[103] # Evaluation of polymeric nanofiltration membranes on metal valorisation from acidic mine waters

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Introduction

Depletion of mining resources requires finding other sources to obtain certain valuable transition metals (e.g. Cu and Zn) and rare earth elements (REE). One of these sources is Acid Mine Drainage (AMD), which could be used as a secondary resource to extract metals. AMD is a by-product of mining industry which presents low pH (1 – 3.5), high content of sulphate ion and heavy metals dissolved. The combination of these properties makes AMD a toxic mixture that will damage aquatic life, destroys ecosystems and taints water. Traditional methods like lime neutralization for sulphate and metal precipitation involve a high amount of reactive and high costs (Simate and Ndlovu, 2014).

Nanofiltration (NF) is a membrane technology that offers appropriate properties to manage AMD. Its advantages are a high permeability for acids and high rejections for multivalent ions (Mohammad et al., 2015). For instance, Mullet et al. (2014) obtained high metal rejection (> 88 % for Ca, Cu, Mg and Mn) with NF270 membrane; whereas sulphate rejection decreased when pH was lowered from 4.5 to 1.5.

Material and Methods

Experiments were performed in a cross-flow set-up equipped with a test cell (GE SEPA™ CF II) with a spacer-filled feed channel. Three different membranes were tested: NF270 (Dow Chemical), Desal DL (GE Osmonics) and HydraCoRe 70pHT (Hydranautics). A synthetic solution mimicking an AMD was treated (Table 1).

Table 1. Chemical composition of the synthetic solution in ppm.

pH	$[SO_4^{2-}]$	$[Cl^-]$	$[Al^{3+}]$	$[Fe^{3+}]$	$[Cu^{2+}]$	$[Zn^{2+}]$	$[Ca^{2+}]$	$[Cu^{2+}]$	$[REE_T]$
1	9400	970	560	500	40	46	24	40	60

The ion fluxes are described according to the Solution-Electro-Diffusion model. Ion transport was subjected to zero-current and electro-neutrality conditions. Virtual ion concentrations are not independent but related by a chemical equilibrium condition at a given constant temperature and ionic strength.

Results and Discussion

NF270 and Desal DL are a polyamide based-membranes and showed similar behaviours, with high metal rejection (>98 %) and low hydrogen (>-10% for NF270 and >10% for Desal DL) and sulphate rejections (>50% for NF270 and >60% for Desal DL). At pH 1, the main sulphate specie in solution is a monovalent anion (HSO_4^-), which is less affected by dielectric exclusion and then responsible for low sulphate rejections. Moreover, its transport is also favoured by the presence of a positively charged surface. According to the isoelectric point of both membranes (2.5 for NF270 and 5 for Desal DL), at pH 1 free carboxylic groups are fully protonated (R-COOH) and amine groups are partially protonated ($R_2NH_2^+$). Cations are rejected, which leads to H^+, which is the more mobile ion and the one with the highest concentration in solution, to permeate easily.

The behaviour of NF270 and Desal DL contrasts with the other membrane (HydraCoRe 70 pHT). This last membrane is a sulphonated polyethersulphone and presents sulphonic groups (R-SO_3^-), which are expected to be ionized leading to a negatively charged membrane. Trivalent metal rejections were around 79 % and for divalent cations were near to 60 %. In addition, sulphate rejection (>70 %) was higher than the other membranes, because of the negative charge of the membrane. Moreover, this membrane has the lowest permeate flux of the tested membranes.

Conclusions

NF270 showed the best performance to treat AMD of the three membranes tested. It allowed to obtain higher permeate fluxes, as well as the possibility to obtain a diluted stream of acid as permeate. In addition, the chemical composition of the membrane was found to have a strong influence over the separation performance.

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