Application of nanofiltration for acidic waters containing rare earth elements: Influence of transition elements, acidity and membrane stability

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A R T I C L E   I N F O

A B S T R A C T

Acid mine drainage (AMD) is considered the main environmental problem in mining operation due to its acidity, metal content (Fe, Al, Zn, Cu) and onerous associated treatment cost. However, the presence of relatively high levels of added value elements (rare earth elements (REE)) could make its valorisation economically affordable. Membrane nanofiltration (NF) has been postulated as a potential recovery technology because it allows the recovery of a sulphuric acid rich stream and a metal rich stream in one step. In this study, the performance of a semi-aromatic polyamide NF membrane (NF270) in filtering model solutions containing common metals (Ca, Al, Zn) in sulphuric solutions (pH 1.5–3.0) was evaluated. In a second stage, the performance was assessed with the same model solutions but also containing REE. NF270 showed high rejections for metallic ions in solution, allowing acid permeation. Ion rejection data were used to determine membrane permeances to ions using the solution-diffusion model considering reactive transport. The stability of the membrane was also studied by comparing performances of a virgin membrane with an aged membrane exposed to 1 M sulphuric acid for 4 weeks. Physicochemical changes of membrane properties after ageing were also analysed by ATR-FTIR, AFM and XPS.

1. Introduction

Acid mine drainage (AMD) is a by-product of the mining industry formed when iron sulphide minerals (e.g. pyrite (FeS$_2$), marcasite, (FeS$_2$), and pyrrhotite (FeS)) are oxidised when in contact with water and oxygen. The sulphuric acid generated has the ability to dissolve soil minerals, which leads to a high content of iron, aluminium, zinc and copper, among others, and to the presence of rare earth elements (REEs) [1]. REEs are presented in igneous and sedimentary rocks and are indispensable for the high-tech industry (e.g. power generation, X-ray imaging, fibre optics, among others) [2]. Although REEs are found in a minor proportion compared to the above-mentioned transition metals, their concentration is relatively high (two orders of magnitude higher than the one presented in natural waters) [3,4]. One of the largest sulphide ore deposits in the world is located in the Iberian Pyrite Bell (IPB), which is situated in the Southern Iberian Peninsula. More than 150 types of AMDs have been described in the Odiel and Tinto basins, which are discharged from galleries, open pits and waste dumps. It has recently been estimated that the total discharge of AMD in the IPB watersheds is around 1 m^3/s in the dry season [5,6] with concentrations

of total REEs varying from 0.3 to 11.7 mg/L with an average concentration of 1.0 mg/L [4]. Therefore, the recovery of REEs from AMD can be considered an environmentally and renewable source for their production, especially in Europe, which is lacking primary resources.

Traditional solutions to treat AMD for metal recovery are: a) neutralization to precipitate metals as hydroxides and sulphate as gypsum [7,8]; and b) biological processing using sulphate-reducing bacteria under anaerobic conditions, leading to the precipitation of metal sulphides [9,10]. Technologies such as adsorption [11,12] and membrane-based technologies such as electro-dialysis [13,14] and nanofiltration (NF) [15–20] have been proposed as emerging solutions. NF is an attractive approach as it makes feasible acid and metal recovery in a single step taking benefit of its ability to discriminate between monovalent and multivalent ions, also allowing high acid permeation.

The application of NF membranes to treat AMD has been previously explored. Published studies reported high metal rejection rates (> 85%) and high acid permeation through the membrane [15–20]. Moreover, it has been observed that higher sulphuric acid concentrations (i.e. lower pH) favour the acid passage through the membrane. This is explained by the fact that, at lower pH, a) sulphuric acid is found

mainly as a monovalent ion (HSO_4^-), which has the ability to permeate more easily than the divalent ion (SO_4^{2-}), and b) functional groups of the NF membrane (e.g. carboxylic and amine groups of the piperazine) are deprotonated and, hence, single-charged anions HSO_4^- are less repelled by the membrane than double-charged anions SO_4^{2-}. However, one of the greatest concerns regarding polyamide-based membranes is the low chemical resistance of the active sites in very high acidic conditions, as described elsewhere [21–24]. Platt et al. [21] reported that the instability of membranes is a function of time exposure, temperature, type of acid and concentration. The chemical instability of NF45 and Desal DK in nitric (5% w/w) is higher than in sulphuric acid (20% w/w) after ageing for one to three months, and decreases with increasing temperature (20 to 80 °C). Manis et al. [22] also reported the instability of Desal DK in 2 M sulphuric acid solutions after ageing the membrane for two months with an increase of permeate flux and a decrease of copper retention, while the MPF-34 membrane kept its properties with little variation. Navarro et al. [23] and Diallo et al. [24] aged Desal 5DL and MPF-34 membranes, respectively, in phosphoric acid and concluded that adsorbed phosphate could have an impact on selectivity by increasing polarity and modulating charge. However, ageing experiments in 2% sulphuric acid at 60 °C by Tanninen et al. [25] for NF270, Desal KH and Desal-5 DK membranes showed marginal changes in pure water flux. After 3 days of immersion, Desal-5 DK exhibited a three times higher filtration flux and a decrease in copper retention, from 96 to 77%. After 7 days, all of the membranes showed more or less the same copper retention (~80%).

The main objective of this work was to study the performance of a piperazine-based polyamide membrane (NF270) in filtering synthetic AMD containing REEs (La, Pr, Nd, Sm, Dy and Yb) under different conditions of acidity (i.e. by varying sulphuric acid concentration), in which a pH range from 2.5 to 1.0 was studied. Experiments of membrane ageing were carried out to quantify the changes in membrane performance after being aged in 1 M sulphuric acid for 1 month. Ions rejection data were modelled with the Solution-Diffusion Model (SDM) to determine the membrane permeances to ions in solution. Equilibrium reactions at the acidity conditions of AMD (e.g. acid/base or complexing reactions) were considered. NF270 membranes were characterised by ATR-FTIR, AFM and XPS to quantify changes in membrane properties after the ageing treatment in sulphuric solutions. The novelties of this work are, on the one hand, the efforts to describe the ion transport mechanisms through the NF membrane considering ion speciation and, on the other, the effect of ageing the membrane on its performance in filtering the synthetic AMD.

2. Experimental methodology

2.1. Membranes, reagents and solutions

Experiments were carried out with samples of commercial NF270 membrane supplied by Dow Chemical. NF270 membrane is a thin film composite made up of three different layers: a piperazine semi-aromatic-based polyamide layer on the top, a polysulphone microporous support and a polyester non-woven backing layer [26,27]. Aged membranes were prepared by the immersion of NF270 sheets in a 1 M sulphuric acid solution for one month at room temperature (20 °C). After this contact time membranes sheets were withdrawn from the sulphuric solution and cleaned with deionised water until the pH of the equilibrated water was close to neutrality.

Synthetic solutions were prepared by adding appropriate amounts of the metal-sulphate, nitrate, chloride and oxide salts and sulphuric acid. The following solutions and salts were used: H_2SO_4 (96 wt%, Sigma-Aldrich); $Al_2(SO4)_3 \cdot 18\ H_2O$ (55%, Panreac); $CaSO_4 \cdot 2\ H_2O$ (100%, Scharlau); $ZnSO_4 \cdot 7\ H_2O$ (100%, Panreac); $CuSO_4$ (100%, Panreac); $La_2(SO_4)_3 \cdot 9\ H_2O$ (99.9%, Alfa Aesar); $Pr(NO_3)_3 \cdot 6\ H_2O$ (100% Fluka AG); $NdCl_3 \cdot 6\ H_2O$ (100%, Fluka AG); $SmCl_3$ (100%, Fluka AG); Dy_2O_3 (99.9%, Fluka AG) and Yb_2O_3 (99.9% Fluka AG).

2.2. Membrane cross-flow experimental set-up

The experimental set-up has been previously described in [28]. Experiments were carried out with NF270 membrane ($0.014\ m^2$), which was placed in a test cell (GE SEPA™ CF II) with a spacer-filled feed channel, and with the possibility to vary the cross-flow velocity (cfv) and trans-membrane pressure (TMP). The solution was kept at a constant temperature (25 ± 2 °C) in a thermostated 30 L tank and it was pumped into the cross-flow cell with a high pressure diaphragm pump (Hydra-Cell, USA) at prefixed required flow rates and pressures. A manometer was located at the entrance of the test cell. Both outputs of the cell (retentate and permeate) were recycled back to the tank to keep a constant concentration in the feed solution. The system was provided with a needle and a by-pass valve to vary the cfv, which was fixed, and the TMP. The first was located at the retentate stream, just at the exit from the test cell. The concentrate passed through a manometer and a flow meter. Just before the discharge of the retentate to the tank, a pre-filter cartridge (100 μm, polypropylene) was placed to avoid erosion products reaching the pump and to eliminate microorganisms. Permeate samples were collected by a three-way valve. Pipes were made of stainless steel.

Membranes were placed in Milli-Q water overnight to remove conservation products. The membrane was compacted at 22 bar and cfv of 1 m/s with deionised water and with the working solution for 2 h and 1.5 h, respectively. Experiments were carried out at a pre-fixed cfv (0.7 m/s) and TMP was varied. Conductivity was measured on-line in the permeate stream and samples were taken when conductivity was stable. Once the experiment was finished, the membrane was cleaned with deionised water at 10 bar for 30 min and at 20 bar for 1.5 h.

Permeate samples were analysed with a conductivity-meter and a pH-meter. A data acquisition system was programmed in LABVIEW® version 8.6 (Laboratory Virtual Instrumentation Engineering Workbench), which collected data from the flow-meter and the pressure-meter.

2.3. Experimental design for membrane performance in sulphuric solutions

Experiments were performed over a range of pH (1.0–2.5) in order to reproduce different acidities typical of AMD. In the first group of experiments (1 to 4 in Table 1), a virgin sample of NF270 was used and the model solutions included four main components: a strong acid (sulphuric acid), a trivalent transition metal ion (Al), a divalent transition metal ion (Zn) and a rare alkaline metal ion (Ca). By increasing the sulphuric acid concentration, pH was varied from 2.5 to 1.0.

Synthetic solutions simulating the supernatant of a pre-treated AMD from La Poderosa Mine at the Iberian Belt (Huelva SW Spain) after being treated by limestone to remove Fe(III) were filtered (experiments

Table 1
Experimental details on the NF270 assays with virgin and aged membranes.

Experiment	1	2	3	4	5
$pH_{initial}$	2.5	1.9	1.5	1.0	1.0
Membrane	Virgin	Virgin	Virgin	Virgin	Aged
H_2SO_4 $_{inl}$ (mM)	18.4	25.1	39.4	84	84
IS (ionic strength, mM)	52	66	96	169	169
$[Al]_{TOT}$ (mM)	12.4	12.7	12.6	20.7	20.7
$[SO_4^{2-}]_{TOT}$ (mM)	26.7	33.5	47.9	97.8	97.8
$[Zn]_{TOT}$ (mM)	0.65	0.65	0.65	0.71	0.71
$[Ca]_{TOT}$ (mM)	6.0	6.0	6.7	0.59	0.59
$[Cu]_{TOT}$ (mM)				0.6	0.6
$[La]_{TOT}$ (mM)				0.068	0.068
$[Pr]_{TOT}$ (mM)				0.072	0.072
$[Nd]_{TOT}$ (mM)				0.064	0.064
$[Sm]_{TOT}$ (mM)				0.045	0.045
$[Dy]_{TOT}$ (mM)				0.063	0.063
$[Yb]_{TOT}$ (mM)				0.043	0.043