Chemical Engineering Journal 345 (2018) 114–125

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Influence of operating conditions on the removal of metals and sulfate from copper acid mine drainage by nanofiltration

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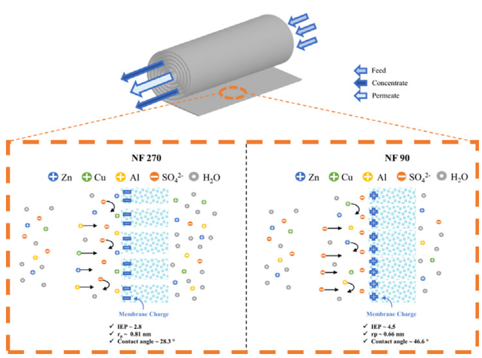
HIGHLIGHTS

- Both spiral wound membranes demonstrated a high metal and sulfate removal capacity.
- No difference in rejections was observed at high pressures in both membranes.
- Increase Reynolds number does not significantly affect the permeate flow.
- VRF measurements provide important information for scaling up AMD treatment.
- NF270 shows excellent performance until ten days of continuous operation.

GRAPHICAL ABSTARCT



ARTICLE INFO

Keywords:
Acid mine drainage
Nanofiltration
Spiral-wound membranes
Heavy metals
Resistance-in-series
Membrane fouling

ABSTRACT

The primary objective of this investigation was to evaluate the ability of two commercial spiral-wound membranes (NF90 and NF270) to remove metals and sulfate from acid mine drainage from an active copper mine. The structural and surface properties of the membranes, hydrodynamic conditions, polarization, and filtration resistance had a significant influence on the effectiveness of the treatment. The obtained results demonstrated a good removal capacity in both membranes (> 94%) at a low operating pressure (15 bar). The increase in pressure had a strong impact on permeate flux, concentration polarization, and contaminant removal rate; however, the increase in the value of the Reynolds number exhibited had no significant effects. The NF270 membrane was selected to perform concentration and long-term tests as it demonstrated a high treatment capacity, high rejections, low resistance, and low polarization at moderate pressures. The permeate flux in the concentration and continuous operation tests decreased by ~45% and ~12%, respectively, due to the increases in resistance of ~63% and ~13%, respectively, while rejection exhibited a slight increase in both tests. The model parameters successfully identified the convective and diffusive contributions to ions transport in all experiments.

1. Introduction

The problem of sulfide mineral oxidation associated with acid mine drainage (AMD) has been an alarming environmental issue for the mining industry worldwide [1]. Although the chemical composition of AMD depends on the climatological and geological conditions of the mining zone, AMD is commonly characterized by low pH and high concentrations of sulfate, heavy metals (Fe, Cu, Pb, Zn, Cd, Co), and

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https://doi.org/10.1016/j.cej.2018.03.070
Received 9 January 2018; Received in revised form 11 March 2018; Accepted 13 March 2018
Available online 15 March 2018

Nomenclature

Symbol	Description (Units)
$\Delta_{hyd}G°$	standard molar Gibbs energy of solvation or hydration of ions ($kJ\,mol^{-1}$)
A_m	effective filtration area (m^2)
C_{Ri}	concentration of solute *i* in the rejected component ($mg\,L^{-1}$)
C_{bi}	concentration of solute *i* in the feed ($mg\,L^{-1}$)
C_{mi}	concentration of solute *i* on the membrane surface ($mg\,L^{-1}$)
C_{pi}	concentration of solute *i* in the permeate ($mg\,L^{-1}$)
D_i	diffusion coefficient ($cm^2\,s^{-1}$)
J_w	permeate water flux ($L\,h^{-1}\,m^{-2}$)
R_{0i}	observed rejection (%)
R_F	mass transfer resistance due to fouling (m^{-1})
R_{F+P}	mass transfer resistance due to fouling and polarization (m^{-1})
R_I	mass transfer resistance due to scaling (m^{-1})
R_M	mass transfer resistance due to the membrane (m^{-1})
R_P	mass transfer resistance due to polarization (m^{-1})
R_T	total resistance (m^{-1})
R_i	real (intrinsic) rejection of solute *i* (%)
k_i	mass transfer coefficient (cm^2/s)
k_w	hydraulic permeability constant ($L\,h^{-1}\,m^{-2}\,bar^{-1}$)
r_i	ion radius (nm)
Δr	hydrated ion layer width (nm)
n	number of water molecules in the hydrated layer (–)
AMD	acid mine drainage (–)
P	pressure (bar)
T	temperature (°C)
V	volume (L)
VRF	volume reduction factor (–)
v	tangential velocity in the module ($m\,s^{-1}$)

Greek Letters

π	osmotic pressure (bar)
σ	reflection coefficient (–)
β	polarization module (–)
μ	viscosity (Pa·s)

metalloids (As, Sb, Se) [2].

In recent years, various technologies have been available for AMD treatment; however, sustainability is deemed the determining factor in selecting an appropriate process [1,2]. Many mining operations use neutralization, in which alkaline agents such as calcium carbonate or lime generate sludge. The treatment of AMD should maximize the recovery of valuable elements such as metals and water in order to compensate for the cost of treatment; however, in neutralization, metal recovery is not economically viable.

Membrane separation has become a promising technology for the treatment of contaminated water due to its efficient species removal capacity [3]. Reverse osmosis (RO) and nanofiltration (NF) are the most commonly used membrane separation processes for metal removal [3]. Both of these processes are capable of retaining salts and metals from the feed solution and therefore demonstrate a high potential for the recovery of species and water from AMD [4–7]. However, RO uses membranes that restrict the passage of salt and are therefore less water permeable than NF. In previous studies, Rieger et al. [8] treated a highly concentrated AMD at laboratory scale by NF (NF99) and RO (RO98pHt). In the range of 10 and 40 bar, total ion rejection between 84% and 87% for NF99 and between 90% and 95% for the RO98pHt membrane were obtained, while permeate fluxes were twice as high for NF. During long-term studies, NF also exhibited lower fouling potential. Using the same membranes with AMD at pilot scale, Ambiado et al. [5] similarly observed high permeate fluxes in NF with only slightly lower divalent ion rejection rates. Under optimum pressure conditions of 15 bar, ion removal reached a maximum of 92% for NF99 and 98% for the RO98pHt membrane, while fluxes were respectively 86.2 L/m^2 h and 16.5 L/m^2 h.

Although NF seems to be an attractive alternative for AMD treatment, fouling is still one of the most difficult parameters to control [9]. Fouling depends on the surface properties of the membrane, feed characteristics, and operating conditions [10,11]. The most important studied parameters for NF are roughness, pore size, hydrophobicity, membrane charge, solute concentration in the feed, feed pH, module type, and the hydrodynamic conditions at different transmembrane pressures. Rana and Matsuura [12] discussed the influence of roughness on NF; however, the results of some earlier scientific studies evince that a greater roughness value significantly increases the probability of surface pore blockage generation [4,13]. Membrane hydrophobicity/hydrophilicity determines its degree of wettability as well as its chemical and mechanical surface stability [14]. Hydrophobic membranes show excellent stability, but at the same time produce greater fouling [12]. The surface charge of the membrane depends on the polymeric material used, functional groups, manufacturing method, and feed solution properties [4,12,14–18]. Thin-film composite (TFC) NF membranes contain ionizable groups, such as carboxyl, sulfonic, and amine groups [6,18], which easily dissociate in the presence of acids or bases. Dissociation affects the electrostatic repulsion between ions or charged molecules and the membrane surface. Finally, operating factors such as pressure [5,14,19], feed velocity [5,14,19], temperature [14,19], recovery [7], and continuous filtration operations [9] also influence permeate water transport, fouling, and membrane polarization. These operating factors are usually assessed on a small scale with a flat sheet membrane with an area of 10–100 cm^2 [20].

Few investigations have addressed the application of NF in the treatment of mining wastewater [4,5,7,8,15,19–21] by comparing NF with RO. All of the results highlight that NF with circular flat sheet [4,7,15,19–22] and spiral-wound membranes [5,20] is the better option for copper [5,19,21] and gold AMD treatment [7,15,20,22]; however, scaling up these results with flat sheet membranes is a challenge due to the problems by of concentration polarization, fouling, permeability efficiency, and cleaning procedures of spiral-wound modules. In addition, the industrial effluents provide valuable information for scaling up of a separation process, although their use in AMD treatment is limited in the published literature [5,7,8,15,20–22]. Therefore, this study aims to assess the performance of two spiral-wound TFC NF membranes (NF90 and NF270) in the treatment of an actual AMD effluent from an active copper mine. The species removal capacity and permeability of both membranes were investigated by varying the operating conditions such as pressure and feed flow and assaying metal and sulfate. The ability of concentrating AMD treatment to recover water and species was also analyzed with NF270 due to its high treatment capacity and continuous operating performance over a long duration. Finally, membrane recovery and resistance due to scaling after continuous AMD treatment and cleaning procedure were assessed.

2. Method and materials

2.1. Membranes

Two commercial spiral-wound membranes (NF90 and NF270) manufactured by Dow/Filmtec were used in this experiment. The membranes were selected based on their molecular cut-off, pore size,