meeks^b, Benjamin Weaver^c, Ilan Wilf^c, Dibakar Bhattacharyya^{a,*}

^a Department of Chemical and Materials Engineering, University of Kentucky, Lexington, KY 40506, USA

^b Southern Company Services, Inc., Birmingham, AL 35203, USA

^c Nanostone/Sepra Membranes, Inc., Oceanside, CA 92056, USA

ARTICLE INFO

Article history:

Received 24 November 2014

Received in revised form

12 March 2015

Accepted 21 March 2015

Available online 20 April 2015

Keywords:

Surface modification

Polyelectrolyte

Nanoparticles

Nanocomposite membrane

ABSTRACT

The remediation of toxic metals from water with high concentrations of salt has been an emerging area for membrane separation. Cost-effective nanomaterials such as iron and iron oxide nanoparticles have been widely used in reductive and oxidative degradation of toxic organics. Similar procedures can be used for redox transformations of metal species (e.g. metal oxyanions to elemental metal), and/or adsorption of species on iron oxide surface. In this study, iron-functionalized membranes were developed for reduction and adsorption of selenium from coal-fired power plant scrubber water. Iron-functionalized membranes have advantages over iron suspension as the membrane prevents particle aggregation and dissolution. Both lab-scale and full-scale membranes were prepared first by coating polyvinylidene fluoride (PVDF) membranes with polyacrylic acid (PAA), followed by ion exchange of ferrous ions and subsequent reduction to zero-valent iron nanoparticles. Water permeability of membranes decreased as the percent PAA functionalization increased, and the highest ion exchange capacity (IEC) was obtained at 20% PAA with highly pH responsive pores. Although high concentrations of sulfate and chloride in scrubber water decreased the reaction rate of selenium reduction, this was shown to be overcome by integration of nanofiltration (NF) and iron-functionalized membranes, and selenium concentration below 10 µg/L was achieved.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Various water sources may contain both toxic heavy metals and chlorinated organic compounds (COCs). Those contaminants are either recalcitrant to environmental degradation, or exist at high concentrations of total dissolved solids (TDS, such as CaCl₂, NaCl, etc.), which brings further complications in treatment.

Membrane technologies allow the separation of solutes in water based on size exclusion, charge exclusion and diffusivity/solubility difference. Commercial membranes such as reverse osmosis (RO) and nanofiltration (NF) membranes have been extensively used for water softening and desalination [1]. However, RO and NF membranes are not effective in rejecting organic pollutants such as trichloroethylene (TCE) and carbon tetrachloride, which have high solubility in membrane synthesis materials. Metal ions can be mostly retained by dense membranes, but concentrated metals in the retentate need further treatment. Non-membrane technologies existing for water remediation are

either energy or capital intensive, such as physical and biological treatment. In recent years, chemical remediation especially reductive and oxidative treatment with iron and iron oxide nanomaterials has been an emerging area for selective removal of various trace contaminants from natural and waste water matrices.

Iron nanoparticles made by borohydride or polyphenol reduction are most commonly used materials in environmental remediation [2–5]. With a second metal coating such as Pd and Ni, more rapid and complete reduction of organic and inorganic pollutants can be achieved [6–8]. Alternatively, toxic organics can be destructed by oxidation of hydroxyl radicals (OH•) from iron oxide catalyzed hydrogen peroxide decomposition [9–13]. However, the direct injection use of iron is complicated by the aggregation and dissolution of nanoparticles, and the use of engineered nanomaterials has already raised public concerns about their potential toxicity [14–16].

One approach to utilize the high reactivity of iron nanoparticles but overcome the aggregation and dissolution issues is to synthesize nanoparticles through ion exchange or adsorption of precursor ions on porous substrates such as silica [17], activated carbon/carbon nanotubes [18], and polyelectrolyte pore-filled membranes [19,20], followed by reduction. The functional groups on those

* Corresponding author. Tel.: +1 859 257 2794.

E-mail address: db@engr.uky.edu (D. Bhattacharyya).

substrates can eliminate the aggregation during the particle formation and release issues to environment during the reaction, as well as allowing the control of particles size [21,22].

We recently reported the development of full-scale polyacrylic acid (PAA) functionalized polyvinylidene fluoride (PVDF) membrane with iron/iron oxide nanoparticles for combined reductive and oxidative degradation of polychlorinated biphenyls (PCBs) in groundwater [23,24]. The same redox chemistry and membrane approach can be used for selenium removal from coal-fired power plant scrubber water, as iron has been reported to reduce selenate (VI) and selenite (IV) to elemental selenium (Se^0) and selenide (-II) [25–27]. Like those on toxic organic degradation, many of these studies were conducted in iron particle suspension without the use of stabilizers.

The scrubber water is generated in the wet scrubber during the flue gas desulfurization (FGD) process. This process is primarily designed for the forced oxidation (using excess air) of sulfur dioxide (SO_2) to sulfates, and subsequent precipitation with the addition of limestone (CaCO_3) slurry. It has co-benefit removals of volatile metals as well as other acid gases. As the limestone dissolves, it reacts with the sulfates and gypsum is precipitated and removed. The remaining scrubber liquor is saturated with gypsum, and also contains excess halides from the dissolution of other acid gases (HCl). TDS in this water varies from 15,000 to 50,000 mg/L, depending on the type of coal used as well as the upstream flue gas treatment unit operations. In addition to major ions such as calcium, magnesium, chloride, and sulfate, volatile metals such as selenium, arsenic and mercury are also present in trace amount. Selenium is an essential element in human and animal nutrition [26], but may be toxic at higher levels due to its interaction with body tissue. Therefore, the control of selenium release to environment from mining, oil refineries, manufacturing and agriculture drainage has been a critical issue [28,29]. This concern over selenium eco-toxicity has also driven its inclusion in proposed Effluent Limitation Guidelines for coal-fired power plants by the US EPA.

The main aim of this study is to understand the effects of surface functionalization on membrane transport and reactivity in toxic metal removal. The specific aims are (i) to quantify the relationship of percent PAA functionalization in membrane pores to water permeability, responsive behavior and ion exchange capacity of membranes, (ii) to determine the reactivity of iron-functionalized membranes for selenium removal in different water matrices, and (iii) to evaluate the performance of full-scale functionalized membranes for power plant water applications.

2. Experimental

2.1. Materials

All chemicals used in the lab-scale membrane study were reagent grade without further purification. Sodium borohydride and selenium powder were purchased from Sigma-Aldrich. Sodium hydroxide, sulfuric acid, hydrochloric acid, nitric acid (trace metal grade), iron and selenium reference standard (1000 mg/L), and ferrous chloride tetrahydrate were obtained from Fisher Scientific. Acrylic acid, ammonium persulfate, N,N'-methylenebisacrylamide (NNMA), ethanol, and sodium selenite were purchased from Acros Organics. Sodium selenate was purchased from Alfa Aesar.

Commercial PVDF400HE and full-scale PVDF400HE-PAA (functionalized) microfiltration membranes were made in Nanostone/Sepron Membranes Inc., Oceanside, CA. The membrane thickness is $200 \pm 5 \mu\text{m}$, including PVDF ($70 \pm 5 \mu\text{m}$) and nonwoven fabric backing ($125 \pm 5 \mu\text{m}$). The average pore size from bubble point tests is 420 nm for non-functionalized membrane and 124 nm for

functionalized membrane. The spiral wound module of PVDF400HE-PAA has an effective area of 0.465 m^2 . The full-scale PV400B-PAA and spongy PVDF-PAA membranes were also studied, and they have different fabric backing and PVDF layer in thickness and pore structure. Commercial DVPP14250 PVDF membranes without fabric backing (hydrophilized, diameter: 142 mm, thickness: $125 \mu\text{m}$, pore size: $0.65 \mu\text{m}$, porosity: 70%) were obtained from EMD Millipore. All solutions were prepared with Milli-Q ultrapure deionized (DI) water ($18.2 \text{ M}\Omega \text{ cm}$ at 25°C). Deoxygenated water was obtained by purging nitrogen gas into DI water for 30 min.

2.2. Functionalized membrane synthesis and characterization

PVDF membranes were functionalized via in situ polymerization method reported in [23]. The polymerization solution contains the monomer acrylic acid (AA, 0.9–4.9 M), initiator ammonium persulfate (1 mol% of AA), cross-linker NNMA (1 mol% of AA), and deoxygenated water.

Iron precursors (e.g. Fe^{2+}) were immobilized in PAA functionalized PVDF membranes through two-step ion exchange process, followed by borohydride reduction to form iron nanoparticles. The iron loading in membranes can be increased by repeated ion exchange and reduction. The amount of iron immobilized and ion exchange capacity (IEC) of membrane were determined by concentration change and acid digestion [9]. Through the oxidative treatment of iron with air or dilute hydrogen peroxide, iron oxides (e.g. ferrihydrite and magnetite) were formed as a passive oxide layer above iron core [9,23]. The whole particle will be converted to iron oxide if enough oxidants are provided.

The surface and cross-sectional morphology of functionalized membranes was obtained in scanning electron microscopy (SEM, Hitachi S4300). Membrane porosity was then estimated by ratio of pore area to total membrane area based on SEM images of membrane top surface. Transmission electron microscopy (TEM, JEOL 2010F) was used to study the base particle properties. The crystal structure of iron/iron oxide was studied by using the selected area electron diffraction (SAED) in TEM. To understand the iron surface transformation and composition change, line scanning and elemental mapping were conducted on single particles using either energy dispersive X-ray spectroscopy (EDS, Oxford INCA) or electron energy loss spectroscopy (EELS, Gatan GIF 2000) in scanning TEM mode. The composition of membrane top layer was studied with X-ray photoelectron spectroscopy (K-Alpha, Thermo-Scientific). Depth profile analysis with ion beam etching was also performed to prove PAA functionalization in membrane pores.

2.3. Water permeability and pH responsive behavior study

Water permeability of PVDF-PAA membranes was evaluated by using a lab-scale stainless steel pressure cell (Sepa ST, GE Osmotics, effective membrane area is 13.2 cm^2) in dead-end mode (Fig. 1A) or a full-scale setup in cross-flow mode (Fig. 1B). Water flux was measured at three different pressures with three replicates at each pressure, and the average values are shown here. For pH responsive experiments, DI water at different pH was passed through the membrane until the permeate pH was identical to feed pH. Water permeability was determined at this equilibrium.

2.4. Selenium removal by iron nanoparticles

Selenium removal was performed with iron nanoparticle suspension, and with iron-functionalized membranes in both batch and convective modes. The effects of TDS on selenium reduction with iron were studied in different water matrices, including DI water, synthetic water containing salts (e.g. CaCl_2 , NaCl, Na_2SO_4 and

Download English Version:

<https://daneshyari.com/en/article/632945>

Download Persian Version:

<https://daneshyari.com/article/632945>

[Daneshyari.com](https://daneshyari.com)