# Effect of Feed Ph in the Nanofiltration of Gold Acid Mine Drainage

**Alice Aguiar, Laura Andrade, Wadson Pires and Miriam Amaral**
*Department of Sanitary and Environmental Engineering, Universidade Federal de Minas Gerais, Brazil*

## ABSTRACT

Acid mine drainage (AMD) is knowingly one of the greatest problems caused by mining activities, not only for the associated environmental impacts, but also due to the large volumes produced and the related costs, the difficulty of its control once started, and its perpetuity. Due to the large volume associated with AMD, membrane separation processes especially nanofiltration (NF) are of great interest. Typically, NF produces a permeate with high quality, which can then be reused in the process. The present work aims to study the effect of different feed pH in the treatment with NF of a gold acid mine drainage effluent. The membranes studied were NF90, NF270 and MPS-34, which were chosen in a previous work for its high potential for AMD treatment. The results showed that the MPS-34 and NF90 membranes operating at natural AMD pH (3.2) obtained higher permeate fluxes than in other conditions. However, the conductivity retention efficiency of the MPS-34 membrane was very low, below 45% for all conditions. The NF270 membrane presented the highest permeate fluxes. Moreover, the retention of conductivity and sulfate were higher with the NF270 membrane than with the NF90 membrane. The fouling resistance of the NF270 at pH 5.5 was slightly smaller than at pH 4.2, indicating that this might be the most adequate condition for the treatment of gold AMD.

**Keywords:** Gold acid mine drainage; Nanofiltration; Feed pH

## INTRODUCTION

Gold mining and gold ore processing are activities of great economic importance. Gold has been used in various applications, ranging from the manufacture of jewelry to the protective covering of satellites and medicinal use due to its distinguished physicochemical properties, such as high corrosion resistance, high electrical conductivity and high infrared radiation reflectance (Kwon et al., 2011; Savage, 2013).

On the other hand, gold mining and processing leads to many environmental impacts. They may vary from natural habitat destruction and consequent loss of biodiversity to the inappropriate disposal of large amounts of waste on the environment (Getaneh & Alemayehu, 2006). Soil, water and plants in areas near gold mining regions can become contaminated by many heavy metals, such as copper, manganese, aluminum, iron, zinc, nickel, chromium, lead, cobalt, etc (Abdul-Wahab & Marikar, 2012). This contamination is most pronounced when the mined rock contains significant amounts of pyrite and other sulfide minerals. These minerals can be oxidized leading to acid generation and consequent increase of heavy metals leaching (Abdul-Wahab & Marikar, 2012).

Metal sulfides oxidation is responsible for the formation of acid mine drainage (AMD), recognized as one of the greatest environmental impacts of mining (Hilsona & Murck, 2001; Akcil & Koldas, 2006). Several authors mention that AMD results from a complex series of chemical reactions involving direct and indirect mechanisms and microbial action (Costello, 2003; Akcil & Koldas, 2006). AMD environmental impacts include acidification of surface and groundwater, soil acidification, biodiversity loss, solubilization of harmful elements such as heavy metals (which could reach human food chain through bioaccumulation and biomagnification), generation of precipitates in water bodies harming benthic flora, etc (Borma & Soares, 2002; Campaner & Silva, 2009).

Therefore, the application of AMD control measures is essential for preservation of environmental quality. AMD traditional treatment consists of adding lime to neutralize the free acidity, oxidize metals and precipitate them as hydroxides (Costello, 2003; Akcil & Koldas, 2006). These technologies may be sufficient to adjust water characteristics to discharge standards; however they are unlikely to generate water with reuse quality, as salts concentrations in the treated effluent are still high.

Membrane separation processes (MSP) are technologies of great potential for mining effluent treatment, especially if the generation of reuse water is also the aim (Al-Zoubi et al., 2010; Sierra et al., 2013; He et al., 2014). Among the MSP, nanofiltration (NF) importance must be highlighted. Nanofiltration is considered an energy efficient and environment-friendly process. NF offers higher fluxes than reverse osmosis and significantly better retentions than ultrafiltration for small molecules such as sugars, amino acids, peptides and even ions (Luo & Wan, 2013).

Solutes separation by NF membranes occurs by several mechanisms including steric hindrance, Donnan and Dielectric effects (Nguyen et al., 2009). Therefore pore size and surface charge of the membrane pores influence salts and molecules retention. As the commercially available NF membranes are usually hydrophilic and prone to be hydrated and ionized in aqueous solution, the conformation and ionization of the membrane's polymer chains will change under different surrounding conditions, especially at different pH and ionic strength. Due to the nanoscale pore dimensions (~1 nm) and electrically charged materials of the NF membranes, even a minor change in pore size or charge pattern would have a clear impact on membrane permeability and molecules retention (Luo & Wan, 2013). Hence, literature findings reveal that membrane separation performance can be highly dependent on solution pH, which in turn can significantly affect the operational conditions selection for a given type of effluent (Capar et al., 2006).

The effect of pH on NF performance is quite complicated as membrane properties and solutes diversity largely varies with pH, and these variations are dependent on membrane material and solute type. Although the behavior of NF membranes in both, single or multi-element solutions of a known composition has already been extensively studied and modeled (Szoke et al., 2003; Teixeira et al., 2005; Nguyen et al., 2009; Dalwani et al., 2011; Luo & Wan, 2013), the operational performance of these processes to treat actual effluents cannot easily be predicted.

Some authors have evaluated the NF of real effluent or water at different pHs (Qin et al., 2003; Capar et al., 2006; Wang et al., 2007), however retention mechanisms and fouling resistance were not thoroughly discussed. As a result, understanding and then manipulating the effect of feed pH on NF can improve effluent treatment, by enhancing separation performance and reducing membrane fouling.

The aim of this study was to evaluate the treatment of a gold acid mine drainage by nanofiltration. Three different commercial NF membranes were tested at feed pH ranging from 3.2 (natural pH) to 6.0.

## METHODOLOGY

### Acid mine drainage

Acid mine drainage was collected from a gold mining company in the state of Minas Gerais, Brazil which has two underground gold mines and an industrial processing plant. AMD was collected in one of the underground mines, on the fourth level below ground. The AMD characteristics vary over the year, in this study the effluent was characterized by a high conductivity (4,510 $\mu S/cm^2$) and sulfate concentration (2,625 mg/L), and initial pH of 3.2.

### Unit description

A bench scale unit was used during the nanofiltration tests. The system is comprised of: one supply tank (ST); one pump; one valve for pressure adjustment; one rotameter; one manometer; one thermometer and one stainless steel membrane cell. Figure 1 shows a schematic of this unit.

The stainless steel membrane cell has 9.8 cm in diameter, providing a filtration area of 75 $cm^2$. The membranes tested were properly cut before being placed in the cell. A feed spacer was placed over the membrane to promote flow distribution. Permeate flow was measured by collecting the volume of permeate in a measuring cylinder over 60 seconds for nanofiltration tests and 180 seconds for reverse osmosis tests. Permeate was collected for analysis and retentate was returned to the supply tank.

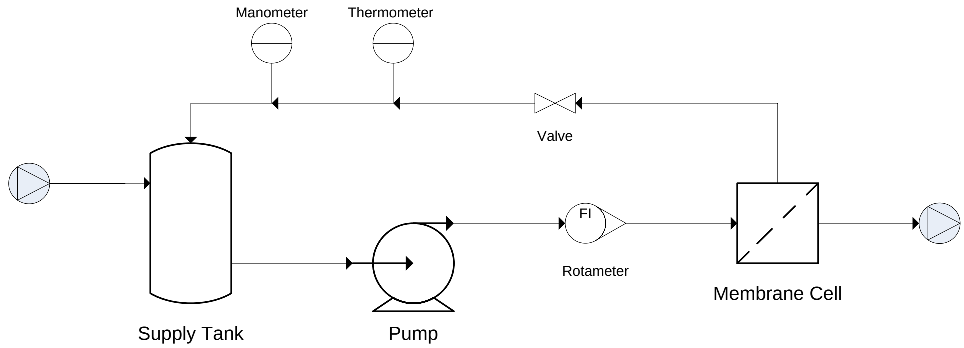


**Figure 1** Schematic of NF unit

**Evaluation of different feed pH values**

A comparative study of three nanofiltration (NF) membranes on the treatment of AMD at feed pH ranging from 3.2 (natural pH) to 6.0 was conducted. The membranes of NF analyzed were NF90, NF270 and MPS-34. Table 1 shows the main characteristics of these membranes as provided by the suppliers, unless otherwise specified.

Process water cannot have acidic pH to prevent possible wear and corrosion of equipment and piping. Thus, for the 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 membranes were tested at different pH values, namely 3.2, 4.2, 5.0, 5.5, and 6.0. Tests with pH above 6.0 were not performed as higher pH values did not enabled better process performance, as will be shown later. A solution 5.0 N of NaOH was used for pH adjustment.

**Table 1** Membranes characteristics as provided by the suppliers

| **Characteristic** | **MPS-34** | **NF90** | **NF270** |
|---|---|---|---|
| Supplier | Koch Membranes | Dow Filmtec | Dow Filmtec |
| Membrane Material | Composite | Composite Polyamide | Composite Polyamide |
| NaCl Retention | 35% [a] | 85-95% [b] | n.a. |
| $MgSO_4$ Retention | n.a. | >97% [c] | 97% [c] |
| Molecular weight cutoff (Da) | 200 [d] | 100 [e] | 200-300 [d] |

n.a. Not available

[a] Feed solution containing 50,000 mg/L of NaCl.

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

[c] Feed solution containing 2,000 mg/L of $MgSO_4$, filtration at 4.8 bar, 25°C, and recovery rate of 15%.

[d] Reference: (Wang & Tang, 2011)

[e] Reference: (Zulaikha et al., 2014)

After pH adjustment, six liters of the AMD was ultrafiltered using a commercial submerged membrane (ZeeWeed) with a filtration area of 0.047 m², PVDF-based polymer and average pore diameter of 0.04 micrometers. UF occurred at a pressure of 0.7 bar up to 4 liters of permeate recovery.

The NF membranes were initially washed in ultrasound bath first with citric acid solution at pH 2.5 followed by 0.1% NaOH solution for 20 minutes each. Water permeability was obtained by monitoring the normalized value of the stabilized permeate flux of clean water at pressures of 10.0; 8.0; 6.0 and 4.0 bar. Normalization to 25°C was accomplished by means of a correction factor calculated by the ratio of water viscosity at 25°C and water viscosity at the temperature of permeation:

$$K = \frac{J}{\Delta P} * \frac{\mu(T)}{\mu(25^{\circ}C)} \quad (1)$$

With the calculated value of water permeability, intrinsic membrane resistance to filtration ($R_m$) was calculated:

$$R_m = \frac{1}{K * \mu(25^{\circ}C)} \quad (2)$$

Nanofiltration was carried out using four liters of pretreated acid mine drainage, during four hours at fixed pressure of 10 bar, feed flow rate of 2.4 LPM and temperatures ranging between 25 and 35°C. Permeate flux, temperature and accumulated permeate volume were measured each 15 minutes. Final permeate was collected for analysis. Retentate was returned to the supply tank. The fouling resistance to filtration ($R_f$) was determined with the values of permeate flux and temperature obtained at the end of the experiment, as demonstrated by the equation:

$$R_f = \frac{\Delta P - \Delta\pi}{\mu(T) * J} - R_m \quad (3)$$

Effluent osmotic pressure (π) for different recovery rates were calculated using the software ROSA 9.1 (The Dow Chemical Company, USA) up to a recovery rate of 65%. The recovery rate is defined as the ratio of the accumulated volume of permeates to the initial volume of effluent. Table 2 shows a summary of the main ions in solution and its respective concentration. These ions concentrations were typical values obtained for the AMD.

**Table 2** Main ions in gold’s acid mine drainage and its concentrations

| **Ions** | **Concentration (mg/L)** |
|---|---|
| Sulfate ($SO_4^{-2}$) | 2,000 |
| Chloride ($Cl^-$) | 10.0 |
| Magnesium ($Mg^{+2}$) | 150 |
| Calcium ($Ca^{+2}$) | 593 |

Feed and permeates were analyzed for conductivity (Hanna conductivity meter HI 9835), total solids and ions concentrations (Metrohm 850 Professional IC, Herisau, Switzerland, equipped with column type Metrosep C4-100/4.0 and Metrosep A Supp 5-150/4.0), in accordance with the Standard Methods for the Examination of Water and Wastewater (APHA 2005).

## RESULTS AND DISCUSSION

### Effluent osmotic pressure

A simulation of the acid mine drainage osmotic pressure calculated using the software ROSA 9.1 (The Dow Chemical Company, USA) for a recovery rate up to 65% is presented on Table 3.

**Table 3** Osmotic pressure of gold's acid mine drainage

| Recovery Rate | Osmotic pressure of retentate (bar) | Recovery Rate | Osmotic pressure of retentate (bar) |
|---|---|---|---|
| 0% | 0.75 | 35% | 1.07 |
| 5% | 0.78 | 40% | 1.15 |
| 10% | 0.82 | 45% | 1.24 |
| 15% | 0.86 | 50% | 1.34 |
| 20% | 0.90 | 55% | 1.46 |
| 25% | 0.95 | 60% | 1.62 |
| 30% | 1.01 | 65% | 1.81 |

As expected, the osmotic pressure of the retentate increases with the increase in the recovery rate, as the concentration of ions in solution increase. The driving force of the nanofiltration is the effective pressure, defined as the operation pressure minus the osmotic pressure. Therefore, an increase in the recovery rate increases the osmotic pressure decreasing the filtration driving force and consequently decreasing the permeate flux.

However, it is important to point out that this software does not provide a full description of the system as it does not have all ions in solution. Hence, small variations in the effluent osmotic pressure are expected.

### Membrane separation

To minimize the influences that variations on initial membrane water permeability could have on the comparison of the effluent permeate fluxes, it is usual to express the ratio of permeate flux to water flux. Figure 2 shows the ratio of permeate flux to water flux as a function permeation time and feed pH for membranes NF90 (Figure 2a), MPS-34 (Figure 2b) and NF270 (Figure 2c).

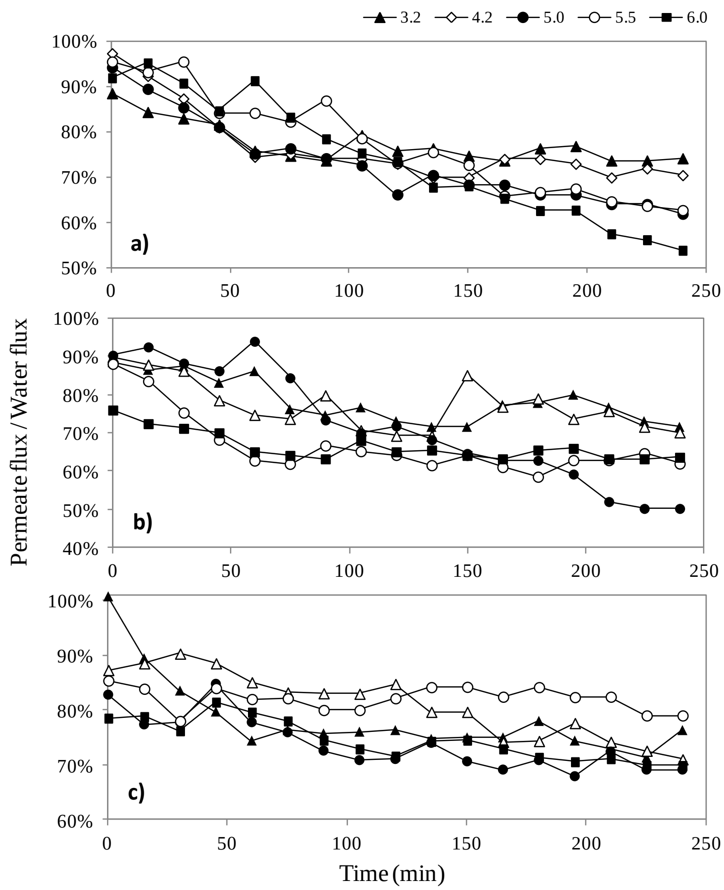


**Figure 2** Ratio of permeate flux to water flux as a function permeation time and feed pH for membranes a) NF90, b) MPS-34 and c) NF270

The NF90 membrane operated best at natural pH (3.2). At this pH the average permeate flux obtained was 52.0 L/h.m² and the average ratio of permeate flux to water flux was 77.4%. However, as can be seen from Figure 2a, there is a considerable decrease in permeate flux at the beginning of the filtration. At the end of the filtration (recovery rate near 40%) the permeate flux was 49.5 L/h.m². At higher pH (6.0) the initial ratio of permeate flux to water flux was very high (91.9%) but it decreased rapidly and at a recovery rate of 40% its value had fallen to 67.9%.

The MPS-34 membrane obtained permeate fluxes similar to the NF90 membrane; and the best feed pH was also 3.2. At this pH the average permeate flux obtained was 51.9 L/h.m² and the average ratio of permeate flux to water flux was 78.3%. Even so, its retention efficiencies were very low, as will be shown later.

Finally, the NF270 membrane presented the highest ratio of permeate flux to water flux of all three membranes. This result is expected as the NF270 membrane has higher water permeability and larger pores than the other membranes (Wang & Tang, 2011; Nghiem & Hawkes, 2007). The NF270 membrane operated better at pH 4.2 and 5.5, as can be seen from Figure 2c the ratio of permeate flux to water flux for these two pH's are consistently higher than the rest. At pH 4.2 the average permeate flux obtained was 68.5 L/h.m², the average ratio of permeate flux to water flux was 81.0% and near the end of the filtration (recovery rate of 40%) the permeate flux was 62.7 L/h.m². At pH 5.5 the average permeate flux obtained was 64.2 L/h.m², the average ratio of permeate flux to water flux was 82.1% and near the end of the filtration (recovery rate of 40%) the permeate flux was 64.4 L/h.m².

Table 4 shows the water permeability, membrane resistance and fouling resistance for the NF270 membrane at feed pH of 4.2 and 5.5 obtained from Equations 1, 2 and 3 respectively. For these two conditions, the values obtained for the water permeability and membrane resistance were very close, which means that the initial conditions of the system were similar. The lower fouling resistance with pH 5.5 indicates that this operational condition might be the most adequate in the treatment of the gold AMD.

**Table 4** Water permeability, membrane resistance and fouling resistance of the NF270 at feed pH of 4.2 and 5.5

| pH | K ($m^3/s.m^2.Pa$) | $R_m$ ($m^{-1}$) | $R_f$ ($m^{-1}$) |
|---|---|---|---|
| 4.2 | $2.56 \times 10^{-11}$ | $4.40 \times 10^{+13}$ | $1.35 \times 10^{+13}$ |
| 5.5 | $2.53 \times 10^{-11}$ | $4.44 \times 10^{+13}$ | $1.20 \times 10^{+13}$ |

The conductivity retention efficiencies obtained for the MPS-34 with all the pH studied were very low (e.g. below 45%). The small permeate fluxes and low retention efficiencies indicate that this membrane is not the most appropriate for this specific application. Table 5 shows the main permeate characteristics for the NF90 membrane at pH 3.2 and NF270 membrane at pH 4.2 and 5.5.

**Table 5** Permeate conductivity, sulfate and calcium concentrations for the NF90 membrane at pH 3.2 and NF270 membrane at pH 4.2 and 5.5

| Membrane | pH | Conductivity (μS/cm²) | Sulfate (mg/L) | Calcium (mg/L) |
|---|---|---|---|---|
| NF90 | 3.2 | 770 | 549 | < 2.5 |
| NF270 | 4.2 | 370 | 258 | < 2.5 |
| NF270 | 5.5 | 405 | 257 | < 2.5 |

It is noted that the retention of conductivity and sulfate were better with the NF270 membrane than with the NF90 membrane. For the NF270 membrane at pH 5.5, the retention efficiencies of conductivity and sulfate were 91.0 and 90.2%, respectively. Calcium retention was high for all three conditions and final concentration was below the method's lowest detection limit.

## CONCLUSION

Average permeate flux for the NF90 and the MPS-34 membranes operating at AMD natural pH (3.2) were very similar, equal 52.0 and 51.9 L/h.m² respectively. However, the permeate flux decrease in the NF90 membrane was considerably higher than the permeate flux decrease in the other membranes. The NF270 membrane showed the highest overall permeate flux and best fluxes were obtained at pH 4.2 and 5.5. At these pHs the average permeate flux were 68.5 and 62.7 L/h.m² respectively for pH 4.2 and 5.5 but permeate flux decline was smaller at pH 5.5 than at pH 4.2. Moreover, fouling resistance was lower at pH 5.5 than at pH 4.2. The retention efficiencies of conductivity and sulfate for the NF270 membrane at pH 5.5 were 91.0 and 90.2%, respectively.

## ACKNOWLEDGEMENTS

The authors would like to thank the Coordination of Improvement of Higher Education Personnel (CAPES) and National Council for Scientific and Technological Development (CNPq) for the postgraduate scholarships provided.

## NOMENCLATURE

| | |
|---|---|
| K | water permeability at 25°C ($m^3/h.m^2.Pa$) |
| μ | permeate viscosity ($N.s/m^2$) |
| J | permeate flux ($m^3/h.m^2$) |
| ΔP | system pressure (Pa) |
| $R_m$ | intrinsic membrane resistance to filtration ($m^{-1}$) |
| $R_f$ | fouling resistance to filtration ($m^{-1}$) |
| ΔP- Δπ | effective pressure (Pa) |

## REFERENCES

Abdul-Wahab, S.A., Marikar, F.A. (2012) The environmental impact of gold mines: pollution by heavy metals. *Central European Journal of Engineering*, v. 2, pp. 304-313.

Akcil, A., Koldas, S. (2006) Acid Mine Drainage (AMD): causes, treatment and case studies. *Journal of Cleaner Production*, v. 14, pp. 1139-1145.

Al-Zoubi, H., Rieger, A., Steinberger, P., Pelz, W., Haseneder, R., & Härtel, G. (2010) Optimization study for treatment of acid mine drainage using membrane technology. *Separation Science and Technology*, v. 45, pp. 2004-2016.

APHA, A. (2005) Standard methods for the examination of water and wastewater, American Public Health Association, Washington, DC.

Burton, F., Leverenz, H., Tsuchihashi, R., Tchobanoglous, G. (2007). Water reuse: issues, technologies, and applications.

Soares, P. S. M., Borma, L. D. S. (2002) Drenagem ácida e gestão de resíduos sólidos de mineração. *Extração de Ouro-Princípios, Tecnologia e Meio Ambiente*. Rio de Janeiro, RJ, pp. 253-276.

Campaner, V.P., Silva, W.L. (2009) Processos físico-químicos em drenagem ácida de mina em mineração de carvão no sul do Brasil. *Química Nova*, v. 32, pp. 146-152.

Capar, G., Yilmaz, L., & Yetis, U. (2006) Reclamation of acid dye bath wastewater: effect of pH on nanofiltration performance. *Journal of membrane science*, v. 281, pp. 560-569.

Costello, C. (2003) Acid mine drainage: innovative treatment technologies. *US Environmental Protection Agency*.

Dalwani, M., Benes, N. E., Bargeman, G., Stamatialis, D., & Wessling, M. (2011) Effect of pH on the performance of polyamide/polyacrylonitrile based thin film composite membranes. *Journal of Membrane Science*, v. 372, pp. 228-238.

Getaneh, W., T. Alemayehu (2006) Metal contamination of the environment by placer and primary gold mining in the Adola region of southern Ethiopia. *Environmental Geology*, v. 50, pp. 339-352.

He, C., Wang, X., Liu, W., Barbot, E., Vidic, R.D (2014) Microfiltration in recycling of Marcellus Shale flowback water: Solids removal and potential fouling of polymeric microfiltration membranes. *Journal of Membrane Science*, v. 462, pp. 88-95.

Hilsona, G., Murck, B. (2001) Progress toward pollution prevention and waste minimization in the North American gold mining industry. *Journal of Cleaner Production*, v. 9, pp. 405-415.

Kwon, Y., Lai, S. C., Rodriguez, P., Koper, M. T. (2011) Electrocatalytic oxidation of alcohols on gold in alkaline media: base or gold catalysis?. *Journal of the American Chemical Society*, v. 133, pp. 6914-6917.

Luo, J., Wan Y. (2013) Effects of pH and salt on nanofiltration—a critical review. *Journal of Membrane Science*, v. 438, pp. 18-28.

Nghiem, L.D., Hawkes, S. (2007) Effects of membrane fouling on the nanofiltration of pharmaceutically active compounds (PhACs): Mechanisms and role of membrane pore size. *Separation and Purification Technology*, v. 57, pp. 176–184.

Nguyen, C. M., Bang, S., Cho, J., Kim, K. W. (2009) Performance and mechanism of arsenic removal from water by a nanofiltration membrane. *Desalination*, v. 245, pp. 82-94.

Qin, J. J., Oo, M. H., Wai, M. N., Wong, F. S. (2003) Effect of feed pH on an integrated membrane process for the reclamation of a combined rinse water from electroless nickel plating. *Journal of membrane science*, v. 217, n. 1, pp. 261-268.

ROSA 9.1 System Design Software, The Dow Chemical Company, USA. Available at http://www.dowwaterandprocess.com/en/resources/rosa_system_design_software. Accessed on: 01/07/2014.

Szoke, S., Patzay, G., Weiser, L. (2003) Characteristics of thin-film nanofiltration membranes at various pH-values. *Desalination*, v. 151, pp. 123–129.

Savage, N. (2013) Mine, all mine! Nature. *Nature*, v. 495(S3).

Sierra, C., J. R. Á. Saiz, et al. (2013) Nanofiltration of Acid Mine Drainage in an Abandoned Mercury Mining Area. *Water, Air, & Soil Pollution*, v. 224, pp. 1-12.

Teixeira, M.R., Rosa, M.J., Nyström, M. (2005) The role of membrane charge on nanofiltration performance. *Journal of Membrane Science*, v. 265, n. 1, pp. 160-166.

Wang, Y.-N. and C. Y. Tang (2011) Protein fouling of nanofiltration, reverse osmosis, and ultrafiltration membranes—the role of hydrodynamic conditions, solution chemistry, and membrane properties. *Journal of Membrane Science*, v. 376, pp. 275-282.

Wang, Z., G. Liu, et al. (2007) Experimental study on treatment of electroplating wastewater by nanofiltration. *Journal of Membrane Science*, v. 305, pp. 185-195.

Zulaikha, S., W. Lau, et al. (2014) Treatment of restaurant wastewater using ultrafiltration and nanofiltration membranes. *Journal of Water Process Engineering*.