Separation of Lead (Pb^{2+}) and Cadmium (Cd^{2+}) from Single and Binary Salt Aqueous Solutions Using Nanofiltration Membranes

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ABSTRACT

The present work reports on the performance of three types of nanofiltration membranes in the removal of highly polluting and toxic lead (Pb^{2+}) and cadmium (Cd^{2+}) from single and binary salt aqueous solutions simulating real wastewaters. The effect of the operating variables (pH (5.5-6.5), types of NF membrane and initial ions concentration (10-250 ppm)) on the separation process and water flux was investigated. It was observed that the rejection efficiency increased with increasing pH of solution and decreasing the initial metal ions concentrations. While the flux decreased with increasing pH of solution and increasing initial metal ions concentrations. The maximum rejection of lead and cadmium ions in single salt solution was 99%, 97.5 % and 98 % at pH 6, 6.5 and 6.2 and 78%, 49.2% and 44% at pH 6.5, 6.2 and 6.5 for NF1, NF2 and NF3 respectively. On the other hand, maximum permeate flux for single NF2 (32.2)> NF3 (16.1)>NF1 (14.2) ($l/m^2.h$) for 100 ppm, higher than binary salt solution was NF2 (23.7) > NF3 (13) > NF1 (8) ($l/m^2.h$) for (10 Pb^{2+}/50 Cd^{2+}) ppm. The NF membranes proved able to achieve high separation efficiency of both lead and cadmium ions in very suitable conditions, leaving wastewaters in a condition suitable prior discharged into the environment.

Keywords: Hollow fiber membrane; Nanofiltration; Wastewater; Heavy metals

فصل ايونات الرصاص والكادميوم من المحاليل الملحية المفردة والثنائية باستخدام الاغشية النانوية

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الخلاصة

تقدم الدراسة الحالية إداء ثلاث انواع من الاغشية النانوية في ازالة ايونات الرصاص والكادميوم العالية التلوث والسمية من المحاليل الملحية المفردة والثنائية المماثلة لمياه الفضلات الحقيقية. تحديد تاثير المتغيرات التشغيلية (6.5 -5.5, pH) نوع الغشاء النانوي وتركيز الايون الابتدائي (10-250) جزء بالمليون) على عملية الفصل وتدفق الماء. لاحظ زيادة الرفض مع زيادة pH المحلول ونقصان التركيز الابتدائي للايون. بينما يتناقص الجريان مع زيادة pH وزيادة التركيز الابتدائي للايون. اعلى رفض للرصاص والكادميوم في المحلول المنفرد كان 99%, 97.5, 98 عند pH 6.2, 6.5, 6 و78%, 49.2, 44 عند pH 6.5, 6.2, 6.5 للاغشية NF1, NF2,NF3 على التوالي. من جهة اخرى, اعلى جريان راشح للمحلول المنفرد كان NF2 (32.2)> NF3 (16.1)>NF1 (14.2) ($l/m^2.h$) عند تركيز ابتدائي

100(جزء بالمليون), اعلى من المحاليل الثنائية NF2 (23.7) > NF3 (13) > NF1 (8) (l/m^2.h) لتركيز ابتدائي
(10 Pb^{2+}/ 50 Cd^{2+}) (جزء بالمليون). الاغشية النانوية اثبتت قابليتها لتحقيق اعلى كفاءة فصل لايوني الرصاص
والكادميوم في ظروف مستقرة جدا, لطرح مياه الفضلات بشكل مناسب الى البيئة.

1. INTRODUCTION

During the last years, attention has been concentrate on the removal heavy metal ions from the wastewater due to its toxicity and thus its impact on human health. Therefore, according to the environmental regulations it is important to remove all of the heavy metals from the wastewater of various industries so that the wastewater requires total control prior discharge to the environment, **Al-Rashdi et al., 2011**.Various traditional processes have been used to remove heavy metals from effluents such as sorptive flotation, **Muhaisn, 2014**. Phytoremediation processes, **Ziarati, and Alaedini, 2014**, **Paz-Ferreiro et al., 2014**. Electrochemical process, **Moosavi, et al., 2014**, adsorption, ion exchange and electrocoagulation, most of these processes suffer from economic limitations and other disadvantages. For example, in adsorption process most of adsorbents do not have adsorption capacities, need long adsorption contact times, slow adsorption kinetics, low of selectivity and still most of adsorbents especially nanoparticles are expensive. Also, solvent extraction and chemical precipitation have considered as polluting processes themselves, **Moore, and Ramamoorthy, 1985, Sarvi, et al., 2014**. The membrane separation processes were found to be efficient, economic, and green (non-polluting) separation processes compare with those traditional and polluting methods mentioned above and gained wide salability in treatment of various industrial wastewaters. There are several membrane separation processes were used for the removal of heavy metals from wastewaters such as Microfiltration (MF), Ultrafiltration (UF), Reverse osmosis (RO) and Nanofiltration (NF), **Kozlowski, and Walkowiak, 2005, Soares, et al., 2005, Ortega, et al., 2008, Evina, et al., 2011**. Nanofiltration membranes (NF) has been used mainly in various industries for removal of heavy metals compare with UF and RO processes due to the high removal efficiency and works under moderate pressure, **Peeters, 1998, Evina, et al., 2011**. Despite the efficient of the use of NF membrane for removal of heavy metals, but the researchers have found that there are several factors affected the performance of NF membranes such as pH, metal ions, type of membrane and metal concentration, **Perkin-Elmer, 1996, Tanninen, et al., 2006**. From the literature it was found that the preparation of hollow fiber NF membranes for heavy metal removal is still rare and few studies have been reported on high concentrated multicomponent solutions using NF membranes. Therefore, in this work effective removals of two heavy metals such as Cd^{2+} and Pb^{2+} from simulated aqueous solutions were investigated using three different NF membranes prepared for this purpose. These two heavy metals are selected due to its severe side effects to human health. The effect of the operating conditions such as pressure, initial feed concentration and pH solution on membrane separation performance and water flux were studied.

2. EXPERIMENTAL WORK

2.1 Materials and Method

Simulated wastewater was prepared by adding the cadmium nitrate $Cd(NO_3)_2.4H_2O$ and lead nitrate $Pb(NO_3)_2$ to the distilled water. Stock solutions

(1000 ppm) of Cd^{2+} and Pb^{2+} were prepared by dissolving the appropriate weight of cadmium nitrate and lead nitrate in distilled water and kept in polyethylene container at room temperature. The desired concentrations were prepared by diluting the stock solution in accurate proportions to different initial concentrations. Several solutions were prepared with different concentrations of (10 - 250 ppm) and pH values of (5- 7). Three different types of polyethersulfone (PES) NF membranes (PES type Radel, was provided by Solvay Advanced Polymers (Belgium)) prepared by using dry/wet phase inversion method coded as NF1, NF2, and NF3 for the purpose of heavy metals removal. The surface morphology and all the specifications of NF membranes are summarized in Table 1. The pH value was measured using a calibrated pH meter (HQ411d, pH /mv, HACH Company) whereas concentrations of metal ion in simulated and treated solutions were examined using (AAS-6200) Atomic absorption flam emission spectrophotometer (Shimadzu company, Japan). The instrument was calibrated regularly and calibration curve was verified before each sample set. The surface charge of the membrane surface depends on the value of the pH, negative charge for solution pH value higher than 5 and positive membrane surface charge when pH value of the solution is less than 4, **Tanninen, et al., 2004, Al-Rashdi et al., 2011.**

2.2 Membrane Filtration Experiments

The permeate flux of distilled water and heavy metals solutions as well as rejection of heavy metals experiments using NF1, NF2, and NF3 hollow fibers were achieved by module cross-flow pattern filtration as shown in **Fig. 1**. NF membranes experiments were carried out at a transmembrane pressure of 1 bar, solution temperature of 25 ± 3 ˚C , different initial metals concentration (10 -250 ppm) and pH (5 -7). Permeate flux (*J*) and heavy metals rejection (R %) was obtained from the following Eq. (1), **Xu, 2002,** and (2), respectively:

$$J = \frac{V}{A \times t} \qquad (1) \qquad \text{and} \qquad R(\%) = \left[1 - \frac{Cp}{Cf}\right] \times 100 \qquad (2)$$

where V is the volume of the permeate (l), t is the collected permeate time (h), A is the membrane surface area (m^2), C_f and C_p are the heavy metal concentrations in bulk feed and permeate solution, respectively. After each set of experiments, for a given feed concentration, the setup is rinsed with distilled water for 60 min at 4 bars to clean the NF membrane experimental system, followed by measurement of pure water permeation flux with distilled water to ensure that the initial membrane flux is restored. Moreover, pH value was adjusted using 1 M NaOH or 1 M HCl.

3. RESULTS and DISCUSSION

Permeability of NF Membrane

Pure water permeability (PWP) measurements as a function of (TMP) for three types nanofiltration membranes were carred out by using Eq. (1) as shown in **Fig. 2**. It can be seen that PWP increased linearly when (TMP) increased from 1 to 4 bar, which may be explained that the performance of the membrane was not significantly affected by the fouling. The membrane pearmeability were found to be 37.9 > 16.6 > 16.4 ($l/m^2.h.bar$), at 1 bar transmembrane pressure for NF2, NF3 and NF1, respectively. The reason of this behavior is due to that of the porosity of NF2 is higher than the others as the following squence:

NF2 67.6 > NF3 58.1 > NF1 52.5 %

PWP considered to be a reference to the fouling of the membrane, concentration polarization and to evaluate cleaning procedure.

3.2 Lead and Cadmium Ions Removal from Single Salt Solutions

3.2.1 Effect of feed pH on NF membranes performance

At the beginning of the work, carried out all the experiments at pH values of (1.5- 11) to determine the effect of pH on the permeate flux and rejection of heavy metal ions, Where noticed that at acidic pH lower 5.5 not happened any rejection for metal ions therefore, the results not dependent. on the other hand, the rejection of heavy metal ions at alkaline pH (7-11) nearly 100 percent and appeared white sediments , this mean the rejection of heavy metal ions because of deposition and not NF membranes, therefore, the results not dependent. Therefore, the effect of pH values on permeates flux and rejection was studied at pH (5.5-6.5).

Fig. 3 to 5 show the effect of the pH feed solution on the permeate flux of the three types of NF membranes for 100 ppm initial Pb^{2+} and Cd^{2+} concentrations at different times, generally, it can be noticed that the permeate flux of all solutions decreases with increase of feed pH from 5.5 to 6.5. Using NF1, permeate flux decreased from 14.2 to 11.7 ($l/m^2.h$) and 10.5 to 9.8 ($l/m^2.h$) with increase of feed pH from 5.5 to 6.5 for Pb^{2+} and Cd^{2+}, respectively.

Using NF2, it can be seen that the same behavior is observed as in NF1, permeate flux decreased from 32.3 to 29 ($l/m^2.h$) and 28.4 to 27.3 ($l/m^2.h$). While for the third type membrane NF3, permeate flux decreased from 16.1 to 14 ($l/m^2.h$) and 14.9 to 12.8 ($l/m^2.h$) with increase of feed pH from 5.5 to 6.5 for Pb^{2+} and Cd^{2+}, respectively.

This phenomenon is mainly attributed to the charge of the membrane surface, with increasing pH from 5.5 to 6.5 the charge of the membrane becomes more negatively due to the increase of OH^-, therefore, adsorption of heavy metal ions occurs at the surface of the hollow fiber membrane because of the electrostatic attraction, which in turn lead to decrease pore size of membrane thus, decrease the permeation flux. The explanation is due to shrinkage of the membrane layer as a result of differences in the hydration of membrane ionized groups, **Ballet, et al., 2004**.In addition, **Wang, et al., 2007;** explain the change due to concentration polarization and membrane fouling**.** Similar behavior was found in the literature, **Tanninen, et al., 2004.**

Fig. 6 to 8 present the effects of pH feed solution on the rejection of the three types of NF membranes for 100 ppm initial concentration of Pb^{2+} and Cd^{2+} at different times. Using NF1, rejection of Pb^{2+} increases from 63.5 to 83.4% with increased pH from 5.5 to 6 while the rejection of Pb^{2+}decreased significantly to 65.5 % at pH value 6.5. Regarding the rejection of Cd^{2+} , it can be seen that the rejection increases from 22 to 68% with an incease of pH value from 5.5 to 6.5. The same behavior of NF2 membrane is observed as in NF1, the rejection of Pb^{2+} increases from 61.4 to 66.5 % with increase pH from 5.5 to 6.5. The rejection of Cd^{2+} increases from 18 to 45% with increase pH from 5.5 to 6.2 while the rejection of Cd^{2+} decreased significantly to 33% at pH value 6.5. Moreover, using NF3 membrane, rejection of Pb^{2+} increased from 36.6 to 67.6% with increase pH from 5.5 to 6.2 while the rejection of Pb^{2+} decreased significantly to 63 % at pH value 6.5. Regarding the rejection of Cd^{2+} increased from 11 to 32% with increase pH from 5.5 to 6.5. From the results mentioned above it can be said that the heavy metals rejection increases with increase of pH value mainly due to increase the negative charge on the membrane surface and then result to increase the attraction between the lead and cadmium ions and the membrane surface, which leads to enhance the membrane separation performance . Similar behavior was found in the literature, **, Tanninen, et al., 2004, Al-Rashdi et al., 2011.**

3.2.2 Effect of initial metal concentration on NF performance

Fig. 9 to 11 show the effect of the initial concentration of Pb^{2+} and Cd^{2+} on the permeate flux for the three types of NF membranes at the best initial pH value obtained from the study of the effect of pH at different times. Using NF1, it can be observed that the permeate flux significantly decreased from 13 to 10.3 ($l/m^2.h$) and 10 to 9.3 ($l/m^2.h$) with increase initial Pb^{2+} and Cd^{2+} concentration from (10-250 ppm), respectively. Using NF2, noticed decrease permeate flux with increase initial metal ions concentration where permeate flux decreased from 32.3 to 28.6 ($l/m^2.h$) and 28.8 to 20.8 ($l/m^2.h$) with increase initial Pb^{2+} and Cd^{2+} concentration from (10- 250 ppm), respectively. While permeate flux for NF3 decreased from 16 to 14.3 ($l/m^2.h$) and 13.9 to 12.4 ($l/m^2.h$) for Pb^{2+} and Cd^{2+} solution, respectively, with increased initial ions concentration from (10-250 ppm).

This decline in permeate flux may be due to the increase of deposition of the metals on the membrane surface with increase of initial metal ions concentration, which leads to clogged pores of the membrane and decrease the pore size and also the exit portion of the solutes with permeate water, leading to a decrease permeate flux. Also from the results above it is worthy to mention here that the Cd^{2+} were more fouled on the membrane surface compared with Pb^{2+}, where permeate flux of NF2 (32.3)> NF3 (16) > NF1(13) ($l/m^2.h$) for Pb^{2+}, NF2 (28.8) > NF3 (13.9) > NF1 (10) ($l/m^2.h$) for Cd^{2+} at initial ions concentrations 10 ppm, while permeate flux of NF2 (28.6) > NF3 (14.3) > NF1 (10.3) ($l/m^2.h$) for Pb^{2+}, NF2 (20.8) > NF3 (12.4) > NF1 (9.3) ($l/m^2.h$) for Cd^{2+} at initial ions concentrations 250 ppm. The same behavior was noticed by **Al-Rashdi, et al., 2013.**

The effect of initial metal ions concentrations on rejection of the three different NF membranes are depicted in **Fig. 12 to 14**. Using NF1 membrane, the rejection was decreased from 99 to 43% and 78 to 41.6% with increased initial ions concentration from (10-250 ppm) for Pb^{2+} and Cd^{2+}, respectively. While the rejection by using NF2 was decreased from 97.5 to 43% and 50.2 to 26% with increased initial ions concentration from (10- 250 ppm) for Pb^{2+} and Cd^{2+}, respectively, and also the rejection by using NF3 was decreased from 98 to 49% and 44 to 25% for Pb^{2+} and Cd^{2+}, respectively. Rejection decreases with increasing the initial concentration of metal ions at the best initial values of pH which be obtained from the single component experiments and at different times, which depends on the type of metal removed by membranes, **Murthy, and Gupta, 1997**, **Peeters, 1998, Bouranene, et al., 2008**. It is a characteristic nature of the NF membranes and interpreted by screen phenomena. The increase in initial ions concentrations leads to screen such formation of cations above the membrane in high pressure side. This cations screen formations neutralizes the negative charge of the membrane. The total charge of the membrane decreases and the repulsion between the membrane and the cations will decrease, **Farares, et al., 2005.**

3.3 Lead and Cadmium Removal From binary aqueous solutions

3.3.1 Effect of initial metal concentration on permeate flux

Data in **Fig. 15**, show the effect of different initial metal ions concentrations in binary model on the permeate flux of NF membranes at optimum pH and 1 bar pressure. It can be noticed that the permeate flux decreases with increasing initial ions concentrations. For binary aqueous solution (Pb^{+2}/ Cd^{+2}) experiments for (10/50 ppm), (50/10 ppm) and (50/50 ppm) initial ions concentrations, the permeate flux of NF1 were 8, 7.7 and 7.6 ($l/m^2.h$), of NF2 were 23.7, 23.3 and 23 ($l/m^2.h$) and of NF3 were 13, 12.7and 12.5 ($l/m^2.h$), respectively. Compared with PWP 16.4, 37.9 and 16.6 ($l/m^2.h$) for NF1, NF2 and NF3, respectively, the permeate flux was in the following sequence: NF2 23.7 > NF3 13 > NF1 8 ($l/m^2.h$) for initial ions concentrations (10/50 ppm), because of that porosity of NF2 67.6 > NF3 58.1 > NF1 52.5%, allow the exit of the largest amount of permeate flux. Also, the decline in permeate flux happen due to several reasons, including, adsorption of soluble hydroxide of the metal on the surface of the membrane, the composition of the cake layer deposited metal hydroxide and concentration polarization, **Al-Rashdi et al., 2011.** In other word,the largest atomic wight has low permeate flux (Pb^{2+} = 207.2 and Cd^{2+} = 112.4 gm/mol), **Bouranene, et al., 2008, Gherasim, et al., 2013.**

3.3.2 Effect of initial metal concentration on rejection

The rejection of two metal ions in the aqueous solution is studied and the results are depicted in Figures 16. For binary aqueous solution model (Pb^{2+}/ Cd^{2+}), using NF1, the rejection of Cd^{2+}47.4 > Pb^{2+} 34%, Cd^{2+} 49 > Pb^{2+} 45.4% and Cd^{2+} 54 > Pb^{2+} 40.4 % at initial concentration (50/50 ppm), (10/50 ppm) and (50/10 ppm), respectively. Moreover, using NF2, the rejection of Cd^{2+} 52.6 > Pb^{2+} 51.3, Cd^{2+} 55.8% > Pb^{2+} 55.4 and Cd^{2+} 61.3 % > Pb^{2+} 52.4% at initial concentration (50/50 ppm), (10/50 ppm) and (50/10 ppm), respectively. While, using NF3, the rejection of Cd^{2+} 42.1 > Pb^{2+} 40.2%, Pb^{2+} 49.3 > Cd^{2+} 45.5% and Cd^{2+} 56 > Pb^{2+} 44.6% at initial concentration (50/50 ppm), (10/50 ppm) and (50/10 ppm), respectively. The explanation of that, the cadmium ions rejection is higher than lead ions rejection, and this higher rejection of cadmium salt is determined by the higher hydration energy of cadmium cation (-1755 kJ/mol of Cd^{2+}) > (-1425 Kj/mol of Pb^{2+}), **Marcus, 1997**. Similar results which highlight the increase in the cation retention with increasing hydration energy were obtained by **Gherasim, et al., 2013**.

4. CONCLUSIONS

In the present study, concluded the maximum rejection of Pb^{2+} in single salt solution were 99, 97.5 and 98%, and of Cd^{2+} were 78, 49.2 and 44 % for NF1, NF2 and NF3, respectively. While the maximum rejection of Pb^{2+} in binary aqueous solution were 45.4, 55.4, 49.3 % , and of Cd^{2+} rejection were 49,55.8 and 45.5 % for NF1, NF2 and NF3, respectively. It can be concluded that the permeation flux and rejection of Pb^{2+}were higher than that of Cd^{2+} at different pH values and initial ions concentration and NF2 was very efficient hollow fiber NF membrane for removal of Pb^{2+} and $Cd^{2+}$and also for binary aqueous solution. Finally, the separation performance of hollow fiber NF membranes is strongly depending on the membrane properties such as mean pore size, pore size distribution, and thickness.

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NOMENCLATURE

A = area, m^2.
C_P = concentrations in permeate solution, ppm.
C_b = concentrations in bulk feed, ppm.
J = permeate flux, $l/m^2.hr$.
ppm = part per million.
PWP = pure water permeability.
R = rejection, %.
t = time, h.
V = volume, l.

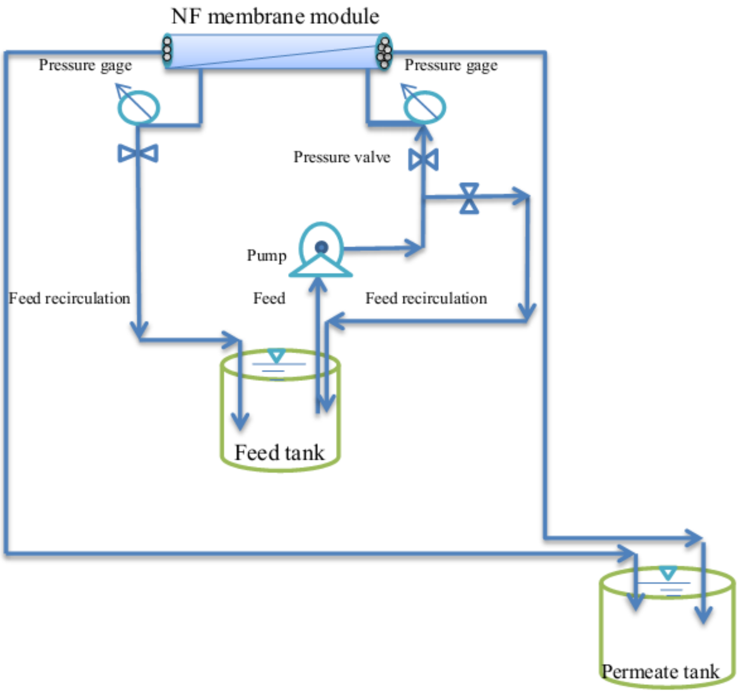


Figure1. A Schematic diagram of the membrane filtration test system.

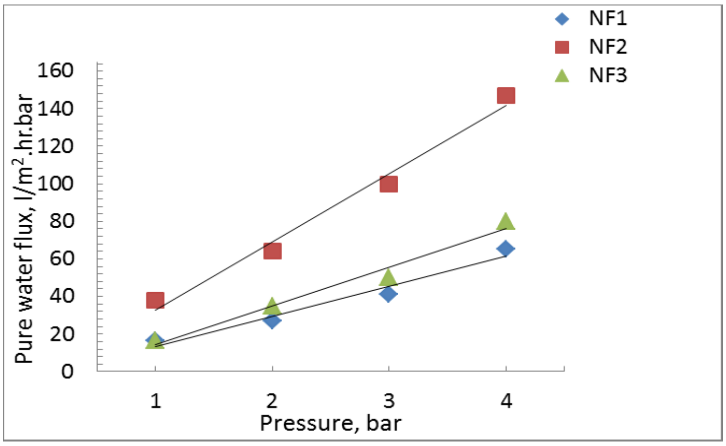
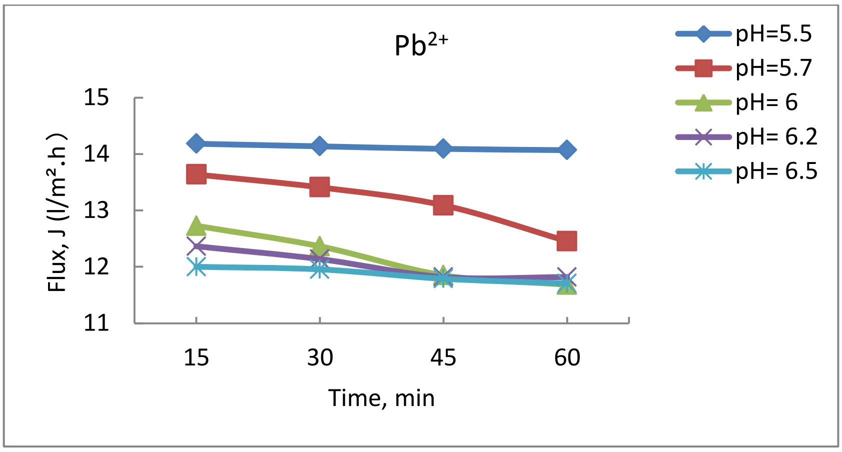


Figure2. Pure water permeability as a function of trans-membrane pressure.



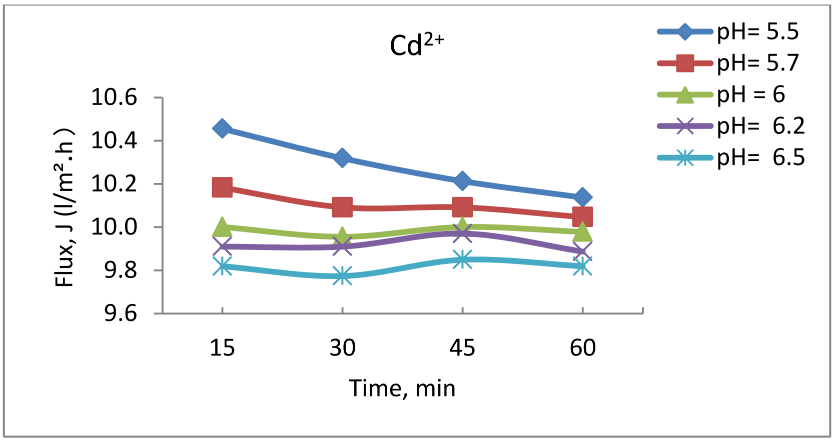
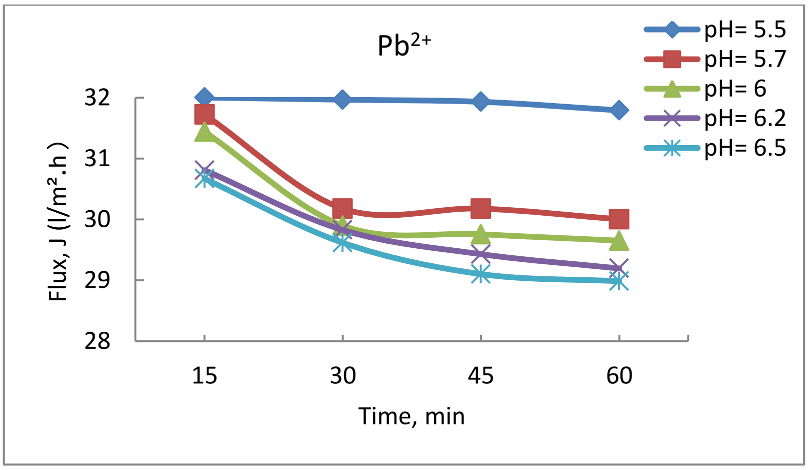


Figure3. Effect feed pH solution on permeate flux of NF1 membrane at different times.



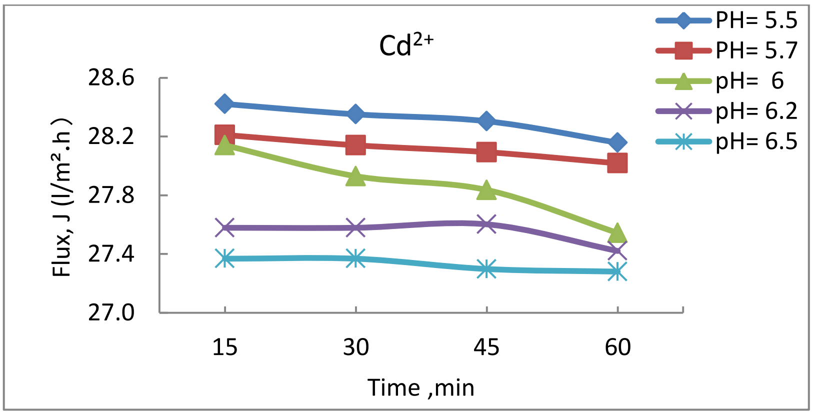


Figure4. Effect feed pH solution on permeate flux of NF2 membrane at different times

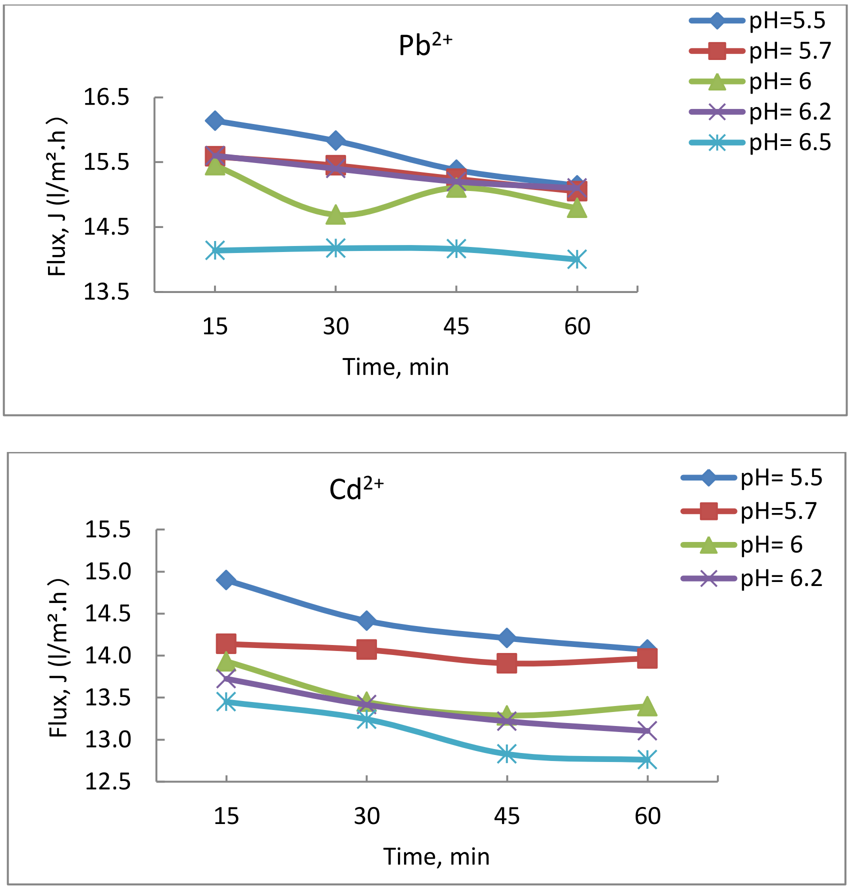


Figure5. Effect feed pH solution on permeates flux of NF3 membrane at different times

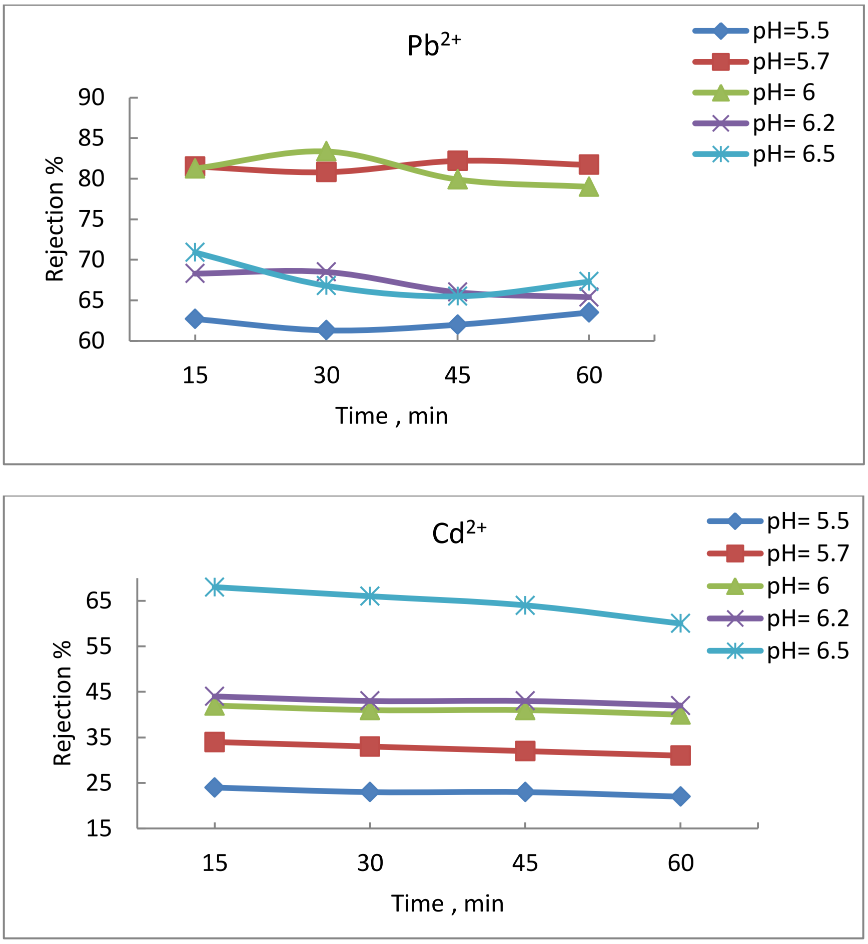
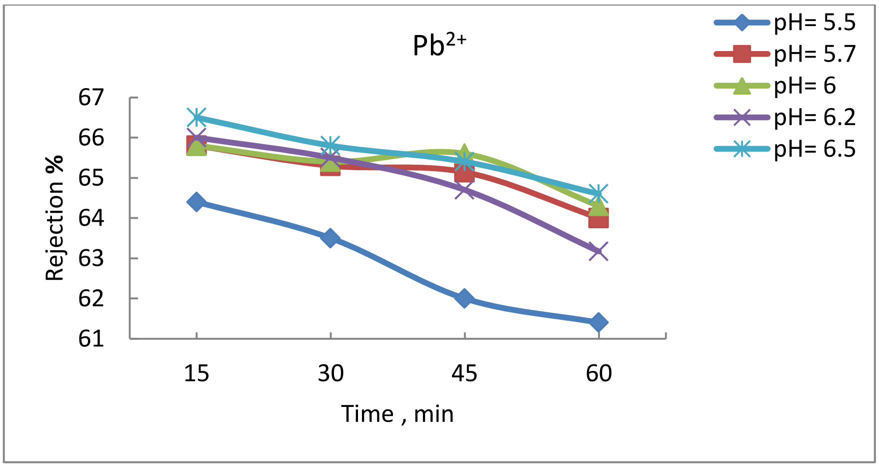


Figure 6 . Effect feed pH solution on rejection of NF1 membrane at (initial con.100 ppm and different times)



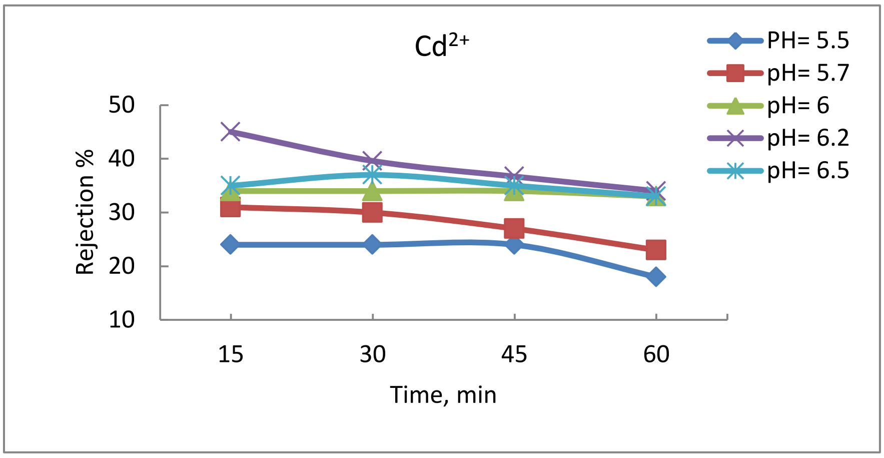


Figure 7. Effect feed pH solution on rejection of NF2 membrane at (initial con.100 ppm and different times)

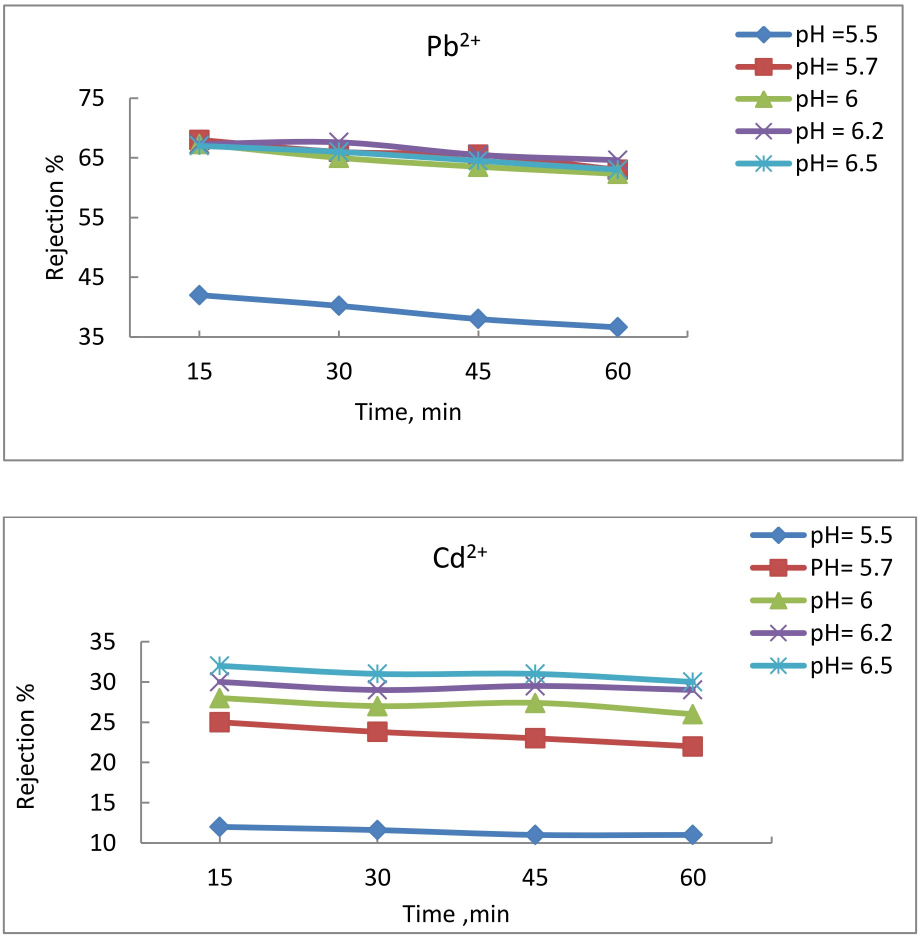


Figure 8. Effect feed pH solution on rejection of NF3 membrane at (initial con.100 ppm and different times)

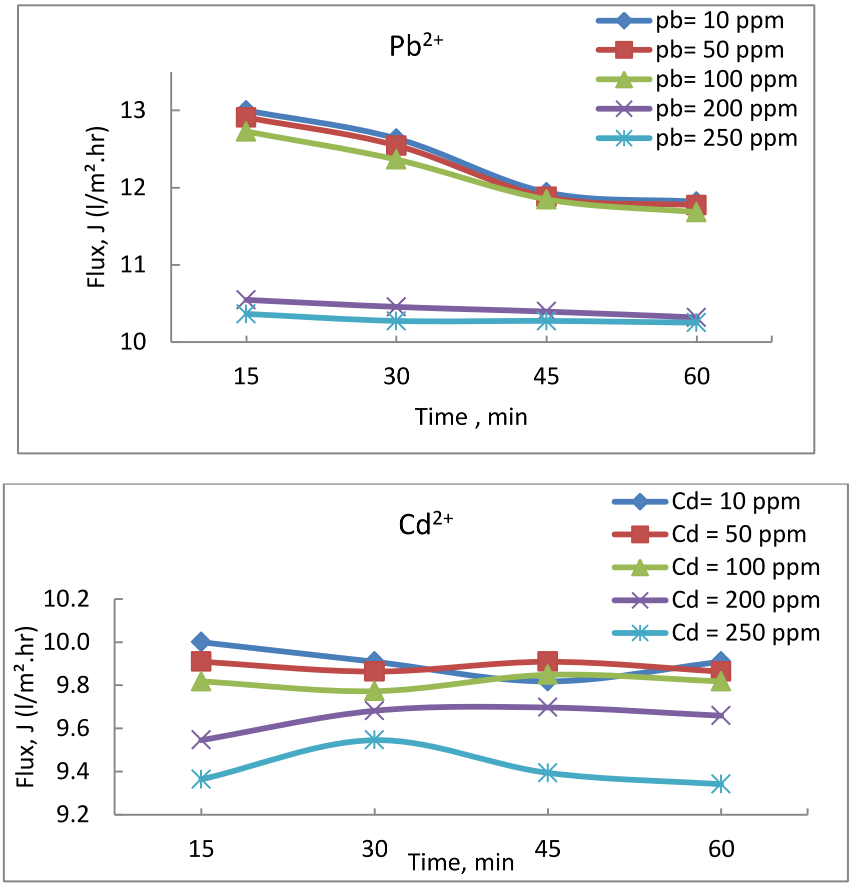
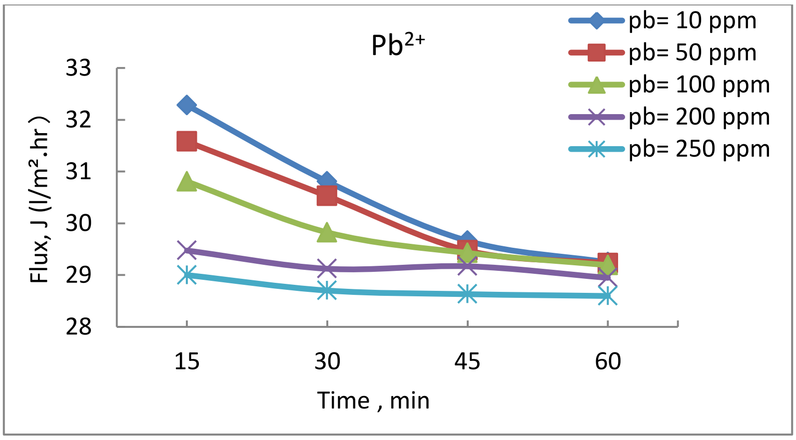


Figure 9. Effect of initial concentration on flux of NF1 membrane at different times



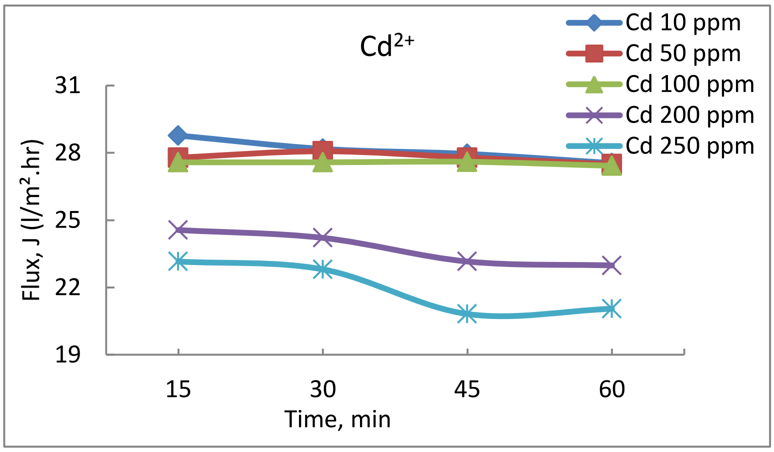


Figure 10. Effect of initial ion concentration on flux of NF2 membrane at different times.

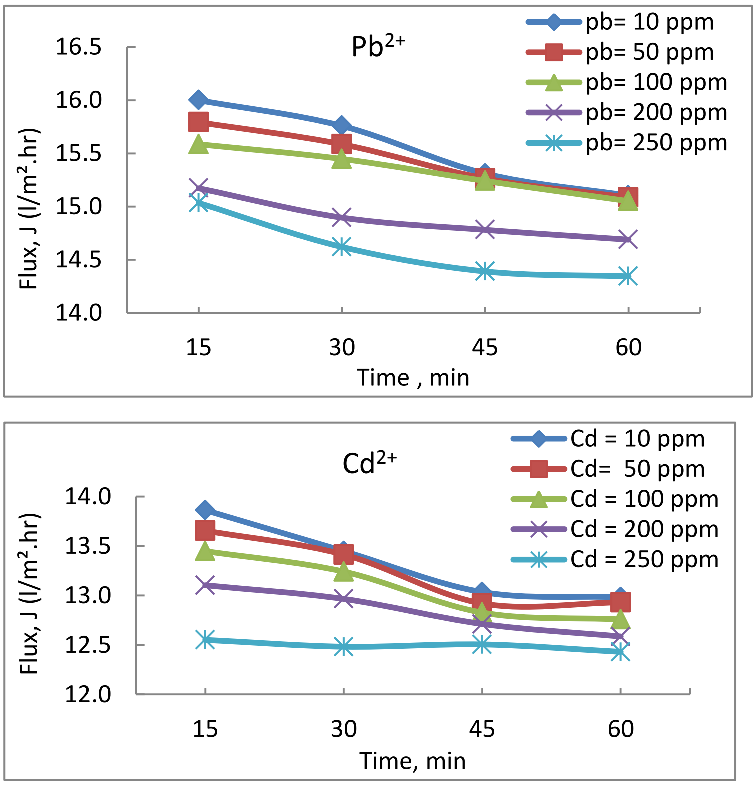


Figure 11. Effect of initial ion concentration on flux of NF3 membrane at different times

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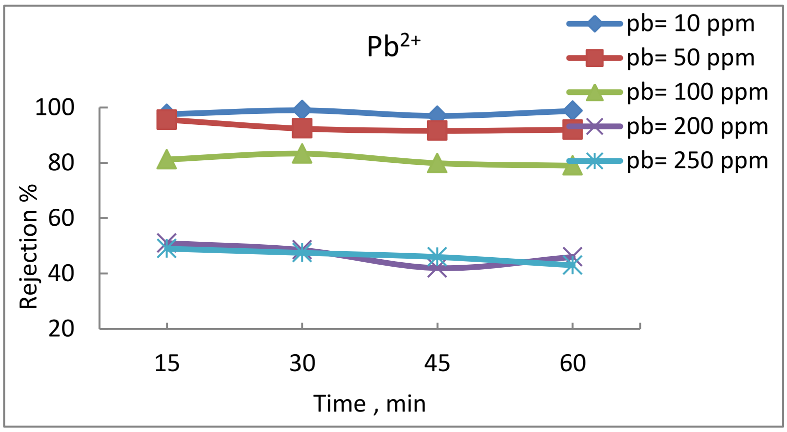


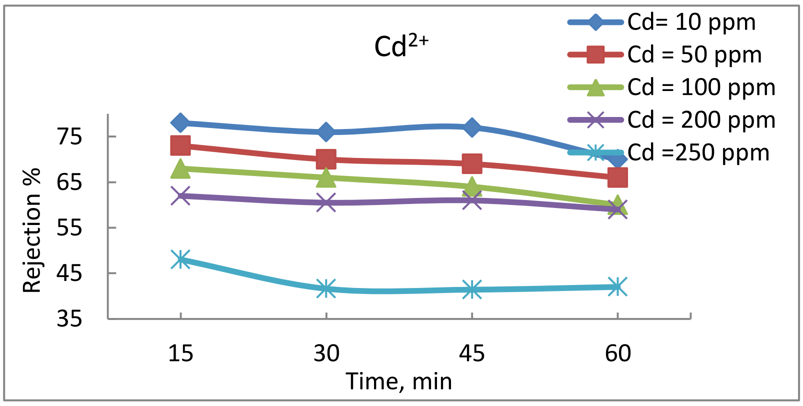
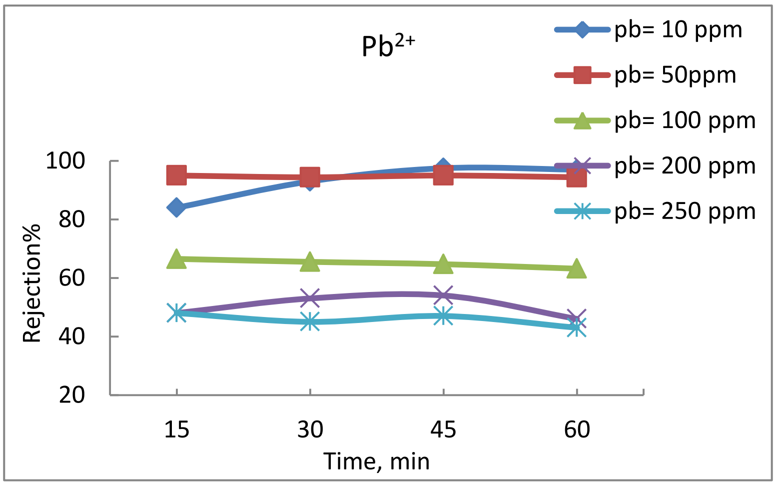


Figure 12. Effect of initial metal concentration on rejection of NF1 membrane at different times



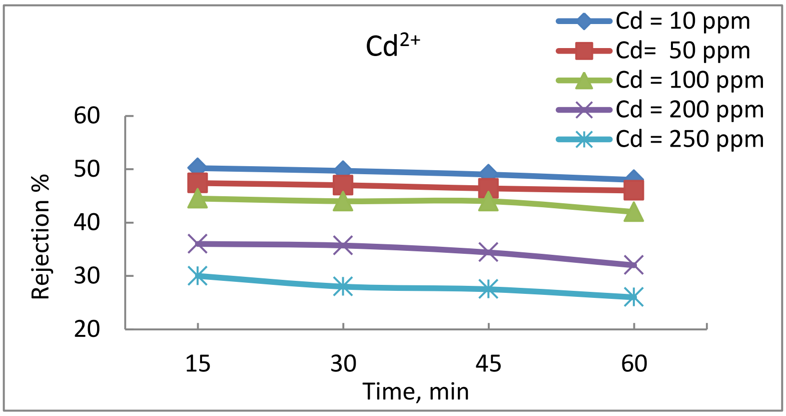


Figure 13. Effect of initial metal concentration on rejection of NF2 membrane at different time

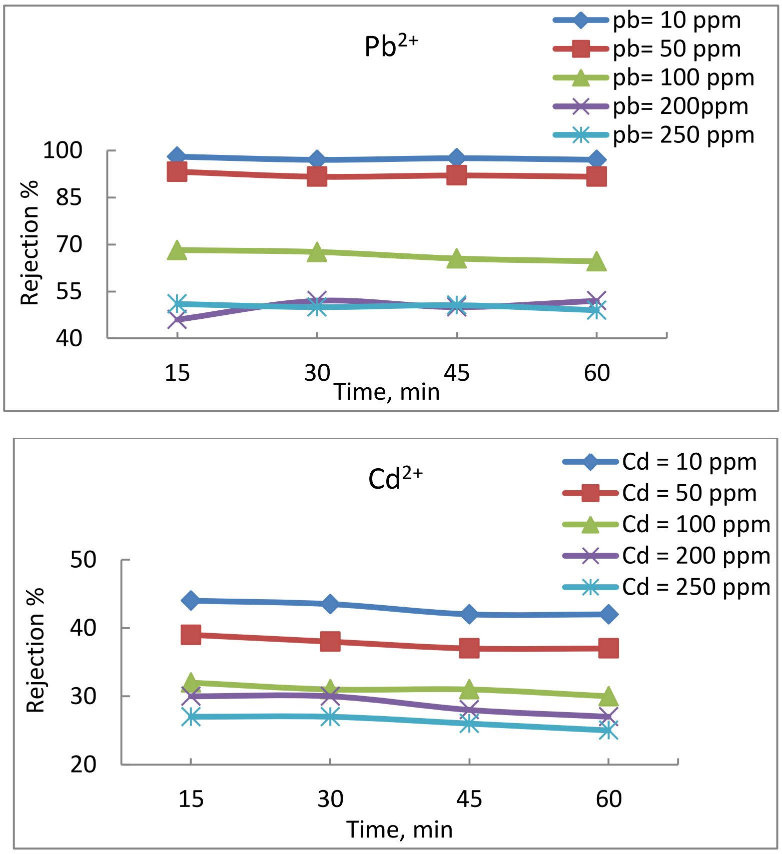


Figure 14. Effect of initial metal concentration on rejection of NF3 membrane at different times

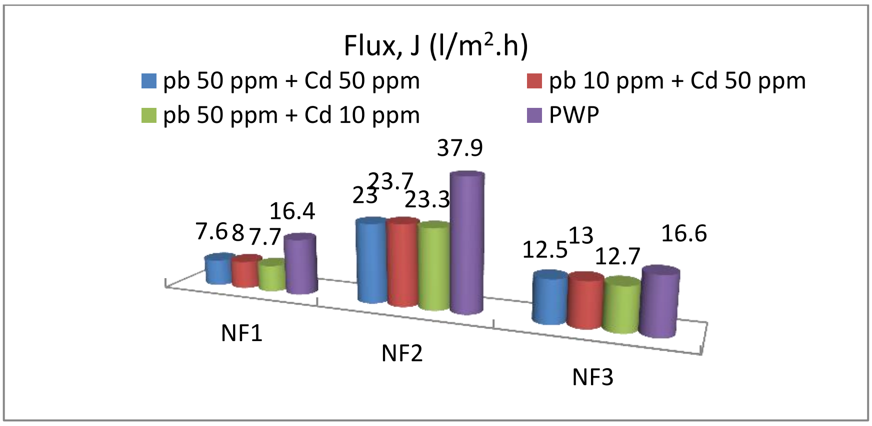


Figure 15 . Effect of initial feed concentration of (Pb^{2+} / Cd^{2+}) on permeate flux for three types of NF membrane (pH 6±0.2 and time 30 min)

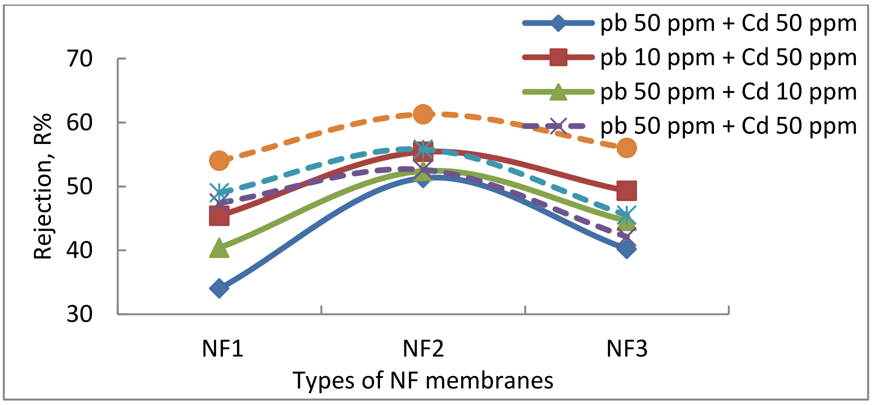


Figure 16. Effect of initial feed concentration of (Pb^{2+} (solid line) and Cd^{2+} (the dotted line)) on rejection for three types of NF membrane (pH 6±0.2 and time 30 min)

Table 1. Characteristics of the NF membranes

Type of membrane	NF1	NF2	NF3
Material	PES (29%)	PES (27%)	PES (27%)
Module	Hollow fiber	Hollow fiber	Hollow fiber
Length (cm)	22.2	22.7	23.1
Active Area (m^2)	4.4×10^{-3}	5.7×10^{-3}	5.8×10^{-3}
Max operating temp (℃)	45	45	45
Average pore size (nm)	52.04	58.11	47.75
pore size distribution (nm)	25 - 100	35 - 130	20 - 115
Porosity (%)	52.5	67.6	58.1
Outer diameter (μm)	1012	958.4	1005
Inner diameter (μm)	620	576	603.6