APPLICATION OF THE SPIEGLER-KEDEM-KACHALSKY MODEL TO THE REMOVAL OF 4-CHLOROPHENOL BY DIFFERENT NANOFILTRATION MEMBRANES

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Abstract

Chlorophenols, commonly found in the wastewaters of numerous industries, are widely considered as priority pollutants and their persistence may cause severe environmental problems. Among the methods described for their removal, pressure-driven membrane processes are considered as a reliable alternative. In this paper we study the influence of different operational variables (applied pressure, feed concentration and pH) on the removal of 4-chlorophenol from synthetic aqueous solutions by nanofiltration using three different polyamide membranes (NF-97, NF-99 and RO98pHt). The Spiegler-Kedem-Kachalsky model was applied to predict the nanofiltration removal process. Model constants for the three membranes were obtained and there was good agreement between the experimental and model rejection data.

Keywords: 4-Chlorophenol; Membrane processes; Nanofiltration; Spiegler-Kedem-Katchalsky model

1. Introduction

The contamination of ground and surface waters with organic pollutants and the increasing scarcity and salinity of available water resources are recognized as problems of growing importance. The negative impact of urban industrial effluents on the world's water resources is a topic of increasing concern. Research conducted in the USA showed that 80% of streams contained organic contaminants [1]. Among these organic contaminants, chlorophenols constitutes a group of environmental pollutants, there are extremely harmful to organisms at even very low concentrations [2-4]. As chlorophenols are non-biodegradable in nature and have carcinogenic, mutagenic and chronic toxic effects, they are considered as priority pollutants by the US Environmental Protection Agency [5] and by the European Union [6]. Spain heads the list of European countries responsible for the direct emission of phenol into the water [7].

Chlorophenols are commonly used as preservative agents for wood and paints and as disinfectants for vegetable fibers. They are also generated by a wide range of industrial processes, including high-temperature coal conversion, petroleum refining and the manufacture of plastics, resins, textile, iron, steel and paper [4, 8-10].

Typical methods for the removal of chlorophenols are biological (enzyme [11, 12] and microbial [13] degradation), chemical (traditional oxidation treatments [14, 15] and advanced oxidation processes [16, 17]), physical (solvent extraction [18], adsorption on different supports [19, 20]), membrane technology [21, 22], and combined methods [7, 23-24].

Membrane technology is considered a useful tool for removing organic pollutants from wastewater, either as single procedure or combined with other physical and chemical water treatment processes [25–27]. For removing phenol and phenolic compounds, nanofiltration (NF) seems to be the most suitable pressure driven membrane process due to its low energy requirements (compared with those of reverse osmosis) and to the high selectivity of nanofiltration membranes to remove multivalent ions and organic contaminants. Several authors have studied phenolic compound removal by nanofiltration [28, 29], but there has been no attempt to model the chlorophenol nanofiltration process.

The development of mathematical models to predict the performance of nanofiltration in the removal of p-chlorophenol is important for the optimal design and operation of these processes. Parameter estimation is an important aspect of any mathematical modelling work. Model parameters are usually estimated by matching the model predictions with experimental data. A good predictive model will allow users to obtain membrane characteristics, to predict process performance as well as to optimize the process. The ability to develop such modelling techniques successfully will result in a smaller number of experiments and subsequently save time and money in the developmental stage of a given process [30].

Some nanofiltration models take into account the transport mechanism, while other models are independent of the same. The solution–diffusion model, solution-diffusion imperfection and extended Nernst-Planck model belong to the former category while the Spiegler-Kedem-Katchalsky model is representative of the latter [31].

The object of this paper is to study the influence of different membranes (NF 97, NF99 and RO98pHt) and different operational conditions (pressure, feed concentration and pH) on 4-chlorophenol removal from aqueous solutions by nanofiltration and to investigate the viability of using the Spiegler-Kedem-Kachalsky model to predict the rejection of 4-chlorophenol with the different membranes studied.

2. Theoretical Background

Membrane performance was measured in terms of membrane rejection, R (%), and permeate flux, J_p. For dilute aqueous mixtures consisting of water and a solute, the selectivity of a membrane towards the mixture is usually expressed in terms of the observed solute rejection coefficient [32]. This parameter is a measure of a membrane's ability to separate the solute from the feed solution, and is defined, as a percentage, by the equation:

$$R = 100\frac{C_f - C_p}{C_f} = 100\left(1 - \frac{C_p}{C_f}\right) \quad (1)$$

where C_p and C_f are the solute concentration in the permeate and feed streams, respectively [33].

The permeate flux was calculated according to the following equation:

$$J_p = \frac{Q_p}{S} \quad (2)$$

where Q_p is the volumetric permeate flux (m^3/s) and S is the membrane active area (m^2).

The transport phenomena of nanofiltration membranes in the pressure-driven process can be described by irreversible thermodynamics. In general, the transport equations for the components through a nanofiltration membrane consist of two components - the diffusion component and the convection component. For a system involving a single solute in aqueous solution, solute retention can be described by three transport coefficients:

i. Specific hydraulic permeability, L_p.

ii. Local solute permeability, P_s.

iii. Reflection coefficient, σ.

Permeability is the flux of a component (solvent or solute) through the membrane per unit driving force (the effective transmembrane pressure). The reflection coefficient is a measure of the degree of semipermeability of the membrane [31].

The Spiegler-Kedem-Kachalsky (SKK) model states that the fluxes of solute and solvent are directly related to the chemical potential differences between the two sides of the membrane. The chemical potential gradient is caused by a concentration or pressure gradient. Solvent transport is due to the pressure gradient across the membrane and solute transport is due to the concentration gradient and/or convective coupling of the volume flow [31].

The transport equation expressed by Spiegler-Kedem-Katchalsky model is as follows [34-36]:

For solvent

$$J_w = L_P \cdot \left(\frac{dP}{dx} - \sigma \frac{d\Pi}{dx} \right) \tag{3}$$

For solute

$$J_s = P_S \cdot \frac{dC_s}{dx} + (1-\sigma) \cdot C_s \cdot J_w \tag{4}$$

Diffusion is represented by the first term in Eq. (4) and the second term of the same equation represents the contribution of convection to the transport.

The following assumptions are made:

- The Spiegler-Kedem-Katchalsky model adequately predicts the transport of solute and solvent, regardless the type of solute and its charge, solvent and membrane.
- The pressure and concentration gradients are the driving forces.
- Solute present in the system is semipermeable to the membrane.
- In the concentration polarization layer thickness, the solute has a value that is independent of the diffusion and mass transfer coefficients.
- L_p, P_s and σ are constants across the membranes so that the equation for the integration of Eqs. (3) and (4) of the membrane can be simplified.

The simplified version of model transport equations can be written as [37]:

$$J_w = L_p \cdot \left(\Delta P - \sigma \cdot \Delta \Pi\right) \quad (5)$$

$$J_s = P_s \cdot (C_m - C_p) + (1-\sigma) \cdot J_w \cdot C_S \quad (6)$$

J_w and J_s are, respectively, the solvent flux and the solute flux; ΔP and $\Delta \Pi$ define, respectively, the pressure drop and osmotic pressure differences across the membrane; C_m and C_p are, respectively, the solute concentrations at the membrane surface and in the permeate; C_s is the logarithmic mean concentration of the solute between the feed and permeate; L_p is the permeability of pure water.

The observed rejections can be explained by SKK theory as follows:

$$R_{obs} = \frac{\sigma(1-F)}{1-\sigma F} \qquad (7)$$

where R_{obs} is the observed rejection (7) and F is a parameter that depends on the solvent flux, the rejection coefficient and solute permeability coefficient according to the expression:

$$F = \exp\left(-\frac{1-\sigma}{P_s}\cdot J_w\right) \qquad (8)$$

The Spiegler-Kedem-Katchalsky model proposes a relationship between the flux of solvent (J_w) and the logarithm of solute membrane parameters, taking into consideration the observed rejection (R) and the reflection coefficient (σ) values in the following equation:

$$Ln[X] = -\frac{(1-\sigma)}{P_s}\cdot J_w \qquad (9)$$

where X can be obtained from the expression

$$X = \left(\frac{1}{(1-\sigma)} - \frac{1}{1-R_{obs}}\right)\cdot\frac{(1-\sigma)}{\sigma} \qquad (10)$$

From equation (6), using the condition that $C_f = C_m$ the following expression can be obtained

$$P_s = \frac{J_s - J_w\cdot C_s\cdot(1-\sigma)}{(C_f - C_p)} \qquad (11)$$

Substituting the value of P_s given by equation (11) into equation (9) gives expression (12)

$$Ln\left[\left(\frac{1}{(1-\sigma)} - z\right)\cdot\frac{(1-\sigma)}{\sigma}\right] + \frac{(1-\sigma)}{a-b\cdot(1-\sigma)}\cdot J_w = 0 \qquad (12)$$

where $z = \left(\frac{1}{1-R_{obs}}\right)$, $a = \frac{J_s}{(C_f - C_p)}$ and $b = \frac{J_w\cdot C_s}{(C_f - C_p)}$

Using a numerical method (Mathematical Program based Runge Kutta¿? Different iterations have been made to minimized the difference values initial and final and obtained the values

that made zero the equation (12) , equation (12) can be solved, and the reflection (σ) and solute permeability (P_s) coefficients can be obtained.

3. Materials and methods

3.1. Chemicals

4-Chlorophenol (99% purity), sulphuric acid (98% purity) and sodium hydroxide (97% purity) were purchased from Aldrich, Probus and Panreac, respectively. 4-aminoantipyrine (AAP) and potassium ferricyanide, were purchased from Sigma-Aldrich Fine Chemicals.

3.2. Membranes

Three different polyamide membranes, NF-99, NF-97 and RO98pHt, manufactured by Alfa Laval (Dow Chemical) were used. The characteristics of the membranes are described in Table 1.

3.3. Membrane test module

All the assays were performed in an INDEVEN flat membrane test module, which is designed for a maximum operating pressure of $70x10^5$ Pa and which provides data concerning the behaviour of the membranes in cross flow conditions with a reduced surface area ($3x10^{-3}$ m^2), low feed flow and short times. Figure 1 shows a diagram of the experimental unit. The feed tank is a closed stainless steel vessel, with a capacity of $12x10^{-3}$ m^3, equipped with a water coiling coil, which allows a constant feed temperature. The membrane module supports the membrane. The feed solution is fed through the membrane module by means of a high pressure pump.

3.4. Experimental procedure

Aqueous solutions of 4-chlorophenol solutions from 0.05 kg/m^3 to 0.25 kg/m^3 were treated in the test module, in which the feed stream was separated into two streams: one purified "permeate" and the other concentrated "concentrate". Both concentrate and permeate were recycled to keep the feed concentrations practically constant and to simulate a continuous process in a quasi-stationary state. Experiments were allowed to reach the steady-state, as revealed by the constant 4-chlorophenol concentration value in the permeate stream. The steady-state was considered to be reached when the difference between the 4-chlorophenol concentration values in the permeate stream in three consecutive measurements was lower than 3%. Rejection percentages and permeate fluxes were calculated in such steady-state conditions as an average value of the last three measurements. All the experiments were run in duplicate and standard deviation values of about 3% were obtained for the whole set of data.

The following experimental conditions were maintained unchanged throughout the experimental series: feed flow 4.17x10^{-5} m^3/s, temperature 25 ± 0.5 ºC and assay time 120 min. Three series of experiments were carried out in the membrane test module, varying the pressure (5x10^5, 10x10^5, 15x10^5, 20x10^5 and 25x10^5 Pa), 4-chlorophenol feed concentration (0.05, 0.10, 0.15, 0.2 and 0.25 kg/m^3) and feed pH (5, 6, 7, 8 and 9). Typical experimental conditions were transmembrane pressure 20 bar, 4-chlorophenol feed concentration 0.15 kg/m^3 and pH 7.

3.5. Analytical method

The 4-chlorophenol concentration was determined using a colorimetric assay as recommended by Standard Methods [38], in which the phenolic compounds within a sample react with 2.08 mM APP in the presence of 8.34 mM potassium ferricyanide reagent. The

reaction product absorbs light at wavelength of 505 nm with an extinction coefficient of 9.5170 mM^{-1} cm^{-1}. The assay mixture consisted of 0.3 cm^3 of ferricyanide solution, 0.3 cm^3 of 4-aminoantipyrine solution and 2.4 cm^3 of 4-chlorophenol sample.

4. Results and discussion

4.1. Influence of main parameters on rejection

Higest rejections and lowest permeate fluxes were obtained using the RO98pHt membrane, while the lowest rejections and highest permeate fluxes were obtained with the NF-99 membrane (Fig. 2 and Fig. 3). According to the manufacturer's specifications, NF-97 and NF-99, membranes are very similar; however, the rejections and permeate fluxes obtained with them differed significantly. Similar results were obtained by other researchers [39].

The influence of 4-chlorophenol feed concentration on rejection and on permeate flux, for the different membranes, is depicted in Figs. 2(A) and Fig. 3(A). There was no significant effect of the 4-chlorophenol concentration on rejection when NF-99 membrane is used, while the rejection coefficient slightly increased as the 4-chlorophenol feed concentration increased when NF-97 and RO98pHt membranes were used. In contrast, the permeate flux decreased as the 4-chlorophenol concentration increased for all three membranes studied. These results agree with those of other studies [40].

The influence of pressure on rejection and on permeate flux for the different membranes are shown in Figs. 2(B) and Fig. 3(B). As can be seen, the rejection coefficient increased with increasing transmembrane pressure when NF-97 and RO98pHt membranes were used.

Although diffusive transport is pressure-independent [41], with increasing pressure convective transport becomes more important [42] and, as a result, rejection also increases.

The behaviour of the NF-99 membrane was, once again, different and no significant effect of pressure on rejection was observed with this membrane. Similar results were obtained by Li and col. using the NF99 membrane for the removal of phenol [39].

An increase in applied pressure leads, as is to be expected from equations (5) and (6), to an increase in the permeate flux for all three tested membranes.

The influence of pH on rejection and on permeate flux, for the different membranes, is shown in Figs. 2(C) and Fig. 3(C). Rejection does not vary significatively in the pH range between 5 and 8, but increases above pH 8. This variation can be explained through the electrostatic interactions between 4-chlorophenol and the membrane functional groups.

Polyamide membranes have free carboxylic acid groups in their structure, and these groups undergo ionization when the pH is increased. It has been reported that this ionization is produced at pH close to neutral values [44]. Due to the ionization of these carboxylic groups the membrane becomes more negatively charged at pH values higher than 6.

As the pKa of 4-chlorophenol is 9.2, its ionization can be expected to be important over pH 8, and so, 4-chlorophenolate (negative charged species) began to be formed above this pH. The result of the interaction between the negatively charged functional groups of the membrane and the negatively charged 4-chlorophenolate is an increase in organic species rejection.

No significant variatiation or permeate flux with pH was observed. A very slight decrease in the permeate flux was observed above pH 7 for all three membranes.

4.2. Comparison between experimental and modeling data

An Advanced Grapher® program was used for the numerical resolution of equation (10). For each experiment using different experimental conditions and different membranes, the reflection coefficient (σ) and the solute permeability coefficient (P_s) were obtained. Average values were calculated as mean using (SPSSv.19) statistical program. These coefficients are shown in Table 2.

From the estimated values of the parameters of the model (σ and P_s) and using equations (5) and (6), values of the rejection coefficient according to the SKK model were calculated and compared with the experimental values. Figure 4 shows that, in general, calculated and experimental rejection coefficients are very close, as shown by the good approximation to the diagonal. The standard deviation values, calculated for the three membranes NF-97, NF-99 and RO98pHt, were 2.32, 1.71 and 2.22, respectively.

4. Conclusions

The influence of different operational variables (applied pressure, feed concentration and pH) on the removal of 4-chlorophenol from aqueous solutions by nanofiltration using three different polyamide membranes (NF-97, NF-99 and RO98pHt) was studied. The highest rejection coefficient of the RO98pHt membrane leads to the lowest permeate flux, while the lowest rejection coefficient of the NF-99 membrane leads to the highest permeate flux. The rejection coefficient increases with the pressure applied and with the feed concentration in NF-97 and RO98pHt membranes, but does not vary in the NF-97 membrane. However, increases significantly at pH values above 8 in the three membranes. Permeate flux increasee

with applied pressure, decreases with feed concentration and shows a slight decrease above pH 7 in the three studied membranes.

The Spiegler-Kedem-Kachalsky model was applied to predict the nanofiltration removal process. Model constants for the three membranes were obtained and good agreements between experimental and model rejection data were obtained.

Symbols

A_w (s/m)	water permeability constant
C_f (kg/m^3)	solute concentration in the feed stream
C_m (kg/m^3)	solute concentration in the membrane
C_p (kg/m^3)	solute concentration in the permeate stream
C_s (kg/m^3)	logarithmic mean concentration of the solute between the feed and permeate
C_w (kg/m^3)	solvent concentration in the permeate stream
F	dimensionless parameter SKK model
J_p (m^3/m^2 s)	permeate flux
J_s (kg/m^2 s)	solute flux
J_w (kg/m^2 s)	solvent flux
L_p (m/s)	solvent permeability constant
P (Pa)	operation pressure
P_s (m/s)	solute permeability constant
Q_p (m^3/s)	volumetric permeate flux
R (%)	membrane rejection
R_{obs} (%)	membrane rejection calculated
S (m^2)	membrane active area

X	auxiliary parameter SKK model
ΔP (Pa)	hydraulic pressure applied across the membrane
$\Delta \Pi$ (Pa)	difference in the osmotic pressure of the solutions on the feed and permeate side of the membrane
σ	reflection coefficient

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Figure captions

Figure 1. Flow diagram of nanofiltration test unit. **(A)** feed tank, **(B)** membrane module, **(C)** pressure pump.

Figure 2. Variation of rejection coefficient with (A) pressure, (B) feed concentration and (C) pH, for the different membranes. Membranes: (*) NF-97, (■) NF-99 and (●) RO98pHt.

Figure 3. Variation of permeate flux with (A) pressure, (B) feed concentration and (C) pH, for the different membranes. Membranes: (*) NF-97, (■) NF-99 and (●) RO98pHt.

Figure 4. Experimental and model rejection coefficient: (*) NF-97, (■) NF-99 and (●) RO98pHt.

Table 1. Main characteristics of the membranes used.

Provider	Alfa Laval	Alfa Laval	Alfa Laval
Manufacturer	Dow Chemical	Dow Chemical	Dow Chemical
Product denomination	NF-97	NF-99	RO98pHt
Type	Thin-film composite	Thin-film composite	Thin-film composite
Composition	Polyamide	Polyamide	Polyamide
Molecular weigh cut-off (MWCO) (Da)	≤ 200	≤ 200	340
Membrane surface area (m^2)	0.003	0.003	0.003
Maximum pressure (N/m^2)	$55x10^5$	$55x10^5$	$55x10^5$
$MgSO_4$ rejection (%)	≥ 97	≥ 98	≥ 99
pH range	3-10	3-10	2-11
Maximum temperature (ºC)	50	50	60

Table 2. Model constants for the three membranes.

Membrane	**NF-97**	**NF-99**	**RO98pHt**
σ	0.7416	0.0986	0.8582
P_s (m/s)	$1.43\ 10^{-5}$	2.42^{-4}	$5.82\ 10^{-6}$

Figure 1.

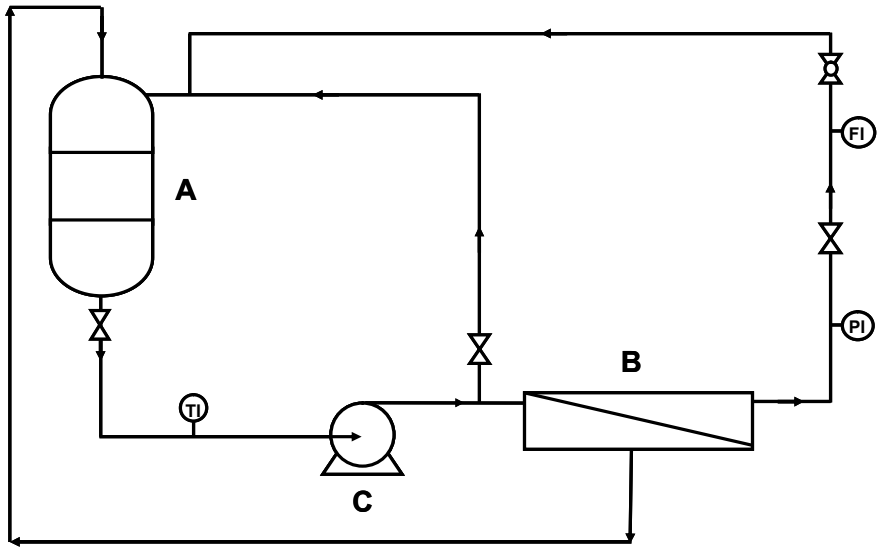


Figure 2

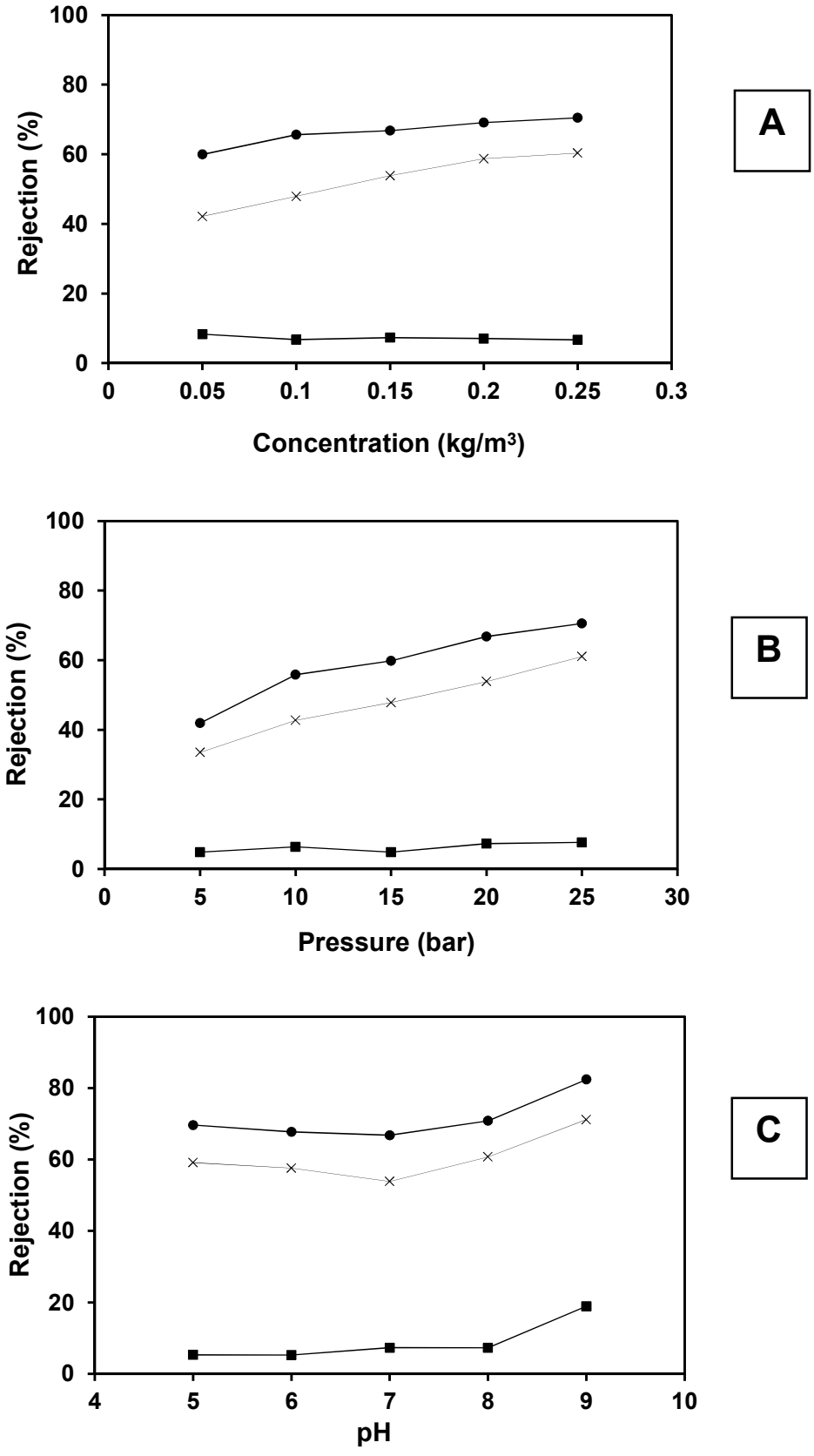

A
Rejection (%)
Concentration (kg/m3)
B
Rejection (%)
Pressure (bar)
C
Rejection (%)
pH

Figure 3

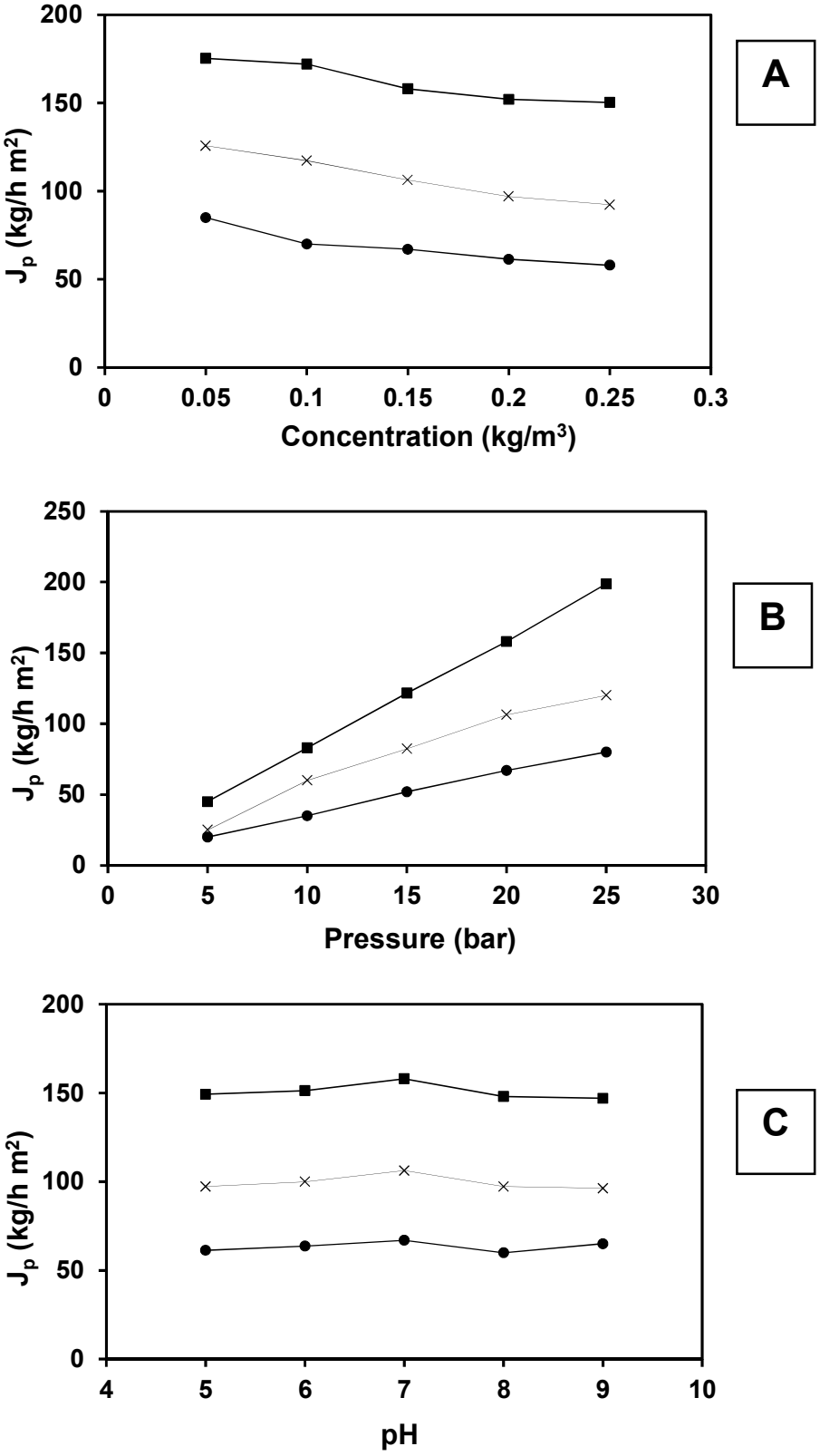
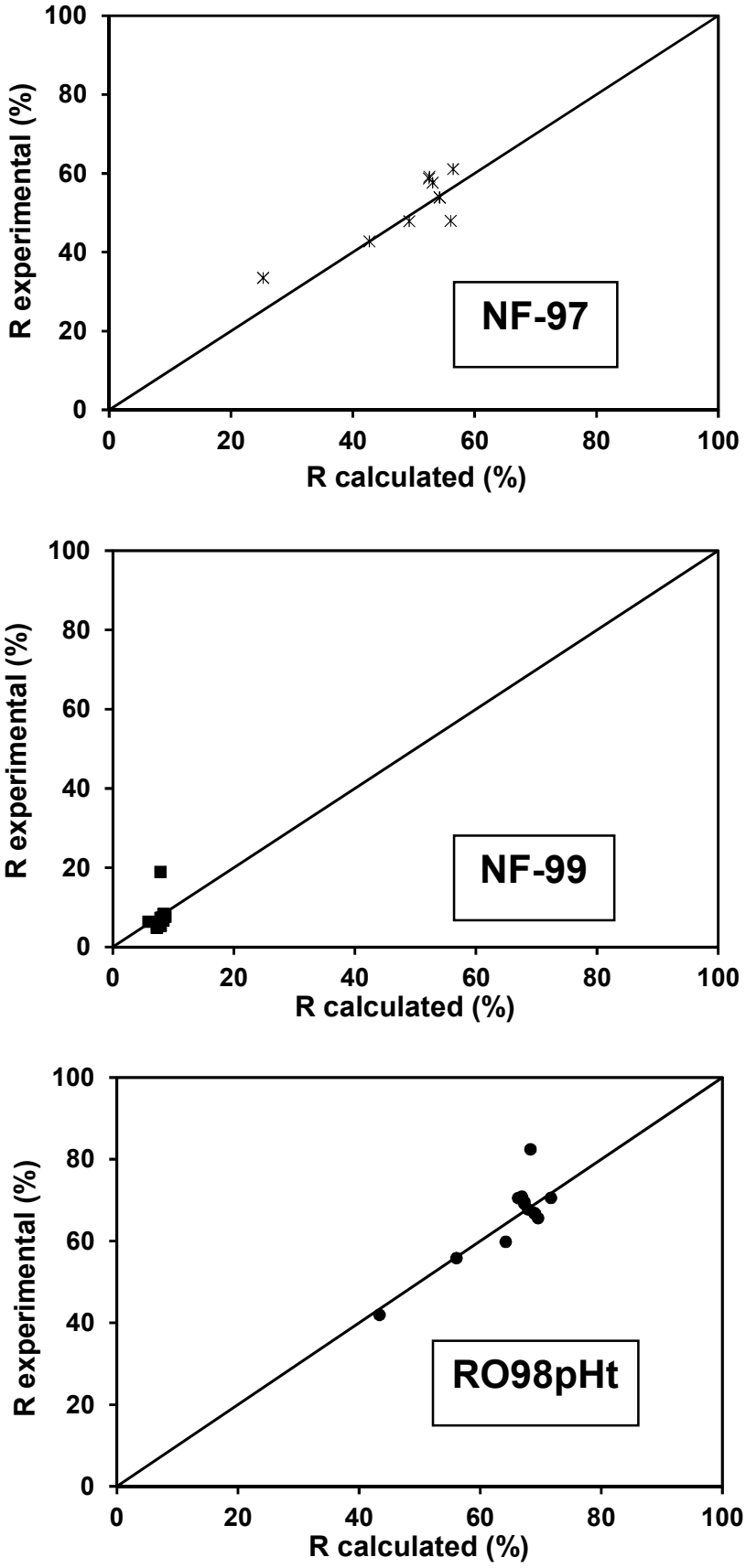

A
J_p (kg/h m^2)
200
150
100
50
0
0
0.05
0.1
0.15
0.2
0.25
0.3
Concentration (kg/m^3)
B
J_p (kg/h m^2)
250
200
150
100
50
0
0
5
10
15
20
25
30
Pressure (bar)
C
J_p (kg/h m^2)
200
150
100
50
0
4
5
6
7
8
9
10
pH

Figure 4


R experimental (%)
R calculated (%)
NF-97
NF-99
RO98pHt
0
20
40
60
80
100