Integration of nanofiltration and reverse osmosis for metal separation and sulfuric acid recovery from gold mining effluent

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ABSTRACT

This work assessed the viability of implementing sequential stages of microfiltration (MF), nanofiltration (NF) and reverse osmosis (RO) to recover sulfuric acid, separate noble metals, and produce high quality reuse water from a gold mining effluent, specifically from a pressure-oxidation process effluent. Additionally, lime demand for neutralization of the proposed treatment streams and current lime demand were compared. It was observed that the NF attained high sulfuric acid permeation, equivalent to 82%, and a substantial acid purification of approximately 77% in relation to feed solution. Moreover, the RO increased the acid content by 99% in relation to feed solution considering a recovery rate of 50%. The final RO permeate had low conductivity and reduced content of total solids and contaminants, thus showing promising potential for industrial reuse. Furthermore, the acid recovery did not led to an important loss of metals of high commercial value which were present in the raw effluent since their retention in the concentrates of the MF and NF was above 95%. The neutralization of the MF and NF concentrates allowed for a 20% reduction in lime consumption in relation current demand.

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1. Introduction

Despite the worldwide economic importance of gold, gold ore mining and processing may cause significant impacts on the environment [1–3]. During gold ore mining and processing, several liquid effluents are generated. Among these liquid effluents, acid mine drainage has been recognized as one of the major environmental problems of mining activity, and is by far its most studied effluent. However, other effluents produced by mining activities are also noteworthy as they usually present high concentrations of heavy metals. Thus, even after neutralization and precipitation processes, these metals from these effluents can be redissolved, resulting in groundwater and surface water contamination [4].

An important processing step for gold ore is pre-oxidation. It is used in the processing of refractory ores which are resistant to direct cyanide leaching. This pretreatment alter or destroy the sulfide matrix thus leaving the gold ore accessible to extraction. The pressure-oxidation process is a frequently used pre-oxidation step for refractory gold ores [5,6].

Like other gold ore processing steps, the pressure-oxidation process generates large volume of liquid effluents with substantial

metal concentrations and high acidity. This effluent is usually treated by the neutralization process using alkalizing agents such as quicklime or hydrated lime, which causes metal precipitation and hence its immobilization [1,7]. Despite this method's simplicity, its main disadvantage is the generation of large volumes of precipitate (sludge) with significant heavy metal content. This sludge still poses an environment threat and must be properly disposed of, which implies in high expenses for final disposal [4,8]. Therefore, the recovery of metals, sulfuric acid and reuse water from this effluent can be a viable alternative to reduce neutralization costs as well as an opportunity to add value to this effluent.

Accordingly, the membrane separation processes (MSP) is a promising technology to treat the pressure-oxidation process effluent. The association of nanofiltration (NF) and reverse osmosis (RO) is of special interest, specially due to the continuous development of membranes more chemically resistant to extreme pH conditions [9].

Nanofiltration is a flexible MSP which combines characteristics of ultrafiltration (UF) and reverse osmosis (RO). These characteristics result in higher permeate fluxes in comparison to RO besides providing high retention of organic compounds and multivalent salts [10]. Due to its particularities, nanofiltration offers a unique opportunity for the separation of metal species from acid streams. The reason for this separation is the membrane isoelectric point

(IEP). Nanofiltration membranes usually exhibit an IEP between 3 and 6, thus at low pH values the membrane is positively charged [11,12]. Consequently, in such conditions, the nanofiltration membranes will strongly reject multivalent metal cations while allowing acidic anions to permeate almost freely through the membrane [9].

On the other hand, RO processes mainly use dense membranes. This process allows retentions above 99% of dissolved salts and of organic molecules of low molar mass [10]. The main use of RO membranes is seawater desalination; and this process accounts for over 20% of all desalinated water produced in the world [1]. Additionally, RO process have become increasingly attractive for industrial effluents treatment, especially when aiming water recovery [13,14]. Due to the high retentions obtained with RO membranes, another frequent application of this technology is in the concentration of existing solutions. Ahsan et al. [15], for example, have reported the use of RO to concentrate acetic acid; they obtained an increase in the acid content of the concentrate greater than 400% in relation to feed solution.

Several studies have reported the use of NF and RO in the treatment of acidic streams contaminated with metal cations. The characteristics of these processes are diverse. They may vary in terms of: the type of acid being purified, which may be sulfuric acid [16,17], phosphoric acid [18–20], or nitric acid [17,21,22]; the acid concentration, that may reach, for example, 35% w/w of H_2SO_4; and the solution contaminants [9]. Despite the diversity of studies found in the literature, few have reported the use of real industrial effluents. Thus the influence of real effluent matrix on permeation properties is usually not taken into account.

Within this context, the present study investigated the viability of implementing sequential stages of microfiltration (MF), nanofiltration (NF) and reverse osmosis (RO) to recover sulfuric acid, separate noble metals, and produce high quality reuse water from a gold mining industry's real effluent, specifically, from a pressure-oxidation process effluent. Furthermore, the reduction of lime demand for the neutralization of the proposed treatment streams compared to current lime demand was evaluated.

2. Experimental

2.1. Pressure-oxidation process effluent

The effluent from the pressure-oxidation process was collected from a gold mining company in the state of Minas Gerais, Brazil. According to the company's data, the effluent is characterized by high acidity (median pH was 1.30) and high metal concentrations. Additionally, some metals of high commercial value are present in this effluent, such as cobalt, nickel and copper, with median concentrations corresponding to 25, 71 and 147 mg L^{-1}, respectively.

2.2. Analytical methods

The raw effluent and the test samples obtained throughout the stages of this work were characterized in terms of the following physicochemical parameters: pH (pHmeter Qualxtron QX 1500); conductivity (Hanna conductivity meter HI 9835); total solids; and free acidity. The analyses were performed in accordance with the *Standard Methods for the Examination of Water and Wastewater* [23]. Sulfate concentrations were determined by ion chromatography (Dionex ICS-1000 ion chromatography, equipped with column type IonPac AS22 and IonPac CS12A) and metal concentrations by atomic absorption spectrophotometer (GBC AVANTA Atomic Absorption Spectrophotometer). Sulfuric acid concentrations were calculated based on the free acidity.

2.3. Proposed treatment for metal separation and sulfuric acid recovery

Fig. 1 shows a schematic of the proposed multistage treatment that was investigated in this work. This proposed multistage treatment comprised the following units: microfiltration (MF), nanofiltration (NF) and reverse osmosis (RO). The streams F, R and P represent, respectively, the feed, the retentate and the permeate fluxes.

As presented in Fig. 1, initially the raw effluent (F_{MF}) enters a MF unit to remove suspended solids from the raw effluent thus protecting the NF membrane of the next stage. The MF permeate is then transferred to the NF unit. The aim of the NF stage was to obtain a metals enriched retentate (R_{NF}) and a permeate containing sulfuric acid (P_{NF}). To concentrate the P_{NF} rich in sulfuric acid, it was then transferred to a RO unit. The RO produced a retentate rich in sulfuric acid (R_{RO}) and a permeate which may be used as reuse water (P_{RO}). Finally, the MF and NF retentates (R_{MF} and R_{NF}) could later be combined and transferred to a subsequent stage for dissolved metals recovery. This last stage was not evaluated on this study.

2.4. Pretreatment procedure

The raw effluent was microfiltrated prior to NF and RO experiments. MF was performed in order to prevent severe damage to the NF membranes caused by the presence of suspended solids from the raw effluent. The MF was performed using a submerged membrane module supplied by Pam Membranas Seletivas Ltda., with filtration area of 0.04 m^2, average pore diameter of 0.4 μm and polyetherimide-based polymer. MF was carried out at a pressure of 0.7 bar up to a recovery rate of 80%.

2.5. Nanofiltration and reverse osmosis membranes

The flat sheet NF and RO membranes used in this study were supplied by Koch Membranes. Some characteristics of these membranes as provided by the supplier are shown in Table 1.

2.6. NF and RO experimental setup

The NF and RO experiments were performed in a bench scale unit. As shown in Fig. 2, the experimental apparatus comprised: a feed tank; a centrifugal pump connected to a speed controller; a rotameter; a valve for pressure adjustment; a stainless steel membrane module; a manometer; and a thermometer.

The stainless steel membrane module has a diameter of 9 cm, providing a filtration area of 63.60 cm^2. The radial inlet radius of the cell is 64 mm, and the channel height is 1 mm. The membranes tested were properly cut before being placed in the cell and a feed spacer was placed over the membrane to promote flow distribution. Permeate was collected for physicochemical analysis, while the retentate was returned to the supply tank. The flux at the permeation temperature [$J(T)$] was calculated by Eq. (1).

$$J(T) = \frac{\Delta V}{A \Delta t} \tag{1}$$

where ΔV is the permeate volume collected, Δt is the collection time, and A is the effective membrane area.

2.7. Cleaning procedure and water permeability determination

Prior to the filtration tests, the membranes were submitted to a cleaning procedure. This procedure consisted of an ultrasound bath with citric acid solution at pH 2.5 followed by an ultrasound bath with 0.1% NaOH solution, for 20 min each.