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Acid mine drainage treatment by nanofiltration: A study of membrane fouling, chemical cleaning, and membrane ageing

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ABSTRACT

This study aimed to investigate the nanofiltration membrane fouling on the NF270 membrane formed during acid mine drainage (AMD) treatment, and the best chemical cleaning procedure to remove this fouling. Moreover, membrane ageing by AMD retentate alone and AMD retentate combined with periodic chemical cleaning solution was assessed. The AMD is a mining effluent with low pH, high concentrations of sulfate, and is mainly composed of dissolved inorganic compounds; its treatment by nanofiltration produces a permeate suitable for industrial reuse. AMD treatment resulted in an inorganic fouling layer, rich in aluminum, arsenic, calcium, chromium, nickel, potassium, and sodium. Among the evaluated cleaning solutions, the best cleaning agent was hydrochloric acid (HCl) at a concentration of 0.20% w/w; this concentration also provided the lowest membrane exposure to the acid. Membrane ageing reduced the NF270 membrane water permeability by 49% after 270 days of exposure to AMD, and by 45% after 270 days of exposure to AMD plus periodic HCl cleaning solution. However, the membrane selectivity to magnesium sulfate and glucose decreased less than 10% in both conditions. These results suggest that the NF270 membrane is stable during AMD treatment.

1. Introduction

Acid mine drainage (AMD) is an effluent formed during the oxidation of sulfide minerals - found in mining waste, tailings, and mine structures of abandoned or active mines [1] - when exposed to oxygen and water. AMD is characterized by low pH, high sulfate concentration, and variable concentrations of metals and metalloids. Nanofiltration (NF) and reverse osmosis (RO) are established technologies for heavy metal retention, and recent studies have successfully applied membrane separation processes (MSP) to treat synthetic and real AMD [2,3]. Moreover, NF has been suggested as the preferable membrane separation process for effluent treatment because of its higher permeate flux, lower required pressure and energy consumption, and lower capital investment and operational cost [4]. In terms of composition, the most widely used RO and NF membranes are polyamide (PA)-based thin-film composite membranes. These membranes provide high selectivity and water permeability; however, they may be degraded by several chemicals, including chlorine [5]. In a previous study, the authors evaluated the treatment of gold AMD by MSP [6]. The best operational conditions were found using the NF270 membrane (Dow Filmtec™), treating AMD after ultrafiltration, at pH 5.5 and with a maximum water recovery (RR) of 60%. In these conditions, the membrane had the lowest fouling tendency and high ionic retention, and at 60% RR, the retention efficiency of the treatment was 95.3, 95.2, and 86.6% for calcium, magnesium, and sulfate, respectively. The permeate obtained was suitable for industrial reuse. Despite the excellent performance achieved, it is essential to evaluate if the membrane performance could be impaired by continuous exposure to the effluent and the chemical cleaning solution.

Some studies have evaluated the stability of NF membranes in extremely acidic conditions and reported that the same type of membrane can be chemically stable or unstable depending on the characteristics of the solution to which it is exposed to [7,8,9,10]. Tanninen et al. [10] evaluated the stability of the NF270 membrane in extreme acidic conditions (8 wt% H_2SO_4 at 40 °C) and found a significant increase in permeate flux and decrease in retention after only 13 days of operation. However, they suggested that this membrane might be a good option for the treatment of less extreme solutions because of its excellent selectivity. Therefore, it is essential to evaluate the stability of the NF270 membrane in a less extreme condition, such as the AMD effluent.

Membrane fouling is an inevitable process and a major problem in NF application [11] since it causes a decline in productivity, deteriorates the permeate quality, increases energy consumption and treatment cost, and shortens membrane lifespan. Membrane fouling must be controlled for an economically feasible operation [12]. It can be partially removed by physical or chemical cleaning. Physical cleaning

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Table 1
AMD main characteristics.

AMD	pH	Conductivity (μS/cm)	Total solids (mg/L)	Total suspended solids (mg/L)	Sulfate (mg/L)	Chloride (mg/L)	Calcium (mg/L)	Magnesium (mg/L)
1st collection	3.76	2573	3102	77	1,959.5	151.5	284	226
2nd collection	3.35	2965	3432	34	2,767.7	14.1	367	299

methods include hydraulic cleaning (back pulse and back flush), ultrasonic vibration, air or CO_2 sparging, and back permeation [13]. Physical cleaning is performed at regular intervals and removes most of the reversible membrane fouling; they are less likely to degrade the membrane and/or decrease the membrane lifespan than chemical cleaning methods [14]. However, its efficiency tends to decrease during membrane operation, as more irreversible membrane fouling accumulates at the membrane surface. Once this occurs, chemical cleaning is recommended [15].

Chemical cleaning involves both chemical and physical interactions. Chemical interactions are related to the reaction between the cleaning agent and the fouling layer. This reaction lessens the structural integrity of the fouling layer, thus facilitating its mechanical removal. In contrast, physical interactions are related to the mass transport of components from the bulk solution to the membrane surface and from the membrane surface to the bulk solution [16]. Periodic chemical cleaning often represents the only way to partially restore the initial permeate flux [17]. There is a large variety of membrane cleaning chemicals commercially available, and they are typically divided into alkaline cleaners, acid cleaners, surfactants, and salt solutions. The selection of the best cleaning agent is directly related to the foulants identified, or expected, on the membrane surface. The membrane material must also be considered when selecting a cleaning agent because some combinations of cleaning agent and membrane material may result in the irreversible loss of membrane performance and shorten the membrane lifespan. Other factors that need to be considered during chemical cleaning are cleaning agent concentration and pH; system temperature, pressure, and flow rate; and cleaning time [11,18].

Wei et al. [11] studied the Desal-5 DK membrane (Osmonics, USA) fouling process during complex pharmaceutical wastewater treatment. Chemical cleaning process was based on the identification of the membrane foulants, which were mostly calcium sulfate and calcium carbonate. Cleaning efficiencies order were NaOH (pH 11) < HCl (pH 2) < citric acid (pH 2) < Na_4EDTA (10 mM). Ang et al. [12] investigated different RO cleaning modes with the membrane LFC-1 (Hydranautics, Oceanside, CA) after wastewater treatment. They observed that the addition of NaOH enhanced the overall cleaning performance when introduced with other chemical agents, due to its ability to loosen the organic fouling layer. However, as far as we know, no study has been published on the cleaning process of membranes fouled during AMD treatment.

Although essential in any NF/RO application, chemical cleaning may accelerate the membrane ageing process [18]. Membrane ageing is considered as the changes from the initial state and properties of the membrane over time. It is a comparative analysis, which cannot be determined quantitatively. Membrane ageing depends on the operational conditions of both the process and the cleaning step. Moreover, membrane ageing can result in decreased process productivity, increased physical and chemical cleaning frequency, modification of the membrane physicochemical properties (such as membrane hydrophobicity and surface roughness), alteration of membrane selectivity, and loss of integrity [13].

Simon et al. [19] studied the effect of chemical cleaning solutions at different concentrations on virgin NF270 membranes (Dow Filmtec™). They measured the membrane zeta potential, hydrophobicity, permeability, and solutes rejection before and after exposure to the cleaning solution for 18 h at 35 °C. Many differences were observed in the membrane characteristics due to membrane ageing; moreover, salt rejection decreased, particularly with caustic cleaning and with acidic cleaning at pH below 1.5. In a later study, Simon et al. [18] evaluated the effect of cleaning temperature on NF270 membrane ageing. They concluded that the cleaning temperature did not exert any discernible impact on the surface charge of the NF270 membrane, but amplified or reduced the impact of the cleaning solution on other membrane properties as well as solute rejection. Do et al. [5] assessed the degradation of PA membranes (NF90, BW30, and NF270; Dow Filmtec™) by prolonged hypochlorite exposure at different solution concentrations and exposure time. X-ray photoelectron spectroscopy (XPS) results showed that chlorine attachment onto the PA surface decreased in the following order: NF90 > BW30 > NF270. However, no study of membrane ageing by HCl or other acidic solutions were found.

Therefore, the aim of this study was to investigate NF membrane fouling during AMD treatment, and the cleaning efficiency of different chemical cleaning agents to this fouling layer. Moreover, this study aimed to evaluate the NF270 membrane ageing caused by prolonged contact with the AMD effluent, and an interchangeable combination of the AMD effluent and the best cleaning agent solution.

2. Materials and methods

2.1. Effluent characterization

AMD was collected on the fourth level below ground of an underground gold mine in the state of Minas Gerais, Brazil. AMD characteristics vary throughout the year, and the main characteristics of the two samples used for this study are presented in Table 1.

2.2. Unit description

The raw AMD was initially filtrated (UF) to prevent severe damage to the NF membranes caused by the presence of suspended solids from the raw effluent. The UF was performed using a commercial submerged membrane (ZeeWeed) module, with a filtration area of 0.047 m^2, average pore diameter of 0.04 μm, and a polyvinylidenefluoride (PVDF)-based polymer. UF was carried out at a pressure of 0.7 bar up to 60% of water recovery.

The nanofiltration experiments were carried out in either a single or a double cell bench-scale unit. Both units comprised the following: a supply tank, a pump, a valve for pressure adjustment, a rotameter, a manometer, a thermometer, and the stainless-steel membrane cell. The membrane cell diameter is 9.8 cm, providing a filtration area of 75 cm^2, and the diameter of the inlet channel is 0.64 cm. A feed spacer with approximate thickness of 1 mm was placed over the membrane to promote flow distribution. Fig. 1 shows a schematic of the double cell unit, the schematic of the single cell unit can be found elsewhere [6].

The flat sheet PA thin-film composite membrane NF270 from DOW Filmtec™ was used in this study. This membrane is a loose NF membrane with relatively low salt rejection. Previous to any test, this membrane was inserted onto the membrane cell and pre-compacted with distilled water at 10 bar, until permeate flux stabilization. All effluent filtration tests were conducted at 10 bar, feed flow rate of 0.14 m^3/h, average tangential velocity (u_0) of 0.38 m/s, and temperature of 25 ± 5 °C.