

# NANOFILTRATION AND REVERSE OSMOSIS APPLIED TO GOLD MINING EFFLUENT TREATMENT AND REUSE

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**Abstract** - Gold mining and ore processing are activities of great economic importance. However, they are related to generation of extremely polluted effluents containing high concentrations of heavy metals and low pH. This study aims to evaluate the optimal conditions for gold mining effluent treatment by crossflow membrane filtration regarding the following variables: nanofiltration (NF) and reverse osmosis (RO) membrane types, feed pH and permeate recovery rate. It was observed that retention efficiencies of NF90 were similar to those of RO membranes though permeate fluxes obtained were 7-fold higher. The optimum pH value was found to be 5.0, which resulted in higher permeate flux and lower fouling formation. At a recovery rate above 40% there was a significant decrease in permeate quality, so this was chosen as the maximum recovery rate for the proposed system. We conclude that NF is a suitable treatment for gold mining effluent at an estimated cost of US\$ 0.83/m<sup>3</sup>.

**Keywords:** Gold mining effluent treatment; Nanofiltration (NF); Reverse Osmosis (RO); Feed pH; Permeate recovery rate.

## INTRODUCTION

Gold mining and ore processing are activities of great economic importance. Gold has been used in many different applications, from raw material for jewelry manufacturing and monetary reserve to more technological applications such as the production of catalysts and nanoparticles. On the other hand, gold ore exploitation and processing bring forth environmental hazards that may go from natural habitat destruction to highly polluted effluent release that may contaminate the environment (Getaneh and Alemayehu, 2006). The effluents generated during ore

processing have low pH and high concentrations of heavy metals and metalloids such as Cd, Cr, Hg, As, etc. as these elements are often associated with valuable components in ores and concentrates (Chan and Dudeney, 2008b; Langsch *et al.*, 2012).

These effluents are usually treated by neutralization, precipitation and sedimentation (Akcil and Koldas, 2006; Correia, 2008; Langsch *et al.*, 2012), although other technologies such as anaerobic bioreactors (Wildeman *et al.*, 2006), sorption (Acheampong and Lens, 2014; Magriotis *et al.*, 2014), coagulation and flocculation (Oncel *et al.*, 2013; Yan *et al.*, 2012), and crystallization (Fernández-Torres *et al.*,

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2012) may also be used. Nevertheless, these methods may: be insufficient to adjust effluent properties to meet discharge and/or reuse standards; require high consumption of chemical products; and generate large volumes of metal-contaminated sludge (Wang *et al.*, 2007).

Membrane separation processes, specifically nanofiltration (NF) and reverse osmosis (RO), are effective technologies to retain salts and metals from aqueous medium (Al-Rashdi *et al.*, 2013; Pages *et al.*, 2013) presenting high potential to treat mining effluents for water reuse. The NF process is an intermediate process between RO and ultrafiltration (UF) that can retain dissolved molecules with molar mass ranging between 200 and 1,000 g/mol and multivalent ions (Yu *et al.*, 2010). Many works have shown that NF is an efficient system for secondary or tertiary treatment of effluents intended to purify water for industrial, agricultural and/or indirect reuse as potable water (Acero *et al.*, 2010a; Acero *et al.*, 2010b; Koyuncu *et al.*, 2000; Shu *et al.*, 2005). The use of NF has been increasing due to advantages such as reliability, ease of operation, low power consumption and high efficiency (Fu and Wang, 2011).

RO systems use membranes that are permeable to water, but substantially impermeable to salts and therefore are suited to separate ions, dissolved metals and organic molecules of low molar mass (Baker, 2004). One of the main applications of RO membranes is seawater desalination (Fu and Wang, 2011). Moreover, RO membranes have increasingly become a popular water recovery technology to treat industrial effluents (Kurt *et al.*, 2012; Qi *et al.*, 2011).

Sierra (2013) studied the nanofiltration process for treating an acid mine drainage from an abandoned mercury mine. NF was able to retain up to 99% of aluminum, iron and arsenic content, and 97% of sulfate content. Other authors (Al-Zoubi and Al-Thyabat, 2012) tested nanofiltration to treat an effluent from a phosphate mine. Retention efficiencies between 61% and 69% for chloride, nearly 100% for sulfate, and 83% for total solids were obtained by the NF process, ensuring a treated effluent with quality similar to the raw water that fed the system. Chan e Dudney (Chan and Dudney, 2008a) evaluated the treatment of wastewater from gold ore bioleaching treated by neutralization, precipitation and sedimentation followed by a post-treatment with RO membrane. It was found that more than 90% of the arsenic that had not been removed by the first treatment was retained by the membrane. Vaclav and Eva (2005) studied a RO pilot plant operation treating three different mine wastewater types, and attained

total solid retention efficiencies ranging between 88% and 98%. Another study evaluated NF and RO membrane performance to treat two synthetic acid mine drainages, including one with higher metal content (Al-Zoubi *et al.*, 2010). It was found that the NF membrane was more suited for such use as it handled a higher permeate flux at lower power consumption, although its rejections were smaller than for the RO membrane.

Despite the successful cases using different membranes for treating mining plant effluents, there remains the need for further examination for each specific application of the most appropriate system (NF or RO) and membrane type selection, and operational conditions such as feed pH and permeate recovery rate. Such assessment would be targeted to find ways to increase retention efficiencies, decrease membrane fouling formation, reduce costs and optimize the whole system. Besides that, although the behavior of NF and RO membranes has already been extensively studied and modeled in both single or multi-element solutions of a known compound (Childress and Elimelech, 2000; Fujioka *et al.*, 2012; Hoang *et al.*, 2010; Nghiem *et al.*, 2004; Nguyen *et al.*, 2009; Toffoletto *et al.*, 2010), the operational performance of these processes to treat actual effluents cannot easily be predicted (Krieg *et al.*, 2005).

Therefore, this study aims to investigate the use of NF and RO for gold mining effluent treatment to obtain water for industrial reuse. Initially, different NF and RO membranes were tested and the one with the greatest application potential was selected. Then, tests were performed in order to define the best operational conditions regarding feed pH and permeate recovery rate.

## MATERIALS AND METHODS

### Effluents from Gold Mining

Two effluents from a gold mining company in Brazil were studied, i.e., an effluent from a sulfuric acid production plant and the water from the calcined dam. At this company, the gold ore extracted from an underground mine undergoes processing (crushing, gravity separation and flotation), and the concentrate is transferred to a pyrometallurgical processing unit. At this stage, it is subjected to a roasting process by which gases containing sulfur dioxide and calcined solids are produced. At the sulfuric acid production plant, SO<sub>2</sub>-rich gas is converted into SO<sub>3</sub>, and then it is adsorbed in an acid solution. The effluent from this phase, that is, the sulfuric acid production

plant effluent, was the first one to be analyzed.

The calcined solids undergo a hydrometallurgical process in which the gold is leached with a sodium cyanide solution. The solid residue is separated from the gold-rich extractant solution through a series of thickeners with counter-current flow. Finally, the solid residue is placed in a calcined dam. The second effluent was made up of water from this dam. The characterizations of both effluents are shown in Table 1.

**Table 1: Characterizations of effluents from gold mining.**

Parameters	Sulfuric acid production plant effluent	Water from the calcined dam
pH	1.59	8.75
Conductivity ( $\mu\text{S}/\text{cm}$ )	10,470	2,612
Turbidity (NTU)	134.0	3.5
Total solids (mg/L)	8,770	3,182
Suspended solids (mg/L)	132	19
Total arsenic (mg/L)	507	0.7
Sulfate (mg/L)	3,912	2,403
Chloride (mg/L)	16	40
Total calcium (mg/L)	374	515
Total magnesium (mg/L)	200	33
Total potassium (mg/L)	33	66
Total iron (mg/L)	125	0.1
Total sodium (mg/L)	14	163

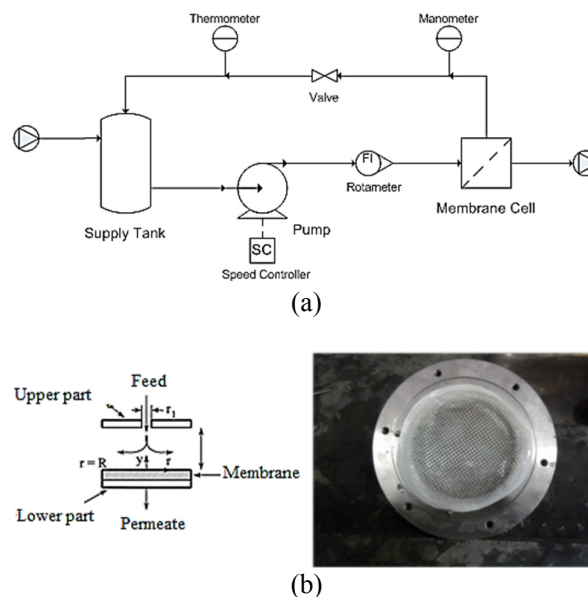
Preliminary tests showed that the performance of the membrane process was improved both in terms of pollutant retention efficiency and membrane fouling when applied to these two effluents combined instead of a single effluent separately. From an operational perspective, the premixed effluent also offered the advantage of acquiring and operating a single treatment unit. Thus, both effluents were mixed at a 1:1 ratio (corresponding to the ratio between the two actual outflow rates) before being transferred to the membrane treatment system. In this work, such a mixture will be referred to only as "effluent from gold mining".

The aim of the present study was to treat both of these effluents and generate reuse water to meet the water demand in all stages of gold processing (beneficiation, hydrometallurgical and pyrometallurgical process).

### Unit description

For the nanofiltration and reverse osmosis filtration tests a bench scale unit was used. The system is comprised of one feed tank, one pump equipped with speed controller, one valve for pressure adjustment, one flowmeter, one manometer, one temperature

gauge, and one stainless steel cell. Figure 1 shows a schematic drawing of this unit. The stainless steel cell has a 9.8 cm diameter that provides a filtration area of 75 cm<sup>2</sup>. The membranes tested were properly cut and placed into the cell. A feed spacer was placed over the membrane to promote an even distribution. Permeate flux was measured by collecting the volume of permeate in a measuring cylinder over a given period of time, that is, 60 seconds for NF and 120 seconds for RO. The concentrate was returned to the feed tank.



**Figure 1:** Schematic of the nanofiltration and reverse osmosis bench scale unit (a) and schematic and photograph of the membrane cell (b).

### Tests Conditions

The effluent from gold mining was first pretreated for each test performed. The pretreatment consisted of ultrafiltration, which was performed using a commercial submerged membrane (ZeeWeed), PVDF-based polymer, average pore diameter of 0.04 micrometers, with a filtration area of 0.047m<sup>2</sup>. UF occurred at a pressure of 0.7 bar.

NF/RO filtration took place at a fixed pressure of 10 bar, feed flow rate of 2.4 LPM (corresponding to a cross flow velocity on the surface of the membrane of 1.9 m/s and Reynolds number of 840), while the permeate was continuously removed and the concentrate returned to the supply tank. Before every test, all membranes were washed in two consecutive ultrasound baths for 20 minutes each, the first containing citric acid solution at pH 2.5 and the second containing 0.1% NaOH solution. After chemical cleaning, the

membrane was flushed with distilled water.

## Evaluation of Different NF and RO Membranes

### Membrane Characteristics

The performances of five different membranes were evaluated during the treatment of the effluent from gold mining. The RO membranes were TFC-HR and BW30, while the NF membranes were MPF34, NF90, and NF270. The characteristics of the membranes studied, as provided by the suppliers, unless otherwise specified, are shown in Table 2. The membranes were provided by the suppliers as flat sheets, and were cut to properly fit into the filtration cell.

### Evaluation of Membrane Performance Regarding Fouling

The NF and RO membranes were investigated regarding their fouling propensity. For this, after membrane cleaning, they were compacted at 10 bar and water permeability was measured by monitoring the stabilized permeate flux at pressures of 10.0, 7.5, 5.0, and 2.5 bar. Water temperature was also monitored and the permeate flux was normalized to 25 °C by means of a correction factor calculated as water viscosity at 25 °C divided by the water viscosity at the temperature of permeation (Drak *et al.*, 2000). With the normalized permeability, the intrinsic membrane resistance to filtration ( $R_{\text{membrane}}$ ) was calculated according to Equation (1):

$$R_{\text{membrane}} = \frac{1}{K \times \mu} \quad (1)$$

where  $K$  is the water permeability at 25 °C in  $\text{m}^3/\text{h} \cdot \text{m}^2 \cdot \text{Pa}$ , and  $\mu$  is the viscosity of permeate (water) in  $\text{Ns}/\text{m}^2$ .

Subsequently, two liters of the pretreated effluent were fed into the NF/RO unit. Permeate flow rate and system temperature were monitored frequently, and the flow rate results were also normalized to 25 °C. The total and fouling resistances to filtration were calculated by Equations (2) and (3):

$$R_{\text{total}} = \frac{P - \sigma \Delta \pi}{\mu \times J_{\text{effluent}}} \quad (2)$$

$$R_{\text{fouling}} = R_{\text{total}} - R_{\text{membrane}} \quad (3)$$

where  $P$  is the applied transmembrane pressure,  $\sigma$  is the reflection coefficient, estimated from the averaged membrane rejection of the major constituents of the effluent (Mattaraj *et al.*, 2008), and  $\Delta \pi$  is the difference in osmotic pressure of the solution in the concentrate and permeate streams. Thus,  $P - \sigma \Delta \pi$  is the effective pressure, in Pa. Additionally,  $J_{\text{effluent}}$  is the permeate flux in  $\text{m}^3/\text{h} \cdot \text{m}^2$ .

The differences in osmotic pressure between NF/RO concentrates and permeates obtained with different permeate recovery rates were estimated by the Equation of Van't Hoff, described in Equation (4):

$$\Delta \pi = RT \Sigma \Delta C \quad (4)$$

where  $R$  is the universal gas constant,  $T$  is the permeation temperature, and  $\Sigma \Delta C$  is the sum of the difference in molar concentrations of the main dissolved species present in the concentrate and the permeate at a given recovery.

**Table 2: Characteristics of the five tested membranes.**

Characteristic	TFC-HR	BW30	MPF34	NF90	NF270
Supplier	Koch Membranes	Dow Filmtech	Koch Membranes	Dow Filmtech	Dow Filmtech
Membrane Material	Polyamide Composite	Polyamide Composite	Composite	Polyamide Composite	Polypiperazine Composite
NaCl retention	99,55% <sup>a</sup>	99,5% <sup>b</sup>	35% <sup>c</sup>	85-95% <sup>b</sup>	n.a.
MgSO <sub>4</sub> Retention	n.a.	n.a.	n.a.	>97% <sup>d</sup>	97% <sup>d</sup>
Molecular weight cutoff (Da)	100 <sup>e</sup>	100 <sup>f</sup>	200 <sup>g</sup>	100 <sup>h</sup>	200-300 <sup>g</sup>
Average pore diameter (nm)	n.a.	n.a.	n.a.	0.68 <sup>i</sup>	0.84 <sup>i</sup>
pH range for continuous operation	4 to 11	2 to 11	0 to 14	3 to 10	3 to 10

n.a. Not available or not applicable

<sup>a</sup> Feed solution containing 2,000 mg/L of NaCl, filtration at 15.5 bar, 25 °C, and recovery rate of 15%.

<sup>b</sup> Feed solution containing 2,000 mg/L of NaCl, filtration at 4.8 bar, 25 °C, and recovery rate of 15%.

<sup>c</sup> Feed solution containing 50,000 mg/L of NaCl.

<sup>d</sup> Feed solution containing 2,000 mg/L of MgSO<sub>4</sub>, filtration at 4.8 bar, 25 °C, and recovery rate of 15%.

<sup>e</sup> Reference: (Xu *et al.*, 2005)

<sup>f</sup> Reference: (Gautam and Menkhaus, 2014)

<sup>g</sup> Reference: (Wang and Tang, 2011)

<sup>h</sup> Reference: (Zulaikha *et al.*, 2014)

<sup>i</sup> Reference: (Nghiem *et al.*, 2004)

Intrinsic membrane resistance and fouling resistance after effluent permeation were calculated for the five studied membranes and compared.

### Evaluation of Membrane Performance Regarding Pollutant Retention

Feed and permeate samples obtained for each test were analyzed for conductivity (Hanna conductivity meter HI 9835), total solids, arsenic concentration (atomic absorption spectrophotometer GBC 932), sulfate and chloride (ion chromatograph Dionex ICS-1000 equipped with AS-22 and ICS 12-A columns), in accordance with the Standard Methods for the Examination of Water and Wastewater (APPA, 2005). The cyanide concentration was not monitored because it was low ( $< 0.5$  mg/L in the gold mining effluent). Membrane retention efficiencies were calculated and compared. According to the fouling propensity and retention efficiency, the best membrane was selected for further trials.

### Evaluation of pH Adjustment as a Tool for Membrane Fouling Mitigation

Process water cannot have acidic pH, so as to prevent possible wear and corrosion of equipment and piping. Thus, for reuse of the treated effluent, its pH must be adjusted to approximately 7.0 (Asano *et al.*, 2007). Such adjustment can be performed before or after the membrane treatment system. Therefore, the membrane selected with the highest potential to treat the effluent from gold mining was tested at different pH values, namely 2.2 (original effluent pH), 3.5, 4.2, 5.0, 5.5, and 6.0. Tests with pH above 6.0 were not performed because higher pH values did not allow better process performance due to high membrane scaling potential, as will be shown later.

A 5.0M NaOH solution was used for the effluent pH adjustment. After adjustment, the effluent was ultrafiltered and four liters the UF permeate was fed into the NF filtration unit. During effluent filtration permeate flux, system temperature and accumulated permeate volume were checked every 15 minutes for 4 hours. Fouling resistance was calculated according to Equations (2) and (3). Osmotic pressures were estimated by Equation (4) for each feed pH at each permeate recovery rate.

Raw effluent, pretreated effluent (after pH adjustment and ultrafiltration) and NF/RO permeates for each feed pH value were analyzed for their pH, conductivity, arsenic, sulfate, chloride, calcium and magnesium concentrations. Calcium and magnesium were analyzed by ion chromatography and the other

parameters determined as described above.

To better understand the membrane behavior at different feed pH values, the zeta potential of the membrane was measured using a SurPASS electrokinetic analyzer supplied by Anton Paar. The zeta potential measurement was carried out with pH values ranging from 2 to 10. The background solution was a synthetic effluent with salt concentrations similar to the actual effluent from gold mining (Table 3), since the actual effluent was not used because it could damage the equipment.

**Table 3: Characteristics of the synthetic effluent used in the analysis of the membrane zeta potential.**

Parameter	Synthetic effluent
pH	1.80
Sulfate (mg/L)	2,403
Chloride (mg/L)	55
Carbonate / Bicarbonate (mg/L)	839
Total calcium (mg/L)	559
Total iron (mg/L)	78
Total magnesium (mg/L)	114
Total potassium (mg/L)	61
Total sodium (mg/L)	99

### Permeate Recovery Rate

To establish the optimal permeate recovery rate (RR), 10 liters of effluent with pH adjusted up to the optimum pre-determined value and then ultrafiltered were fed into the NF/RO system. The permeation occurred with continuous permeate removal. Flux was measured for every 100 mL of permeate obtained, while permeate conductivity and sulfate and calcium contents were analyzed for each 500 mL of permeate.

After the filtration, water flux through the fouled membrane was measured at a pressure of 10 bar. The membrane cleanup procedure was performed using two consecutive ultrasound baths for 20 minutes each, first with citric acid solution at pH 2.5 then with 0.1% NaOH solution. Water flux of the clean membrane was measured at a pressure of 10 bar. These results, combined with effluent permeate flux analyzed during the concentration experiment and initial flux through the virgin membrane were used to calculate the flux decrease due to concentration polarization, reversible fouling and irreversible fouling according to Capar *et al.* (2006).

To evaluate salt precipitation on the membrane surface, which results in scaling, the calcium sulfate supersaturation index on the membrane surface ( $SI_m$ ) was determined for different RR according to Equation (5) (Huang and Ma, 2012; Schäfer *et al.*, 2005).

Calcium sulfate was chosen as representative of salt precipitation because it has low solubility and a high concentration in the effluent from gold mining (Table 1) presenting, therefore, greater precipitation potential. It is noteworthy that in aqueous systems the hydrated specie  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  is more likely to be formed; however, the solubilities of the two salts is quite similar and therefore  $\text{CaSO}_4$  can be taken as the scaling model.

$$\text{SI}_m = \left( \frac{C_{\text{Ca}^{2+}_m} \times C_{\text{SO}_4^{2-}_m}}{K_{\text{sp}'}} \right)^{0.5} \quad (5)$$

where  $C_{\text{Ca}^{2+}_m}$  and  $C_{\text{SO}_4^{2-}_m}$  are the molar concentrations of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  at the membrane/solution interface and  $K_{\text{sp}'}$  is the solubility product constant for calcium sulfate based on molar concentration.

The supersaturation index is important since it can be related to the variation in Gibbs free energy ( $\Delta G$ ) through Equation (6). For  $\text{SI}_m > 1$ , the  $\Delta G$  is less than zero and the precipitation process is thermodynamically spontaneous.

$$\Delta G = -RT \ln(\text{SI}_m) \quad (6)$$

Molar concentrations at the membrane surface ( $C_{\text{im}}$ ) were determined by Equation (7) (Song *et al.*, 2013).

$$C_{\text{im}} = e^{J_v/k_i} (C_{\text{ib}} - C_{\text{ip}}) + C_{\text{ip}} \quad (7)$$

where  $C_{\text{im}}$ ,  $C_{\text{ib}}$  and  $C_{\text{ip}}$  are the concentrations of species  $i$  at the membrane/solution interface and in the bulk solution and permeate, respectively;  $J_v$  is the permeate flux; and  $k_i$  the mass transfer constant of species  $i$ , determined through the Sherwood number ( $Sh$ ) for a radial cross-flow membrane cell (Equations (8), (9) and (10)) (De *et al.*, 1995).

$$\text{SH} = \frac{k_i \cdot h}{D_i} = 1.05 \left( \text{Re} \cdot \text{Sc} \cdot \frac{h}{r} \right)^{0.38} \quad (8)$$

$$\text{Re} = \frac{\rho \cdot u_o \cdot d_h}{\mu} \quad (9)$$

$$\text{Sc} = \frac{\nu}{D_i} \quad (10)$$

where  $\text{Re}$  is the Reynolds number;  $\text{Sc}$  is the Schmidt number;  $\rho$  is the solution density;  $\mu$  and  $\nu$  are the

kinematic and dynamic viscosities, respectively;  $u_o$  is the average cross-flow velocity (Minnikanti *et al.*, 1999);  $d_h$  the cell hydraulic diameter;  $D_i$  is the diffusion coefficient of component  $i$  (Wang *et al.*, 2005);  $h$  is the half channel; and  $r$  is the membrane cell radius.  $K_{\text{sp}'}$  can be calculated through the mass transfer constant based on activity ( $K_{\text{sp}}$ ), as shown in Equation (11).

$$K_{\text{sp}} = a_{\text{Ca}^{2+}_m} a_{\text{SO}_4^{2-}_m} = K_{\text{sp}'} \gamma_{\text{Ca}^{2+}_m} \gamma_{\text{SO}_4^{2-}_m} \quad (11)$$

where  $\gamma_{\text{im}}$  and  $a_{\text{im}}$  are the activity coefficient and the activity of species  $i$  at the membrane surface. In solutions with ionic strength lower than 0.5 M, the activity coefficients can be calculated by the Davies equation (Sawyer *et al.*, 2003).

The final permeate obtained under the best operational conditions (NF/RO membrane, feed pH and recovery rate) was characterized for its total dissolved solids, conductivity, arsenic, sulfate, chloride, calcium and magnesium concentrations. These results were compared with the average quality of the process water used by the gold mining company and the industrial reuse possibility was discussed.

## Economic Aspects

A preliminary investment and cost estimate of the NF/RO membrane system for treating effluent from gold mining was conducted. The variables considered in this estimate were membrane replacement costs, power consumption costs, system maintenance, chemical products for membrane cleanup, alkalizing agent for pH adjustment, personnel costs and unit depreciation.

The alkalizing agent considered for pH adjustment was NaOH. The volume of NaOH solution used to adjust the effluent pH value was measured and used to estimate the process neutralizing cost. The NaOH price was US\$ 0.43 per kg. NF and UF membrane prices were US\$ 90 and US\$ 135 per square meter, respectively. These prices were based on a preliminary estimate provided by a large commercial membrane supplier. The required membrane area was calculated based on the total flow rate of 280 m<sup>3</sup>/h (effluent flow rate informed by the mining company), permeate flux of 20 L/h.m<sup>2</sup> for NF and 100 L/h.m<sup>2</sup> for UF (obtained in this study). Membrane lifespan was estimated as 3 years (Van der Merwe, 1998), while depreciation time was up to 15 years. Personnel costs included payroll for hiring four technicians/operators and 13 annual salaries plus 70% corresponding to labor costs (payroll taxes

and benefits) (Zancula, 2013). According to the membrane supplier, system maintenance charges correspond to 5% of the initial investment. The cleaning agents cost was US\$ 0.10/m<sup>3</sup> of effluent. Power consumption expenditure estimated by ROSA 9.1 software was 0.27 kWh/m<sup>3</sup> and the electricity tariff employed was US\$ 0.15/kWh (CEMIG, 2014).

## RESULTS AND DISCUSSION

### Evaluation of Different NF and RO Membranes

The membranes used in this study are comprised of a thin selective layer of polyamide. Although the selective layer of all five membranes is formed by the same base polymer, their complete compositions are unknown and they are likely to be very different (Nghiem and Hawkes, 2007). Thus, membrane properties that affect retention capacity and fouling propensity differ from one membrane to another. Although the literature presents several studies evaluating different membranes applied to many industrial effluents (Balannec *et al.*, 2005; Bellona *et al.*, 2012; Chang *et al.*, 2014; Richards *et al.*, 2010), effluent composition and its specific physicochemical properties directly influence treatment performance and the results obtained for a given system cannot be simply replicated to another. Thus, membrane evaluation for each given application is required.

The resistance of clean RO membranes (Table 4) is much higher than that of clean NF membranes, and this is consistent with the more closed polymeric structure of the former (Tu *et al.*, 2011). This makes permeate flux through RO membranes very low, about 7 to 12 times lower than the permeate flux through NF membranes. Fouling resistance shows

the trend for different membranes of undergoing adsorption, pore blocking or solid deposition over the membrane surface in contact with the effluent (Mattaraj *et al.*, 2011). Thus, proneness to fouling may be related to membrane characteristics such as pore size, hydrophobicity, and surface charge. It can be seen that RO membranes, especially TFC-HR membranes, exhibit a prompter interaction with the effluent, and more intense fouling. Conversely, although the MPF34 membrane had one of the lowest fouling, the NF270 membrane had the highest permeate flux, nearly 60% higher than the NF90 and MPF34 membranes.

**Table 4: Membranes performance to treat the effluent from gold mining regarding intrinsic membrane resistance, fouling resistance and final permeate flux.**

Membrane	Intrinsic membrane resistance (x10 <sup>12</sup> /m)	Fouling resistance (x10 <sup>12</sup> /m)	Fouling in relation to membrane resistance	Final permeate flux (L/h.m <sup>2</sup> )
TFC-HR	451.4	93.0	21%	7
BW30	470.8	82.5	18%	7
MPF34	60.8	5.4	9%	59
NF90	64.9	10.4	16%	54
NF270	33.0	11.4	34%	89

Table 5 shows the results of pollutant retention efficiency obtained for the five membranes tested. Initially, the high retention efficiencies of both NF and RO membranes must be highlighted. The high sulfate concentration in the effluent from gold mining is considered to be the major hindrance to water reuse. Sulfate can precipitate with metal cations, causing fouling in equipments and pipes. It can be seen that the permeates obtained for all membranes had a low sulfate concentration (< 200 mg/L).

**Table 5: Results for physico-chemical parameters of the raw effluent and permeates obtained with different membranes and their respective retention efficiencies.**

Membrane /Sample	Conductivity (μS/cm)	Total solids (mg/L)	Arsenic (mg/L)	Sulfate (mg/L)	Chloride (mg/L)
Raw effluent	5,393	4,342	340	1393	48,7
TFC-HR	244 (95%)	114 (97%)	83 (75%)	8 (99%)	11 (78%)
BW30	555 (90%)	460 (89%)	197 (42%)	55 (96%)	2 (97%)
MPF34	2,715 (50%)	864 (80%)	231 (32%)	182 (87%)	18 (63%)
NF90	314 (94%)	126 (97%)	109 (68%)	23 (98%)	8 (84%)
NF270	1,843 (66%)	710 (84%)	212 (38%)	63 (95%)	24 (51%)

Note: Values in brackets are the retention efficiencies

Among the parameters evaluated, the only one for which the efficiency was mediocre was arsenic retention. However, it is important to point out that, even though this element may be very hazardous to human health and the environment, it has no adverse effect on the industrial process. The main objective of this treatment system is to generate industrial reuse water, which can be used in gold processing for applications that do not involve direct contact with the operators. Therefore, because the treated effluent will not be discharged into water bodies, the discharge standard for arsenic does not need to be met. Moreover, arsenic is not associated with problems of corrosion or fouling and may even act as a corrosion inhibitor for zero-valent iron (Triszcz *et al.*, 2009). Thus, obtaining a final permeate with an arsenic content of 230 mg/L is not critical. The continuous reuse of this effluent would lead to an arsenic buildup in the system, and when the steady-state was reached the arsenic concentrations of the raw effluent and treated effluent (reuse water) would be 780 and 530 mg/L, respectively (considering the worst retention efficiency of 32%, removal efficiency independent of feed concentrations, and full replacement of process water with the treated effluent with no new water addition).

The reverse osmosis membrane TFC-HR showed the highest pollutant retention efficiency among the tested membranes. According to Fujioka (Fujioka *et al.*, 2012), TFC-HR is a low pressure RO membrane typically applied for effluent treatment and reuse processes due to its high efficiency. On the other hand, the second RO membrane studied (BW30) showed slightly lower pollutant retention efficiency. These results are consistent with the findings of Balanec *et al.* (2005) who evaluated eight different membranes to treat a simulated dairy plant effluent.

Among the NF membranes, NF90 showed the best results for the parameters evaluated, and was even comparable to those obtained using the TFC-HR membrane. NF90 and RO membranes have very similar characteristics (Krieg *et al.*, 2005), and therefore NF90 may present high conductivity removal efficiency, especially for an effluent in which the major contaminants are divalent ions (sulfate, calcium, magnesium, etc.), such as the one here studied.

According to Wang and Tang (2011), the NF270 membrane has higher water permeability, lower salt retention efficiency, and a surface smoother than the NF90 membrane. Additionally, Nghiem and Hawkes (2007) stated that NF270 membrane pores are larger, which may explain its lower performance. The MPF34 membrane showed the lowest retention capacity for all the parameters analyzed. Although the

molecular weight cutoff of the MPF34 membrane is lower than that of NF270 (Table 2), other parameters such as surface charge and hydrophobicity may affect the ion retention capacity in aqueous solution, and may account for the lower retention efficiency observed. Furthermore, the pore size of NF membranes is affected by the ionic strength of the medium; therefore, the molecular weight cutoffs of the membranes differ in the presence of different solutions (Hong and Elimelech, 1997). By assessing different NF membranes used for sulfate retention in brine, Bargeman *et al.* (2009) also observed lower retention capacity for MPF34 in comparison to NF270.

The membrane area required for an application is inversely proportional to permeate flux, and the cost of NF or RO systems depends on the membrane area required. Therefore, even though RO systems have shown good pollutant retention efficiency, their use proved to be cost-prohibitive for the application studied. Although NF membranes have a slightly higher cost per m<sup>2</sup> than RO membranes (Nghiem, 2005), the membrane area required by RO systems in this application is significantly greater, which makes its cost substantially higher. An alternative to avoid the increase in membrane area would be to operate the system at higher pressure. However, to achieve the same permeate flux of NF membranes keeping the same membrane area, the operating pressure of RO would have to be above 70 bar, which is also not feasible due to excessive power consumption. Furthermore, as can be seen in Table 5, NF90 retention efficiencies were similar to those of RO membranes, besides allowing for a much higher permeate flux. As a result, the NF90 membrane was selected as it showed the highest potential for the studied application.

### Evaluation of pH Adjustment as a Tool for Membrane Fouling Mitigation

Effluent pH adjustment alters its physicochemical properties because it promotes precipitation of metals and salts. Therefore, pH adjustment followed by precipitation can be considered a pretreatment stage, which can be associated with a suspended solids removal process, like ultrafiltration. Pretreatment of the effluent from gold mining by pH adjustment between pH 2.2 (the original pH) and pH 6.0 followed by ultrafiltration was studied and the physicochemical parameters of the raw effluent and the pretreated effluent are shown in Table 6. A pH increment prompts precipitation of ions in solution, reducing the conductivity and also calcium and magnesium concentrations. Arsenic concentration was

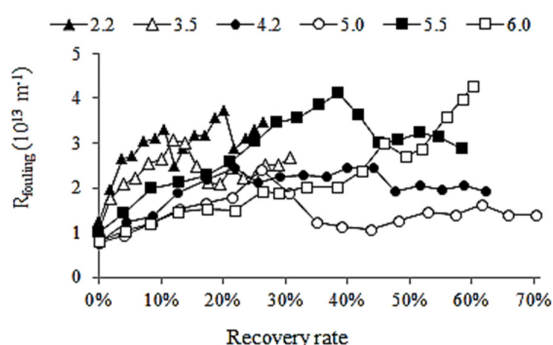
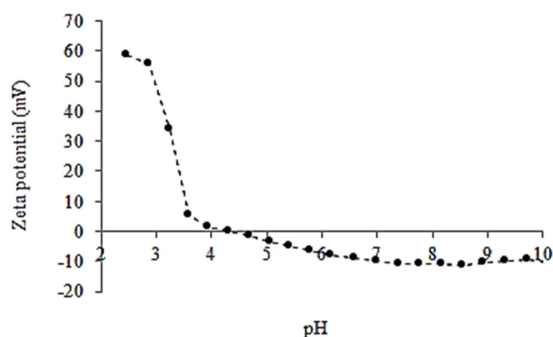


**Table 6: Physicochemical parameters of effluent from gold mining after pre-treatment with pH adjustment.**

Feed pH	Raw effluent	2.2	3.5	4.2	5.0	5.5	6.0
Conductivity ( $\mu\text{S}/\text{cm}$ )	5,821	4,550	3,330	3,260	3,250	3,310	3,300
Arsenic (mg/L)	275	251	247	230	211	204	203
Sulfate (mg/L)	2911	2785	2783	2931	2832	2871	2891
Chloride (mg/L)	70	52	48	64	50	61	56
Calcium (mg/L)	383	198	193	210	196	207	201
Magnesium (mg/L)	104	71	67	83	69	80	75

also gradually reduced as the pH rose. Because arsenic solubility is high (USA, 2007), the decrease of its concentration in solution is due more to coprecipitation with other metal hydroxydes such as iron and aluminum (Jia *et al.*, 2012).

The nanofiltration of the effluent from gold mining with NF90 was performed with the ultrafiltration permeates at different pH values. The filtration was carried out for 4 hours at constant pressure and variable flux; therefore, the maximum recovery rate (RR) obtained for each condition was different. Figure 2 shows fouling resistance as a function of both feed pH and recovery rate.

**Figure 2:** Fouling resistance as a function of feed pH and recovery rate.**Figure 3:** Zeta Potential of NF90 measured with a salt solution with concentrations similar to the effluent from gold mining.

Nanofiltration at the original effluent pH resulted in the highest fouling. Over 4 hours of filtration, an upper limit of just 27% of recovery was achieved. From the membrane zeta potential as a function of pH, it can be seen that, at pH 2.2, the membrane has a high positive surface charge (Figure 3), which leads to the adsorption of sulfate and other anions on the membrane, accelerating fouling and reducing permeate flux.

On the other hand, within the same filtration time, 70% of the feed at pH 5.0 was permeated, with the highest productivity among the evaluated conditions. Despite the high RR achieved, which greatly increases salt concentration in the feed solution, the fouling resistance was only  $8 \times 10^{12} \text{ m}^{-1}$  in the 4-hour filtration process. This feed pH allowed for the lowest fouling resistance, probably because at this pH the membrane has a small negative charge, and therefore repels anions, which prevents fouling formation.

Filtration at pH 4.2 also showed a good performance with fouling resistance of  $1.5 \times 10^{13} \text{ m}^{-1}$  up to a RR of 62%. Nanofiltration at high pH values above 5.0 allowed for a better performance than at low pH values (highest maximum RR achieved); however, the fouling resistances were higher than at pH values between 4.2 and 5.0. In such conditions the membrane has a negative surface charge and may form complexes with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  present in the effluent in high concentrations, which leads to an increase in fouling formation (Childress and Elimelech, 1996). Besides, at higher pHs the solubility of salts is reduced, which can lead to membrane fouling by precipitation. The best results at pH values near the membrane isoelectric point are consistent with the literature (Childress and Elimelech, 2000).

Table 7 presents the NF90 permeate conductivity as a function of feed pH. It is possible to see that pH adjustment did not compromise permeate quality, as the permeate conductivities obtained at feed pHs of 3.5, 5.0, 5.5 and 6.0 are similar to that obtained for the nanofiltration of the effluent without pH adjustment (2.2). The sole exception was observed for a

**Table 7: NF-90 permeate conductivity as a function of feed pH.**

Feed pH	2.2	3.5	4.2	5.0	5.5	6.0
NF-90 permeate conductivity <sup>a</sup>	382 (91.6%)	186 (94.4%)	624 (80.9%)	274 (91.6%)	372 (88.8%)	401 (87.8%)

<sup>a</sup> Values in brackets are the NF retention efficiencies

feed pH of 4.2. It is known that NF membranes may retain pollutants through steric hindrance and electrostatic repulsion. The first is the most important mechanism for neutral molecule retention, and the second for ionic species retention (Childress and Elimelech, 2000; Nguyen *et al.*, 2009). At pH values near the isoelectric point, the membrane surface has a near neutral charge. Under such condition, only steric hindrance will prevent the passage of solute through the membrane, decreasing its retention efficiency, as observed.

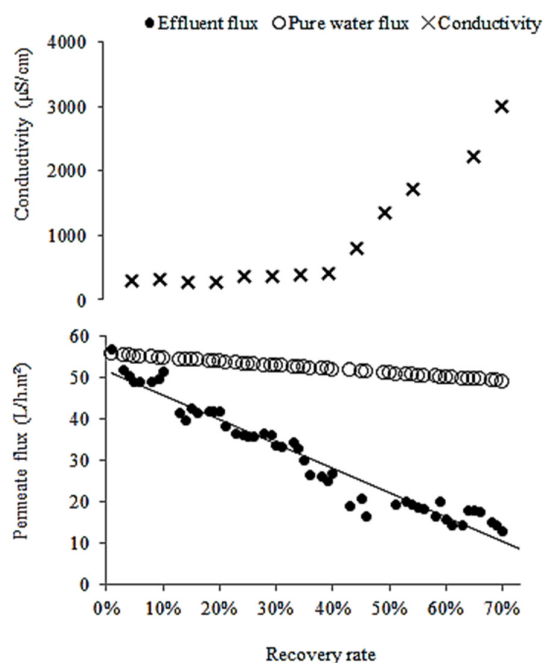
Accordingly, a feed pH equal to 5.0 was selected as the most suited for the application studied since it allowed simultaneously for good permeate quality and the lowest fouling formation. Furthermore, it is worth pointing out that continuous operation at very acidic pH may damage the membrane structure and reduce its lifespan, which is also an advantage produced by the effluent pH adjustment (Manis *et al.*, 2003).

### Permeate Recovery Rate

After membrane and feed pH selection, the permeate recovery rate (RR) was studied. The permeate RR is one of the main design parameters of systems with membranes operating under a pressure gradient (Greenlee *et al.*, 2009). While microfiltration and ultrafiltration usually operate at 90-96% RR, for NF and RO these values are substantially lower (Bi *et al.*, 2014). Since these membranes are much more permeable to water than to solutes, increasing the RR induces an increase in salt concentration and osmotic pressure in the concentrate and membrane fouling formation. Thus, for a constant operating pressure, increasing the RR leads to a reduction in permeate flux. In this study, this decrement occurred in an almost linear manner, that is,  $R^2 = 0.947$  for a linear fit, with a reduction of nearly 0.6 L/h.m<sup>2</sup> for each 1% increase in the RR (Figure 4).

This decay is partly explained by the reduction in the effective pressure for permeation ( $\Delta P - \sigma \Delta \pi$ ). In Figure 4, the pure water flux was calculated considering the membrane permeability constant and equal to that measured at the beginning of the experiment. The pure water flux reduction is thus attributed only

to a decrease of the effective pressure. However, it can be seen that the effluent flux decay rate is more pronounced, which indicates that fouling is also occurring.



**Figure 4:** Permeate flux, theoretical pure water flux at the instant of effective pressure and conductivity as a function of the recovery rate.

Moreover, permeate quality remains almost constant up to a RR of 40%. From this point onwards there is a significant increase in permeate conductivity. The conductivity retention efficiency with 5% of RR was 93.8%; this value slowly decreased to 91.3 when the RR reached 40%. However, for RR above 45%, removal efficiency reached values lower than 83%. Using a synthetic solution of MgSO<sub>4</sub>, Bi *et al.* (2014) found that the degree of concentration polarization on NF membranes increased from ~1 to 1.45, while the RR increased from 20% to 70%, which was found to cause a decrease in the observed efficiency (pollutant concentration in the permeate in relation to pollutant concentration in the feed solution). However, no significant change was observed in its real efficiency, that is, in the permeate pollutant

concentration compared to the concentration on the membrane surface. Additionally, the authors stated that the concentration polarization degree should be kept below 1.2 in actual applications to be technically and economically feasible. According to Luo and Wang (2013), higher salt concentration increased bulk viscosity, which decreased solute back-diffusion away from the membrane, thus inducing more concentration polarization.

Table 8 presents the percentage of permeate flux decrement during filtration due to concentration polarization, reversible fouling formation and irreversible fouling formation. One may notice that, when the NF90 membrane is used for filtration of effluent from gold mining with a RR of 70%, there will be a 77% decrease in permeate flux in comparison to initial water flux through a clean membrane. Of these 77%, 30% are due to concentration polarization, 15% to reversible fouling formation and 32% to irreversible fouling formation. The high percentage attributed to concentration polarization may be associated with the high RR reached (70%), and it may be controlled in milder operational conditions (lower RR). The percentage of flux decrement due to reversible fouling is related to the formation of loose precipitates over the membrane surface, or physical interaction (van der Waals interaction) between effluent components and membrane polymeric structure. Finally, irreversible fouling is caused by sticky precipitates that cannot be easily removed by chemical cleanup. The RR must be kept low in order to: prevent solute supersaturation in the concentrate; reduce the adhesion risk of sticky precipitates that may reduce membrane lifespan; and prevent loose precipitate adhesion, which would require more frequent cleanup procedures (Nanda *et al.*, 2010).

**Table 8: Percentage of permeate flux decrement during filtration due to concentration polarization and reversible and irreversible fouling formation.**

Flux decrement	
Concentration polarization	30%
Reversible fouling formation	15%
Irreversible fouling formation	32%
Total	77%

The supersaturation ratio of  $\text{CaSO}_4$  on the membrane surface ( $\text{SI}_m$ ) for different values of the RR are presented in Table 9. As the RR increases, the salt concentration in the concentrate and the concentration polarization process intensify, consequently increasing the  $\text{SI}_m$ . The  $\text{SI}_m$  increment was higher

when the RR rose from 50 to 60%, when it increased by 15%. Moreover, the  $\text{SI}_m$  was higher than 1 even for feed solution (RR = 0%). However, although precipitation may be expected when  $\text{SI}_m > 1$ , a significantly higher value of the supersaturation ratio must be exceeded in order to result in scaling, due to kinetics and metastability effects (Schäfer *et al.*, 2005). According to Gabelich and co-workers (2011), scaling can be prevented if  $\text{SI}_{\text{CaSO}_4} < 2.3$ , which is the case for the studied effluent at RR up to ~ 60%. It is noteworthy that the SI calculation was based on the diffusivity coefficient of ions in dilute single-component solutions. Because ion mobility in real effluents is smaller, the actual mass transfer coefficient can be lower, and the  $\text{SI}_m$ , greater than the ones calculated.

**Table 9: Supersaturation index of  $\text{CaSO}_4$  on the membrane surface at different RR values.**

RR	0%	10%	20%	30%	40%	50%	60%	70%
$\text{SI}_m$	1.33	1.64	1.73	1.84	1.98	2.03	2.33	2.34

A RR of 40% was recommended for this process because operation at higher RR favors the development of both reversible and irreversible fouling formation. Additionally, it was observed that the permeate flux decrement was almost constant in relation to the RR increase. However, a significant reduction in permeate quality was observed at RR greater than 40%.

It is noteworthy that a higher water recovery may be achieved with multiple NF steps, particularly if intermediate precipitation steps are applied. In this approach, a primary NF/RO step recovers water up to a  $\text{SI}_m$  below the threshold of membrane mineral scaling. Mineral scale precursors are subsequently removed from the concentrate via precipitation and solid-liquid separation techniques. That lowers the concentrate mineral scaling propensity and thereby enables additional water recovery in a secondary NF/RO step (Gabelich *et al.*, 2011; Rahardianto *et al.*, 2007; Rahardianto *et al.*, 2010)

To verify the permeate applicability for industrial reuse, the physical-chemical properties of the treated effluent obtained with the optimal operational conditions (NF90 membrane, at feed pH 5.0 and RR of 40%) were compared with process water quality used in the gold mining company (Table 10). With the exception of arsenic, all parameters showed high retention efficiencies and proved the effectiveness of the proposed treatment. The permeate met water reuse quality, since its pollutants concentration for all monitored parameters were smaller than those of

process water. Arsenic was the sole pollutant to show a higher concentration in the permeate than in process water. However, as already discussed, this metal has no fouling and/or corrosion potential and thus does not qualify as a critical parameter.

**Table 10: Quality parameters for the final treated gold mining effluent and cooling water and treatment retention efficiencies.**

Parameter	Treated effluent	Retention efficiency	Process water
Total dissolved solids (mg/L)	146	97%	1374
Conductivity ( $\mu\text{S}/\text{cm}$ )	398	91%	710
Chloride (mg/L)	15	89%	20
Sulfate (mg/L)	168	94%	304
Calcium (mg/L)	24	94%	104
Magnesium (mg/L)	6	95%	11
Arsenic (mg/L)	116	58%	<2

### Economic Aspects

Although effluent pH adjustment reduces fouling formation and improves membrane retention efficiency, it represents the largest investment percentage of the proposed treatment system. However, pH adjustment is mandatory for mining wastewater reuse, since its original pH is very low. The other major costs observed were membrane replacement and depreciation of the initial unit investment (Table 11). The preliminary cost per  $\text{m}^3$  of the mining effluent treatment was only US\$ 0.83.

**Table 11: Annual Expenditures for treating effluents from gold mining with NF.**

Item	Annual cost (US\$)	Percentage
Membrane replacement	301,538.46	15%
Power consumption	100,561.03	5%
System maintenance	226,153.85	11%
Chemical agents (cleaning)	226,412.31	11%
pH adjustments	776,636.19	38%
Personnel costs	102,000.00	5%
Depreciation of initial investment	295,625.94	15%
Total	2,028,927.77	-
Cost per $\text{m}^3$ of effluent	0.83	-

### CONCLUSION

It may be concluded that:

- In an effluent in which the major contaminants are bivalent ions, such as effluent from gold mining

with high concentrations of sulfate, calcium and magnesium, effluent treatment with NF membranes was more effective than with RO membranes, because they allow permeate fluxes 7 to 12 times higher and compatible retention efficiencies. In this study, NF90 showed the best performance.

- A feed pH of 5.0 provided both greater permeate flux and higher retention efficiencies. Slightly above the membrane isoelectric point (pH 4.3), at pH 5.0 the membrane has a small negative charge and therefore it repels anions, which prevents fouling formation.

▪ Permeate flux decreased linearly as the permeate recovery rate increased. Additionally, there was a significant increase in conductivity for RR above 40%. Consequently, a RR of 40% was selected as the ideal for this process.

- The proposed treatment system, operating in optimal conditions, provided a final treated effluent with high quality at an approximate cost of US\$ 0.83/ $\text{m}^3$ .

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