Evaluation of NF membranes as treatment technology of acid mine drainage: metals and sulfate removal

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ABSTRACT

Acid mine drainage (AMD) are acidic streams rich in dissolved ferrous and non-ferrous metal sulfates and minor amounts of non-metals. Nanofiltration (NF) has been postulated as a potential technology in the metallurgical and mining industry to recover strong acids as H_2SO_4 and concentrate metallic ions from acidic mine waters. The performance of semi-aromatic polyamide (NF270) and sulfonated polyethersulfone (HydraCoRe 70pHT) NF membranes were evaluated at different trans-membrane pressures. Different synthetic solutions were filtered under spiral wound configuration at two pHs (2.0 and 2.8): i) a solution of Na_2SO_4 and ii) a solution mimicking AMD from dams, containing Na_2SO_4 and Fe^{2+}, Zn^{2+} and Cu^{2+}. NF270 showed metal rejections higher than 90%, while for HydraCoRe 70pHT they were in between 60 and 70%. Metal rejection values decreased when solution acidity was increased. Chemical composition of the membrane active layer and the aqueous metal-sulfate speciation were found to have a large impact on membrane separation process. Solution-Electromigration-Diffusion-Film model was used to estimate the membrane permeances to ions from the measured ion rejections. Furthermore, a full scale unit vessel containing six spiral wound membrane modules was simulated. NF270 showed a higher capacity for concentrating metal and sulfate ions (100%) than Hydracore 70pHT (50%).

1. Introduction

Acid mine drainage (AMD) are strong acidic streams rich in dissolved ferrous and non-ferrous metal sulfates, and non-metallic species (e.g., As, Se) [1] occurring in galleries, mine workings, open pits, waste rock piles, and mill tailings in both operating and abandoned polysulfide mining sites [2–4]. AMD generation is straightforward and its final composition is a function of the geochemistry of the mineral deposits, presence of oxygen, water availability, microorganisms and temperature [5]. Due to the environmental threats posed by AMD, research has been focused on the development of cost-effective and sustainable solutions for the AMD treatment [6]. However, despite AMD is identified as the main concern for mining and extraction industries, no single successful initiative has developed the required combination of scale, resources and affordability to deal with the problem.

The main effort to treat AMD has been allocated to the development of remediation techniques based on source control and migration control [7]. Source control techniques are directed towards controlling the formation of AMD at source and are based on avoiding the contact of oxygen and/or water with sulfide minerals [3,8,9]. Alternatively,

sulfide oxidation can also be hindered by separating selectively sulfide minerals from the waste [8]. However, many attempts to prevent AMD generation have proven to be unprofitable [10] with the risk of contaminating surrounding water bodies such as the underground aquifers. Different remediation options have been developed for the management of AMD once it has been generated and has eventually contaminated the surrounding water bodies. Among them are: i) its containment to prevent migration of contaminants (e.g., using geotechnical measures), ii) active treatments using an energy source (e.g., pump-and-treat systems, by which AMD-contaminated water is pumped, treated and, optionally, injected to the aquifer) and iii) passive treatments without any energy source (e.g., permeable reactive barriers, by which AMD-contaminated groundwater is treated in-situ by an appropriate reactive material placed under ground in the path of the polluted water flow) [11–15]. Few efforts have been made so far in treating AMD for the recovery of sulfuric acid and/or dissolved transition metals [5]. These studies have involved AMD treatment with traditional technologies (chemical precipitation, adsorption, coagulation–flocculation, flotation and electrochemical methods [16,17]), membrane technologies [18,19], ion-exchange membranes (IXM) [20], membrane distillation

(MD) [21], forward osmosis (FO) [22] and reverse osmosis (RO) [23].

Some recent studies have proposed the treatment of AMD by nanofiltration (NF) [18,19,24–28]. NF has the additional advantage of selectively separating single-charged ions with a wide range of rejection values, which makes feasible to concentrate metallic ions and, at the same time, recover acids from AMD [29,30]. Research studies have highlighted that H_2SO_4 rejection by NF depends on its speciation. For instance, Visser et al. [25] treated sulfuric acid solutions with aromatic and semi-aromatic polyamide-based NF membranes and found that at neutral pH (pH > pK_a = 1.9), when sulfuric acid is presented mainly as SO_4^{2-}, the rejection percentage was higher than 99.9%, but at low pH (pH < pK_a1.9), when the prevalent form of sulfuric acid is HSO_4^-, the rejection percentage was below 20%. Another factor that must be taken into account in the membrane performance is its iso-electric point (IEP), which is defined as the pH value at which membrane exhibits zero charge [24]. It has been found that at pH lower than the IEP, the membranes present a positively charged surface, thus leading to high metal rejection [18,19,23,24,31]. For example, Mullet et al. [24] filtered AMD with two polyamide NF membranes (NF270 and TriSep TS80) working at recovery ratios of 70% and observed that, at pH values lower than the IEP, cation rejection was maximized. Therefore, as reported by these previous studies, sulfuric acid can be, under appropriate pH, recovered in the permeate stream, while metal species are retained in the concentrated side.

Among the different models to describe the separation performance of a NF membrane, the solution-diffusion model is widely applied [32–35]. Yaroschuck et al. [32] coupled the solution-diffusion model to film model theory for single salts (Solution-Diffusion-Film model (SDFM)), and latter extended to electrolyte mixtures (Solution-Electromigration-Diffusion-Film model (SEDFM)) [33–36]. SEDFM allows to obtain the membrane permeance to a given ion, which depends upon both the membrane and ion properties.

This study evaluated the valorization of acidic mine waters, i.e. the recovery of sulfuric acid and valuable metals (Fe, Zn and Cu) with two NF membranes under a spiral wound (SW) configuration: a) semi-aromatic polyamide based composite membrane (NF270) and b) a sulfonated polyethersulfone based composite membrane (HydraCoRe 70pHT). SEDFM was used to determine the membrane permeances to ions. The main novelty of this work is the effort to describe the transport mechanisms of ions in AMD through NF membranes taking into account the different chemical properties of the membranes and the ions speciation. It must be stressed that the HydraCoRe 70pHT is a novel membrane that has not been used to treat acidic waters according to the literature review.

2. Materials and methods

2.1. Water composition

Two synthetic acid solutions of Na_2SO_4 (at pH 2.8 and 2.0) with and without metal ions (Fe^{2+}, Zn^{2+}, Cu^{2+}) were used in this study. Their composition is given in Table 1. The second type of water mimicked an AMD generated in a poly-sulfide mine in the South of Spain (Río Tinto). This mine is located in the South-Portuguese zone of the Iberian Peninsula, in the so-called Iberian Pyrite Bell, which is one of the main poly-sulfide deposits worldwide, mainly composed of pyrite (FeS_2),

chalcopyrite ($CuFeS_2$), sphalerite (ZnS) and galena (PbS) [37]. The compositions of the synthetic waters were based on average values of the AMD stored in the pond of the mine along one year. Major components (Na^+, SO_4^{2-}, Fe^{2+}, Zn^{2+}, Cu^{2+}) were considered for the experimental design, while metals at concentrations below 20 mg/L (Ca, Mg and Al, among others) were not included. The two pH values were selected according to the limit values reported in the mining operation site.

For the first type of water, a solution containing 0.1 M H_2SO_4 was prepared and NaOH 50% was carefully added until the desired pH value was obtained (2.8 and 2.0). For the second type of water mimicking an AMD, appropriate amounts of Fe, Cu, Zn from their respective sulfate salts were dissolved in the solution described above and pH was adjusted by the addition of H_2SO_4. Speciation diagrams obtained with Hydra/Medusa software [38] are shown in Appendix A.

2.2. Membrane set-up and procedure

Two different membranes were tested under SW configuration: NF270 (from Dow Chemical) and HydraCoRe 70pHT (from Hydranautics). NF270 is a thin-film composite based on a semi-aromatic polyamide active layer, where carboxylic (R-COOH) and amine (R-NH$_2$) groups are present. NF270 has an IEP value of 3, and the membrane z-potential has a value of 2 and 5 mV at pH 2.8 and 2, respectively [39]. This membrane is suitable for operation at pH from 2 to 11 up to a maximum pressure and temperature of 41 bar and 45 °C, respectively. HydraCoRe 70pHT is based on a sulfonated polyethersulfone active layer. Coatings of sulfonated polysulfone or sulfonated polyethersulfone have been applied to a porous support to create negatively charged membranes (due to the presence of R-SO$_3$H groups) with good chemical resistance to acids and chlorine [40–42]. According to literature, HydraCoRe 70pHT is a negatively charged membrane with zeta potential value constant (-85 mV) for the pH range from 3 to 11 [43]. Breite et al. [44] also reported negative values of z-potential from pH 3 to 11 for synthetized membranes containing sulfonic groups. In addition, membranes containing sulfonic groups (widely used in electrodialysis and diffusion dialysis) have pK_a values between 0 and 1 [45]. Thus it was expected qualitatively that at the acidity conditions in this study (pH of 2.0 and 2.8) the membrane was negatively charged [45]. HydraCoRe membrane allows operation at a wider range of pH, with values lying between 1 and 13.5 and maximum temperature and pressure of 70 °C and 41 bar, respectively. HydraCoRe 70pHT membrane is suitable for color removal. Nevertheless, the presence of a high negative surface charge might make this membrane suitable for acid removal too. Fig. 1 shows the chemical active layer of both membranes.

Feed solution (50 L) was kept in a refrigerated tank at 25 ± 2 °C and was pumped to the membrane module by a diaphragm pump, passing previously through a pre-filter cartridge. The solution reached the membrane module and two output streams were obtained, the permeate and the retentate. Both generated streams (retentate and permeate) were recirculated to the feed tank solution. In order to control the trans-membrane pressure (TMP) and cross-flow velocity (cfv), one by-pass valve before the entrance of the module and a needle valve in the retentate stream were used. These two valves allowed to vary the TMP, which was directly correlated with the trans-membrane flux. Several parameters such as pressure, conductivity and flow-rate were monitored during the experiments by means of manometers, conductivity-meters and flow-meters. NF270 and HydraCoRe 70pHT modules had an active area of 2.6 m^2 and 6.4 m^2, respectively. Fig. 2 shows a scheme of the experimental setup used.

The experimental procedure started with the membrane compaction at 20 bar for 2 h by filtering feed solution. After that, feed flow rate was fixed at 14.3 L/min and pressure was gradually varied from 4.5 to 20 bar. Samples from the permeate side were collected and analyzed at different TMP. Once an experiment was finished, the membrane was cleaned with de-ionized water at 10 bar for 1 h and at 20 bar for 1.5 h.

Table 1
Concentrations of the both types of water.

pH	[H$^+$] (mmol/L)	[Na$^+$] (mmol/L)	[SO$_4^{2-}$] (mmol/L)	[Fe^{2+}] (mmol/L)	[Zn^{2+}] (mmol/L)	[Cu^{2+}] (mmol/L)
2.8	1.6	200	100	–	–	–
2.0	10	190	100	–	–	–
2.8	1.6	49	80	45	4	5
2.0	10	46	94	56	7	3