Evaluation Of Antibiotics Removal From Wastewater By Nanofiltration

De Souza, D. I.[1], Gıacobbo, A.[1], Rodrıgues, M. A. S.[2], Bernardes, A. M.[1,*]

[1]Programa de Pós-Graduação em Engenharia de Minas, Metalúrgica e de Materiais – PPGE3M, Universidade Federal do Rio Grande do Sul – UFRGS. Av. Bento Gonçalves, n. 9500, Porto Alegre/RS, Brasil. Tel: +555133089428 - Fax: +555133089427

[2]Instituto de Ciências Exatas e Tecnológicas – ICET, Universidade Feevale, Rodovia 239, n. 2755 – Vila Nova, Novo Hamburgo/RS, Brazil. Tel: +555135868800

*corresponding author:

e-mail: amb@ufrgs.br

Abstract Pharmaceuticals constitute a wide group of human and veterinary medicinal compounds largely used worldwide. Antibiotics are one of the most important pharmaceuticals found in the water, being amoxicillin one of the most commercially used due to its high antibacterial activity and large spectrum against a great variety of microorganisms. These chemicals find their way into the water via wastewater from drug manufacturing plants, hospitals, and private households. Thus, it is highly important to employ an adequate treatment for wastewater containing antibiotics. Unfortunately, although their low efficiency in removing antibiotics from wastewaters, conventional biological treatment is still the most often used treatment for this purpose. On the other hand, considering their inherent characteristics, membrane separation processes, as nanofiltration, may be performed for removing the antibiotics presented in wastewaters. At the present work, the performance of nanofiltration in removing antibiotics from wastewaters was assessed. Two nanofiltration membranes, two antibiotics (amoxicillin and norfloxacin) at different concentrations and pH of wastewater were evaluated. The results pointed out that the pH did not influence permeability, and rejections for both antibiotics were always higher than 97% in all experiments showing the viability of nanofiltration for antibiotics' removal and water reuse.

Keywords: **N**anofiltration, Antibiotics Removal, Wastewater.

1. Introduction

With new analytical technologies, pharmaceutical compounds have been found as pollutants in µg - ηg per L in different biotic or abiotic environmental matrices, being the antibiotics an important group of pharmaceuticals and considered as organic contaminants of emerging concern Antibiotics residues have been found in rivers (López-Roldán, 2010), wastewater from drug manufacturing plants (Larsson, 2015), wastewater from hospitals (Rodriguez-Mozaz *et al*, 2015) and domestic sewage (Tuc *et al*, 2016). They can be found either in soil and sediments (Wu *et al*, 2015), as well as in foods (Done; Halsen, 2015).

The European Community Directive 2013/39/EU has treated emerging contaminants as those which are not yet part of routine monitoring programs, but may pose significant regulatory risks related to their potential toxicological or eco-toxicological effects and their levels in the aquatic environment (EU, 2013).

In Brazil, a survey on the occurrence of organic compounds of emerging concern was carried out in 22 states in 2011 and 2012. This study covered different classes of emerging compounds and antibiotics were found in water and in domestic sewage (Machado *et al*, 2016). Homem and Santos (2011) made an extensive survey with data from 2005 to 2011 showing several matrices, from several countries, including Brazil, with antibiotic contaminants. In water-based surface waters, amoxicillin concentrations ranged from 1.0 to 1,640 $ng.L^{-1}$, norfloxacin from 2 to 3,700 $ng.L^{-1}$, erythromycin from 0.5 to 100,000 $ng.L^{-1}$, and sulfamethoxazole from 0.3 to 309,000 $ng.L^{-1}$.

According to the European Centre for Disease Prevention and Control (2014), amoxicillin (AMX) is one of the most consumed antibiotics in the European Union, used alone or combined with clavulanic acid. AMX is a ß-lactam antibiotic from aminopenicillin family.

Another concerning antibiotic is Norfloxacin (NOR). NOR is a fluoroquinolone antibiotic, being one of the most consumed in seven countries of Latin America (Wirtz, 2010). This synthetic compound is not easily biodegradable. It has stability, structural complexity and antimicrobial activity. NOR limits the efficiency of conventional water treatment plants once it reduces or exterminates the microorganisms of biological treatment systems (Li and Zhang, 2010). efficiency of NOR ranged from 5 to 78%, being insufficient.

Although many methods have been investigated for this purpose, there is still a deficit in researches addressed to the removal of antibiotics from water and wastewater.

Membrane separation processes, as reverse osmosis, ultrafiltration and nanofiltration, may be used as wastewater treatments for the removal or concentration of chemical compounds from water and wastewater (Homayoonfal, Mehrnia, 2014). In this sense, the present work was performed aiming to evaluate the performance of two nanofiltration membranes in removing antibiotics.

2. Materials and Methods

2.1. Feed solutions

Binary aqueous solutions with amoxicillin and norfloxacin (99.9% pure) were prepared in order to simulate synthetic wastewaters from pharmaceutics' industries. AMX solutions were made with 250 $mg.L^{-1}$ at pH 2.1, 5.7 and 10.0, and with 50 $mg.L^{-1}$ at pH 5.7. NOR solutions were prepared with 23 and 34 $mg.L^{-1}$ at pH 6.2.

All the feed solutions were made with distilled/deionized water (DDW), totalizing a feed volume of 4 L for each solution, and the pH was adjusted with 1M NaOH or 1M HCl solutions.

2.2. *Membranes characterization*

Permeation experiments were carried out with two flat-sheet nanofiltration membranes, NF 270 and NF 90 (FilmTec; Minneapolis, MN) with average pore radius around 0.42 nm and 0.34 nm (Nghiem *et al* 2004). They are polyamide thin film composite membranes. The thin film (skin) is a mixture of aromatic and aliphatic polyamide with amine and carboxylates end groups. Skin is over a layer of polysulfone on a polyester support layer (Dow, 2004).

The isoelectric point (pHi) of the membranes are 3.5 to NF 270 and 4.0 to NF 90. In pH higther than pHi the membranes present a negative superficial charge and in pH smaller than the pHi there is a positive charge. (Nghiem *et al*, 2005).

Membranes were characterized in terms of their hydraulic permeability (Lpw), as described elsewhere (Giacobbo *et al*., 2013), at transmembrane pressures (ΔP) of 5, 7, 10, 15 and 20 bar, and in terms of rejection coefficients to reference solutes: NaCl, Na_2SO_4 and $CaCl_2$ The permeation of reference solutions for membranes characterization was performed at ΔP of 10 bar, feed solution of 2,000 $mg.L^{-1}$ and at a feed flowrate of 3.3 $L.min^{-1}$.

The solute rejection coefficient (*R*) was defined as:

$$R\ (\%) = \left[\frac{C_f - C_P}{C_f}\right] x\ 100 \qquad \text{Eq. (1)}$$

where C_f, is the average between feed final and initial solution concentration, C_p is the concentration of permeate.

2.3. Nanofiltration permeation experiments

Permeation experiments were carried out in laboratory flat-cell units with a membrane surface area of 14.5 x 10^{-4} m^2, and with a feed flowrate of 3.3 $L.min^{-1}$, thoroughly described elsewhere (Giacobbo *et al*., 2013).

Experiments were performed in total recirculation mode, so that the permeate and the retentate streams were recirculated to the feed tank in order to evaluate the variation of the permeation fluxes (Jp) and of the solute rejection coefficients with ΔP. The stabilization time for each experimental run was 30 min, after which permeate samples were taken for chemical analysis.

After each experiment the membranes were washed with DDW and/or 0.1% NaOH solution at 30 °C, when necessary, until recover the L_{PW} at least 90% of the initial value.

2.4. Analytical methods

Total organic carbon (TOC) was analyzed with a TOC-LCPH carbon analyzer (Shimadzu). pH and conductivity were measured using a Tek PHS-3B pH meter and an AKSO 8306 conductivity meter, respectively. AMX and NOR were analyzed by high performance liquid chromatography-HPLC-UV (Thermo Scientific).

3. Results and Discussion

3.1. Membranes characterization

The NF 270 and NF 90 membranes presented hydraulic permeabilities (Lpw) of 12.88 and 6.86 $kg.h^{-1}.m^{-2}.bar^{-1}$, respectively. In terms of rejection to the reference solutes (R%), the NF 270 membrane reached 52%, 98%, 71% for NaCl, Na_2SO_4 and $CaCl_2$, while the NF 90 presented rejection of 90%, 99% and 97%, respectively. These results are in line with the manufacturer's data.

3.2. Effect of pH and transmembrane pressure (ΔP) in rejection and permeation flux

Figure 1 shows the permeation flux of AMX solutions and rejections in different pH and ΔP. Rejection has been evaluated through the TOC. In all assays, the rejections were similar, always higher than 98%, such that the pH did not influenced significantly the AMX rejection.

Regarding Lps (solution permeability) and Lpw presented by the NF 270, one can verify a drop of 22.3% at pH 2.1, 17% at pH 5.7 and 5.7% at pH 10.0, while in NF 90 there was a drop of 20.3% at pH 2.1, 9.0% at pH 5.7 and 3.2% at pH 10.0. For both membranes, increasing pH results in increasing fluxes, being this result in accordance with the manufacturer data which states at pH above 9 causes the membrane to swell promoting an increase in permeation fluxes.

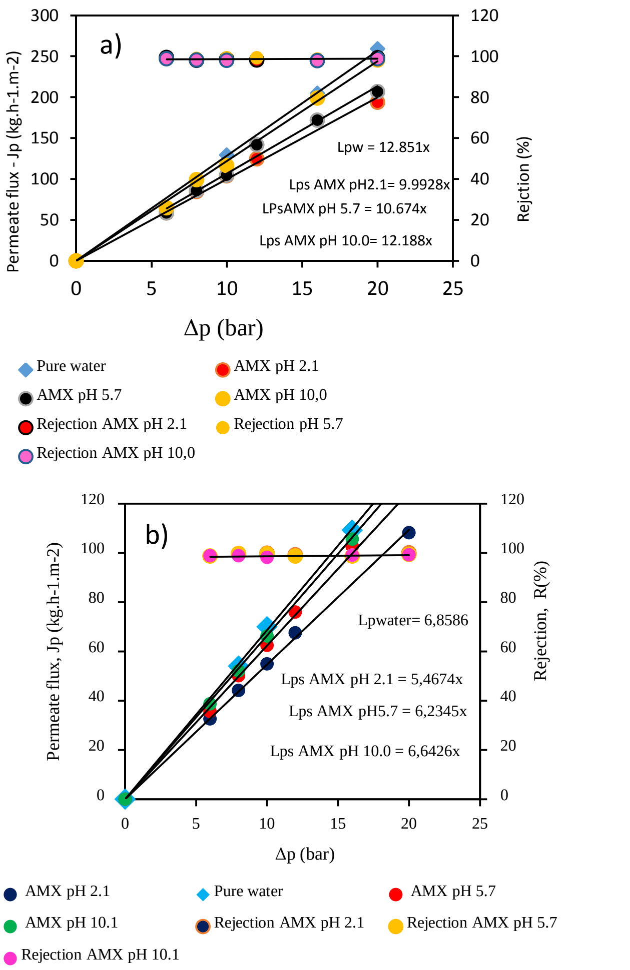

Figure 1. Permeation fluxes and AMX rejection as a function of ΔP at different pHs (2.1-10.0); feed flow rate of 3.3 L.min^{-1}; feed solution: 250 mg.L^{-1} AMX; and temperature: 25 °C. (a) NF 270 membrane and (b) NF 90 membrane.

Separation of ionic species from aqueous solutions across NF membranes is controlled by different mechanisms such as solute adsorption on the membrane surface, molecular size (steric exclusion) of the compound, repulsive forces and others. AMX has three pKa as zwitterion pka1= 2.4, pka2= 7.4, pka3=9.6 and in AMX aqueous solutions with pH lower than 2.4, AMX is a cation, above pH 7.4 is an anion and between 2.4 and 7.4 AMX is a neutral compound (Homayoonfal and Merhnia, 2014). At NF 270 the AMX rejection in terms of TOC was the same (R= 98.7%; 98.8%; 98.8%) for the three evaluated pH, suggesting that the separation was due to AMX molecule size and steric exclusion.

For the NF 90 the AMX rejection in relation to TOC was slightly higher at pH 2.12 (R = 99.6%) because the membrane is in contact with an acid solution, lower than the membrane pHi, which is around 4.0. Thus, the membrane becomes more positive due to the protonation of the amine groups. So, if the membrane is positive and also the AMX, a repulsion of the AMX occurs on membrane surface increasing the rejection. This could increase the concentration polarization near the surface of the membrane, which can explain the flux decrease. As the pH increases to 10, the flux increases and the rejection decrease for both membranes. In accord to orientations of manufacturer, clean nanomembranes with alkaline solutions at pH above 9 causes a membrane swelling and an increase in flux (can be up to 40%) and a reduction in rejection. Acid solutions at a pH below 4 cause the membrane to shrink and there is an increase in rejection and a decrease in flux (Filmtec).

Figure 2 shows results of the experiments with AMX 50 mg.L^{-1} and pH 5.7 for both membranes: (a) NF 270 and (b) NF 90.

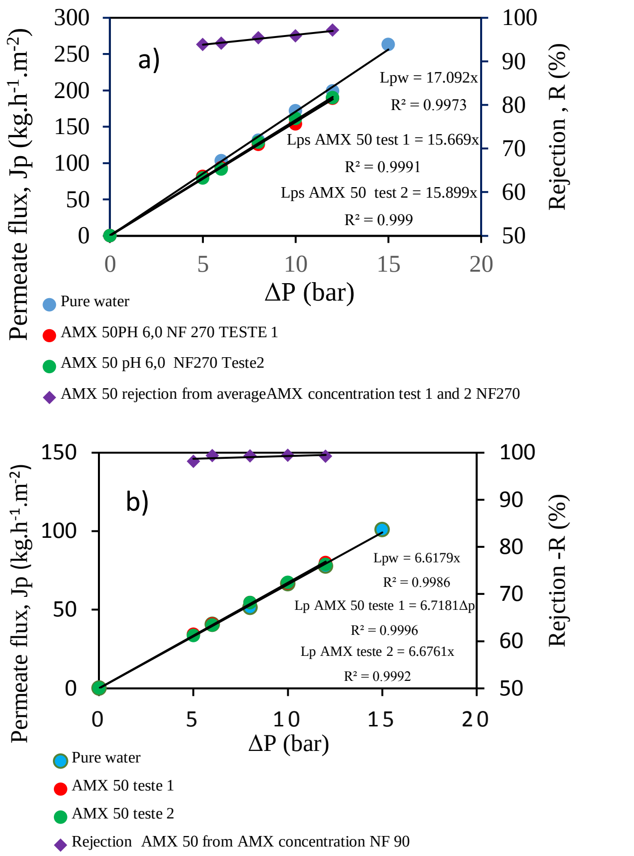

Figure 2. Permeation fluxes and AMX rejection as a function of ΔP at pH 5.7; feed flow rate: 3.3 L.min^{-1}; feed solution: 50 mg.L^{-1} AMX; and temperature: 25 °C. (a) NF 270 membrane and (b) NF 90 membrane.

For both membranes the highest rejections were always at the highest ΔP. Besides, both membranes presented Lps (solution permeability) similar to the Lpw (hydraulic permeability), discarding the hypothesis of occurrence of concentration polarization and fouling on the membrane surface.

In Figure 3 is presented the permeation fluxes and rejections for NOR solutions with 23 and 34 mg.L^{-1} and pH 5.7 for both membranes: (a) NF 270 and (b) NF 90.

With the NF 90 membrane the permeability to the Norfloxacin solutions were closed to the one achieved with water. On the other hand, with NF 270 there was a decrease in permeability, from 17.09 kg.h^{-1}.m^{-2}.bar^{-1} (Lpw) to 11.6 kg.h^{-1}.m^{-2}.bar^{-1} (Lps). This fact can be attributed to the occurrence of concentration polarization and/or reversible fouling on the surface of NF 270 membrane.

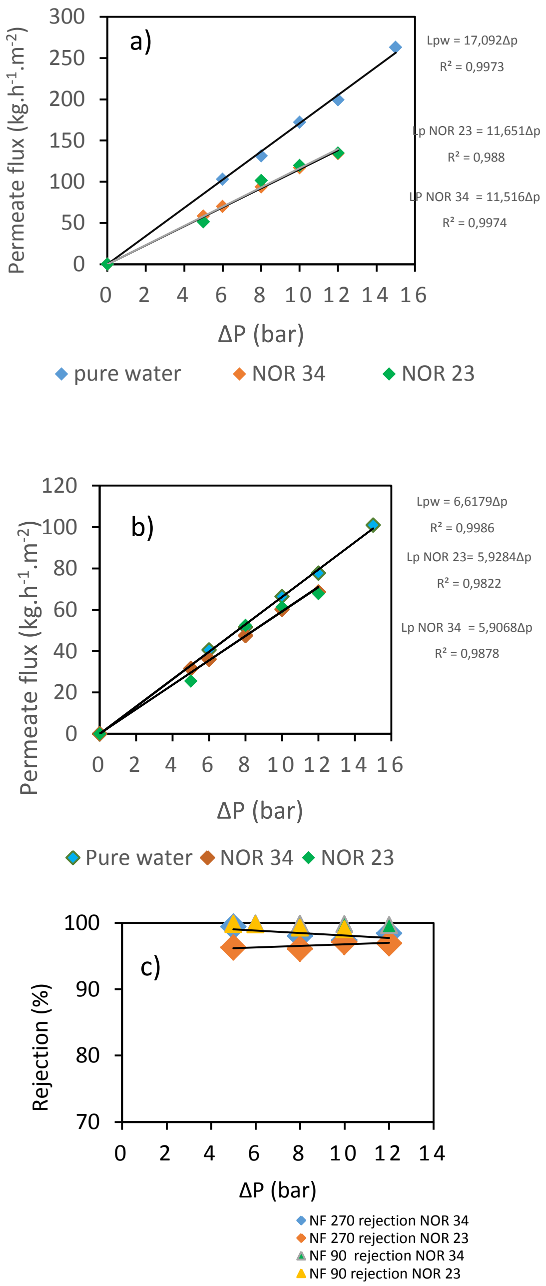

Figure 3. Permeation fluxes and rejection as a function of ΔP at pH 5.7; feed flow rate: 3.3 $L.min^{-1}$; feed solution: 23 and 34 $mg.L^{-1}$ NOR; and temperature: 25 °C. (a) NF 270 membrane, (b) NF 90 membrane and (c) rejection for both membranes.

The rejection was between 96.1 and 97.1% for NF 270 at different pressures, i.e., slightly lower than the ones obtained with NF 90 (above 99% at all pressures). The different concentrations of NOR 23 and 34 $mg.L^{-1}$ did not alter the rejection.

4. Conclusions

pH had no significant influence on amoxicillin rejection, but influenced the permeate flux. Alkaline solutions with pH above 9 cause the membranes to swell and an increase in flux and reduction in rejection. Some solutes can get closer membrane to the membrane and deposit on surface, decreasing flux. Nanofiltration was shown to be viable for separation of antibiotics considering that the rejections were greater than 97%.

Other permeation experiments and studies of interaction and rejection of these and other drugs will be performed.

Acknowledgements

The authors are grateful to the Brazilian funding agencies (FINEP, CNPq, CAPES, FAPERGS and SCIT/RS) for their financial support.

References

Adams, C. *et al* . (2002) Removal of Antibiotics from surface and distilled water in conventional water treatment processes. J. Environ. Eng. 128: 253-260.

Done, H.Y. , Halsen, R.U. (2015) Reconnaissance of 47 antibiotics and associated microbial risks in seafood sold in the United States. Journal of Hazardous Materials. 282: 10–17.

DOW. Filmtec membranes. Basics of RO and NF: Membrane Description. In Tech Manual Excerpt. 2004. http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_0042/0901b80380042dd8.pdf?filepath=liquidseps/pdfs/noreg/609-02004.pdf&fromPage=GetDoc

EU. Directive 2013/39/EU oh The European Parliament and of The Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. http://data.europa.eu/eli/dir/2013/39/oj

European Centre for Disease Prevention and Control. (2014) Surveillance of antimicrobial consumption in Europe 2012. Stockholm: ECDC. http://ecdc.europa.eu/en/publications/publications/antimicrobial-consumption-europe-esac-net-2012.pdf

Filmtec Membranes. Cleaning and Disinfection Procedures for FILMTEC™ NF200 and NF270 Elements. http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_004d/0901b8038004d1e2.pdf?filepath=liquidseps/pdfs/noreg/609- 00388.pdf%26fromPage=GetDoc. Acessed on March 10th, 2017.

Giacobbo, A., *et al.* (2013) Nanofiltration for the recovery of low molecular weight polysaccharides and polyphenols from winery effluents, Sep. Sci. Technol. 48:2524–2530.

Gulkwoka *et al.* (2007) Removal of antibiotics from wastewater by sewage treatment facilities in Hong Kong and Shenzhen, China.

Homayoonfal; Mehrnia. (2014) Amoxicillin separation from pharmaceutical solution by pH sensitive nanofiltration membranes. Separation and Purification Technology. 130: 74–83.

Homem, V.; Santos, L. (2011) Degradation and removal methods of antibiotics from aqueous matrices - A review. J. Environ. Management 92: 2304 – 2347.

Larsson DGJ. (2013) Pollution from drug manufacturing: review and perspectives. Phil. Trans. R. Soc. B. 369: 20130571.

Li, B.; Zhang, T. (2010) Biodegradation and adsorption of antibiotics in the activated sludge process. Environ. Sci. Technol. 44: 3468–3473.

López-Roldán, R., *et al.* (2010) Advanced monitoring of pharmaceuticals and estrogens in the Llobregat River basin (Spain) by liquid chromatography–triple quadrupole-tandem mass spectrometry in combination with ultra performance liquid chromatography–time of flight-mass spectrometry. Chemosphere. 80:1337–1344.

Machado, K.C. *et al.* (2016) A preliminary nationwide survey of the presence of emerging contaminants in drinking and source waters in Brazil. Sci. Total Environ. 572: p.138–146.

Nghim, L.D. *et al.* (2005) Pharmaceutical retention mechanism by nanofiltration membranes. Environ.Sci. Technol.39: 7698-7705.

Pereira, C.D.S. *et al.* (2016) Occurrence of pharmaceuticals and cocaine in a Brazilian coastal zone. Sci Total Environ 548–549, p 148–154.

Rodriguez-Mozaz, S. *et al.* (2015) Occurrence of antibiotics and antibiotic resistance genes in hospital and urban wastewaters and their impact on the receiving river. Water Research, 69: 234-242.

Tuc *et al.* (2017) Fate of antibiotics from hospital and domestic sources in a sewage network. Science of the Total Environment 575: 758–766.

Wirtz, V.J., Dreser, A., Gonzales, R. (2010) Trends in antibiotic utilization in eight Latin American countries, 1997–2007. Rev. Panam. Salud Publica 27: 219–225.

Wu *et al.* (2014) Distribution and risk assessment of quinolone antibiotics in the soils from organic vegetable farms of a subtropical city, Southern China. Sci Total Environ 487: 399–406.)