Removal of Heavy Metal Ions from Aqueous Solutions by Nanofiltration

Petr Mikulášek*, Jiří Cuhorka

Institute of Environmental and Chemical Engineering, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic
petr.mikulasek@upce.cz

This report presents the results of investigations on the removal of toxic Pb(II) ions from aqueous wastewaters by using two commercial thin-film composite polyamide NF membranes. The influence of the operational variables, i.e. the pressure applied, feed solution pH, and feed solution concentration, on the ability of the NF membranes to remove ions was evaluated.

It has been found, for example, that the rejection of lead ions increases with the higher operational pressure, increasing also with higher metal concentration in feed. The solution pH is a parameter which had influenced to a greater extent the separation by the AFC 40 membrane. The maximum rejection of Pb(II) ions achieved above 80 % for AFC 40 and 98 % for AFC 80, respectively, proving that these NF membranes have real potential for efficient removal of metal ions from highly polluted wastewaters The results obtained are discussed in correlation with both the NF membrane properties (pore size and charge) and with the chemistry of the investigated solutions. The role of the steric and electrical interactions in the rejection mechanism of the NF membranes has been finally assessed. The Spiegler-Kedem model describes with high accuracy the experimental rejection data on the concentration range investigated, offering also information about the proper separation mechanism.

1. Introduction

The pollution with heavy metals is a problem of great concern nowadays associated with the industrial production of high amounts of wastewaters containing heavy metals. Heavy metals are extremely dangerous for the human health and for the environment because of their toxicity, non-biodegradability, and tendency to be accumulated in living organisms (Moore and Ramamoorthy, 1985). Therefore, due to the nowadays environmental legislations, the treatment of wastewaters for removal of heavy metals is a task of critical importance (Fane, 1996). The membrane processes are non-polluting separation methods used in wastewater treatment. In pressure driven membrane separation processes such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), a pressure gradient over the membrane enables the solvent (water) to permeate the membrane. Solutes existing in the feed solution are rejected to a certain extent, which depends on the membrane type (Baker, 2004). Among these, nanofiltration is a promising and innovative technology which can be widely applied in drinking water and industrial effluents treatment. NF membranes allow passage of dissolved molecules with molecular weight less than 200-1000 Da and of some salts, rejecting the other ones. Thus, nanofiltration is widely used for water softening applications as monovalent ions are allowed to pass, whereas bivalent ions are rejected to a degree determined by the feed stream. As NF membranes have a less dense structure compared to RO membranes, these configurations require lower operational pressure and energy consumption, also assuring a higher water flux. These membranes have particular separation performance which results from an interplay of size exclusion and charge interactions between the solutes and the membrane material. Thus, the electrical charge and the membrane morphology play a decisive role in the rejection or passage of various ions and the dissolved molecules present in solutions (Schafer et al., 2002).

2. Materials and methods

2.1 Materials

The NF system was operated with a tubular module (model: "MIC-RO 240", PCI Membrane Systems, Poland), equipped with two tubular NF membranes (AFC 80 or AFC 40, respectively). The main characteristics of these membranes are summarized in Table 1.

Table 1: Technical specification of the AFC 80 and AFC 40 membranes

Membranes structural parameters	AFC 80	AFC 40	Data origin
Membrane type	Thin-film composite, tubular configuration		Supplier
Material	Aromatic polyamide skin layer on polysulfone substrate		Supplier
NaCl rejection (%)	80[a]	~60%[b]	[a]Supplier; [b](Deon et al., 2012)
Mean pore radius (nm)	0.262-0.315[c]	0.53[d]	[c](Gherasim et al., 2013); [d](Deon et al., 2007)
Thickness to porosity ratio $\Delta x/A_k$ (µm)	3.450-6.32[c]	17.5-21.6[d]	[c](Gherasim et al., 2013); [d](Deon et al., 2007)
Water permeability L_p at 25 ºC (L m^{-2} h^{-1})	1.45 ± 0.1[c]	7.4± 0.1[e]	[c](Gherasim et al., 2013); [e]this work (experimental)
Isoelectric point (IEP)	3.6[c]	–	[c](Gherasim et al., 2013)

2.2 Experimental set-up

By using a cross-flow separation unit schematically shown in previously published article (Gherasim et al., 2013), the NF experiments were performed at constant temperature of the feed solution of 25 ± 0.5 °C assured by heat exchanger. The pressure was applied in the range of 10-50 bar and 5-45 bar for AFC 80 and AFC 40 membranes, respectively. By measuring the pure water flux, a permeability for the AFC 40 membrane of L_p = 7.4 ± 0.1 L m^{-2} h^{-1} bar at 25°C was evaluated from the slope of the plot of flux vs. applied pressure.

The permeate flux was determined by weighing using an electronic balance connected to a personal computer, with the fluxes recorded automatically by software. By measuring the solute concentrations in feed solution (C_f) and in permeate solution (C_p), the rejections observed were calculated from the rejection data according to the following formula:

$$Rejection\ (\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{1}$$

2.3 Experimental procedures and analytical methods

All the reagents were of analytical reagent grade or the highest purity available, and were used as received. Lead nitrate $Pb(NO_3)_2$ and HNO_3 were supplied by Penta Co., Czech Republic. Thoroughly demineralized water (with conductivity < 1 µS/cm, pH 6.0 ± 0.2) was used for preparation of all the aqueous solutions. Synthetic lead polluted wastewaters were prepared by adding the required amounts of $Pb(NO_3)_2$ into demineralized water. When being dissolved in water, lead nitrate solutions show natural pH about 5.7. The pH value for the lead nitrate solutions was further adjusted by using HNO_3.

The elemental analysis of heavy metals concentration in feed and permeate was carried out with the sequential, radially viewed ICP (Inductively Coupled Plasma) atomic emission spectrometer (model "INTEGRA XL 2"; GBC, Dandenong, Australia); the analytical line used being 220,353 nm. The apparatus was devised with the concentric nebulizer and the glass cyclonic spray chamber (both Glass Expansion, Australia). The nitrate concentration was determined by flow injection analysis (model "FIA compact-MLE", MLE Dresden, Germany). The pH value of solutions was measured with a pH meter (model "HI 9126", Hanna Instruments, USA) in conjunction with the combined glass electrode (HI 1230B, Hanna Instruments, USA) calibrated with a set of commercial buffers.

In order to assure the desired reproducibility of the results, all the experiments were performed in duplicate. The values reported represent an average of two identical experiments; the relative standard deviation being up to ±5 %.

3. Results and discussion

The pH of the aqueous solution is a very important factor in NF, due to the fact that the separation process combines the size exclusion and electrical interaction between the ions in the feed aqueous solution with the charged NF membranes. The pH of aqueous solution influences the membrane charge and also the chemistry itself as the solutions of lead nitrate are stable at pH<6 (Bouranene et al., 2009). The membranes used in the present work have a polyamide top layer, being the so-called amphoteric membranes as the partial hydrolysis of polyamide leads to formation of ammonium ($-NH_4^+$) and carboxyl (-COOH) groups. Thus, below the IEP the carboxyl groups are not dissociated and the amine groups protonated; thus, the overall membrane charge being positive. On the contrary, above the IEP the carboxyl groups are dissociated and the membrane is charged negatively. The IEP of the AFC 80 membrane is at pH 3.6 (see Table 1). Additionally, the adsorption of the differently charged or polarizable solutes from the solution — especially, the divalent ions — may lead to a modification of the membrane charge. Indeed, it has been shown that in the solutions of $Pb(NO_3)_2$, the IEP of the AFC 80 membrane is shifted from pH 3.6 to a higher values of about 5.7 (Gherasim et al., 2013); the same behavior was observed for an AFC 30 membrane with IEP about 5.3 because this membrane is similar to both AFC 80 and AFC 40 (Bouranene et al., 2008). This behavior can be attributed to the adsorption of lead ions on the membrane surface, which can switch the membrane charge from negative to positive in the range of pH 4-6 (Bouranene et al., 2008).

The Figures 1 and 2 show the effect of solution pH on the flux and upon the lead nitrate rejection for both membranes and at different pressures applied. The feed solutions contain 100 mg Pb/L at pH 3 and 5.7 respectively. The condition of the overall electroneutrality allows us to consider the relation $R_{cation}=R_{anion}$; therefore, the lead nitrate rejection is thought to be identical with the lead rejection (determined experimentally).
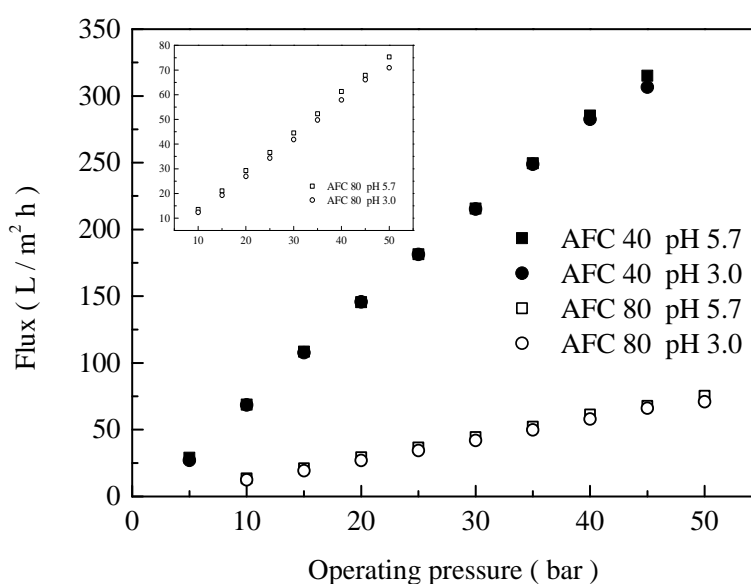

Figure 1: Effect of pH on the flux by AFC 80 and AFC 40 membranes at different operational pressures for feed solutions containing 100 mg Pb/L (t=25°C).

As Figure 1 shows, the membrane flux remains linear while the increasing pressure indicates insignificant concentration polarisation. Also, the flux by AFC 40 membrane is significantly higher than that through the AFC 80 membrane. This is consistent with the data in Table 1, which shows that AFC 80 membrane has smaller pores in comparison with AFC 40 membrane. Thus, it can be expected that steric effects would play a more important role in the rejection behavior of AFC 80 with respect to the electric effects. Also, the situation should be opposite for AFC 40 membrane whose pores are much larger than those of the Stokes radii of lead and nitrate ions which are r_s=0.260 nm and r_s=0.129 nm, respectively (Bouranene et al., 2009). Hence, the

electric interaction should play the major role in the rejection behaviour of this last membrane. Indeed, the insert in Figure 1, containing a magnification of the plots for the AFC 80 membrane, supports these assumptions. Thus, it can be observed that the flux by AFC 80 membrane is decreasing with the decreased pH, while for the AFC 40 membrane the flux is almost identical for both pH values.
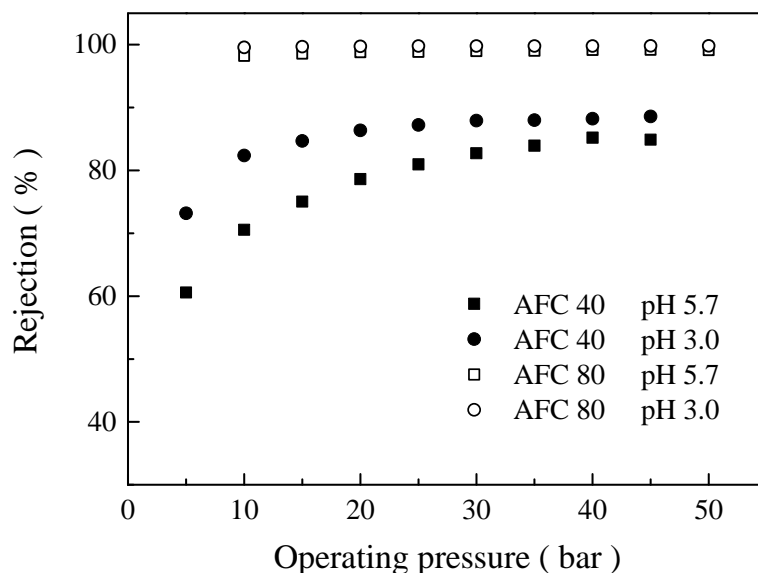

Figure 2: Effect of pH on the lead nitrate rejection from feed solutions containing 100 mg Pb/L at different operational pressures (t=25°C).

A possible explanation for this behavior could be a decrease in the pore size dimension when the membrane is charged by the increased repulsion between the charged functional groups of the membranes (Childress and Elimelech, 2000). Therefore with decreased pH, the positive charge of both membranes increases whereas the pore sizes might decrease, but this influences mainly the flux and rejection behavior of the AFC 80 membranes with very small pores (see Table 1).

The rejection behavior illustrated in Figure 2 shows that lead nitrate rejection by AFC 80 membrane is very high (>98 %) and almost the same for both pH values, while for AFC 40 membrane, the rejection is lower and significantly decreases with the increasing pH. Therefore, these data also confirm that the AFC 80 membrane rejects predominantly the lead ions due to the steric effects determined by the hindered transport of ions in small pores; AFC 40 membranes has larger pores, which allows us to pass the ions more easily, but at pH 3, the higher positively charged membrane rejects the lead ions more effectively than at pH 5.7, thus increasing the lead nitrate rejection with decreased pH.

The Figure 3 shows the effect of the pressure applied and of the lead concentration in feed upon the rejection of the NF membranes investigated.

Data in Figure 3 show that the increase of lead concentration in feed does not significantly influence the retention by AFC 80 membrane which is otherwise very high (>98 %). This is yet another experimental result which supports the hypothesis of a predominant steric rejection mechanism of lead nitrate by AFC 80 membrane. By contrast, for the AFC 40 membrane, the increase of lead concentration in feed increases the lead nitrate rejection in the low pressures domain, decreasing this parameter in the range of high pressures. Additionally, the metal retention significantly increases by enhancing the operational pressure for both solutions' concentrations investigated. These behaviors can be explained by considering an increase in the positive charge of the AFC 40 with higher lead concentration in feed, due to the higher adsorption of lead ions in the AFC 40 membrane. Indeed, it has been shown that the membrane charge can be related with the solute concentration in feed by the Freundlich type isotherm (Bowen and Mukhtar, 1996). Also, when increasing the applied pressure, the metal is repulsed by charge interactions with the membrane, but the water flux through the membrane will further increase in consequence of the higher driving force. This would result in a decrease in the solute concentration in permeate due to the so called "dilution effect" and subsequently lead to an increase in the rejection value with the increase in the pressure applied (Childress and Elimelech, 2000).
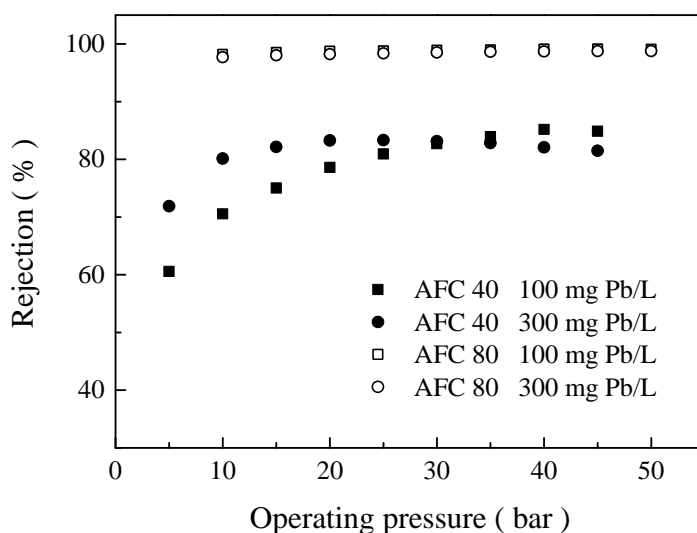
Figure 3: Influence of operating pressure and metal concentration in feed on the rejection of Pb(NO₃)₂ by AFC 40 and AFC 80 membranes (t=25°C, feed solutions at pH 5.7).
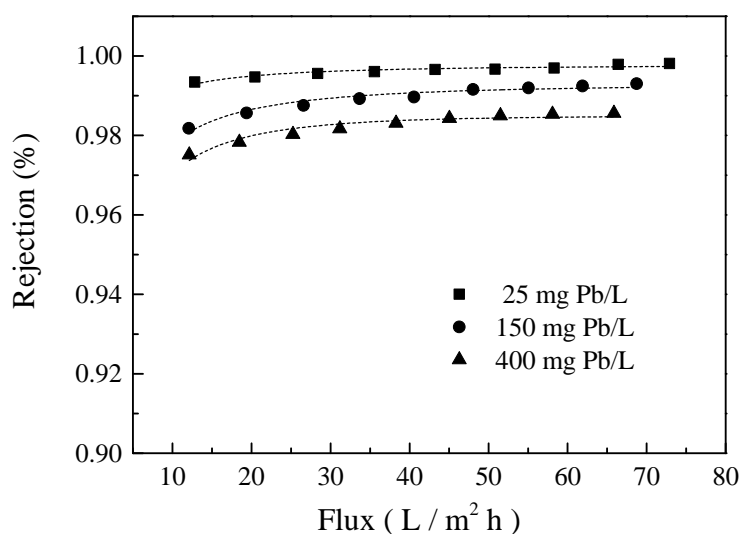

Figure 4: Experimental data (points) and Spiegler-Kedem model predictions (lines) for aqueous solutions with different lead concentrations.

The fitting of the experimental data with the Spiegler-Kedem model (Spiegler and Kedem, 1966) shows that the model agrees well the experimental results. The values of the reflection coefficient are very high, being 0.997, 0.992, and 0.984 for the solutions containing 25, 150, and 400 mg Pb/L, respectively. These values allow us to make some remarks about the transport mechanism in the NF process investigated. Thus, very high reflection coefficients are in accordance with a very high rejection rate of the AFC 80 membrane presented in Figure 4. Additionally, when considering that the solute transport by diffusion is negligible at very high fluxes, the reflection coefficient is a measure of the degree for the convective transport of the solute (Schaep et al., 1998). Therefore, the values of the reflection coefficients — being close to unity obtained herein — indicate that the convective transport is totally blocked and the resultant steric hindrance effect is principal in the separation of lead ions by the AFC 80 membrane. This means that the solutes dimension is very close to that of the pore dimension, which is in good agreement with the previous data: the pore radius being 0.264 nm and the Stokes radius of lead ion 0.260 nm (Bouranene et al., 2009). Thus, the metal

retention determines the retention of salt solution, and the separation can be attributed to the predominant steric-hindrance effect; the membrane charge effect being negligible in the separation processes investigated. This finding corresponds well to our previous study, showing that the AFC 80 membrane is uncharged around pH 5.7 in lead nitrate solutions (Gherasim et al., 2013). Finally, the reflection coefficients are slightly decreasing as the feed solution concentration increases, thus predicting a decrease in the rejection with the increase in the feed concentration. The same behavior has also been observed experimentally (see Figure 4). Therefore, the Spiegler-Kedem model can be used to predict and, at the same, to explain the removal of Pb(II) ions from aqueous solutions by the NF membrane investigated.

4. Conclusions

In this study, the removal of polluting and toxic Pb(II) ions under different operational conditions was investigated by using two polyamide NF membranes. It has been found that the rejection of lead ions increases with the increased pressure, as well as with the increased metal concentration in feed. The solution pH is a parameter influencing into a greater extent the separation by the AFC 40 membrane. The maximum rejection of Pb(II) ions is reaches above 80 % for AFC 40 and 98 % for AFC 80, respectively, proving that these NF membranes have a real potential some promise for efficient removal of polluting and highly toxic lead ions from wastewaters. The results obtained were discussed in correlation with both the NF membrane properties (pore size and charge) and the chemistry of the solutions investigated. The role of the steric and electric interactions in the rejection mechanism of the NF membranes was confirmed.

The processes are characterized with high accuracy by the Spiegler-Kedem model, and the membrane transport parameters determined from the fitting of the experimental data with the model describe very well the NF processes for a wider range of the concentration. Finally, as found out, the transport mechanism of the solute is mainly convective in nature, being almost totally hindered by the size of the metal ions, which finally determines the salts' retention. Thus, the Spiegler-Kedem model can be used to interpret and predict the removal of lead by NF from single nitrate solutions.

References

Baker R.W., 2004, Membrane Technology and Applications, Wiley, Chichester, United Kingdom.

Bouranene S., Fievet P., Szymczyk A., El-Hadi Samer M., Vodonne A., 2008, Influence of operating conditions on the rejection of cobalt and lead ions in aqueous solutions by a nanofiltration polyamide membrane, J. Membr. Sci. 325, 150–157.

Bouranene S., Fievet P., Szymczyk A., 2009, Investigating nanofiltration of multiionic solutions using the steric, electric and dielectric exclusion model, Chem. Eng. Sci. 64(17), 3789-3798.

Bowen W.R., Mukhtar H., 1996, Characterisation and prediction of separation performance of nanofiltration membranes, J. Membr. Sci. 112(2), 263-274.

Childress A., Elimelech M., 2000, Relating nanofiltration membrane performance to membrane charge (electrokinetic) characteristics, Environ. Sci. Technol. 24, 3710-3716.

Deon S., Dutournie P., Bourseau P., 2007, Modelling nanofiltration with Nernst-Planck approach and polarization layer, AIChE J. 53, 1952-1969.

Deon S., Escoda A., Fievet P., Dutournie P., Bourseau P., 2012, How to use a multi-ionic transport model to fully predict rejection of mineral salts by nanofiltration membranes, Chem. Eng. J. 189-190, 24-31.

Fane A.G., 1996, Membranes for water production and wastewater reuse, Desalination 106, 1-9.

Gherasim C.V., Cuhorka J., Mikulášek P., 2013, Analysis of lead(II) retention from single salt and binary aqueous solutions by a polyamide nanofiltration membrane: Experimental results and modelling, J. Membr. Sci. 436, 132-144.

Moore M., Ramamoorthy S., 1985, Heavy Metals in Natural Waters, Springer-Verlag, New York, USA, 112-119.

Schaep J., van der Bruggen B., Vandecasteele C., Wilms D., 1998, Influence of ion size and charge in nanofiltration, Sep. Purif. Technol. 14, 155-162.

Schafer A.I., Fane A.G., Waite T.D. (Eds), 2002, Nanofiltration-Principles and Applications, Elsevier, Oxford, United Kingdom.

Spiegler K., Kedem O., 1966, Thermodynamics of hyperfiltration (reverse osmosis): criteria for efficient membranes, Desalination 1, 311-326.