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Application of the solution-diffusion model for the removal of atrazine using a nanofiltration membrane

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ABSTRACT

The solution-diffusion model was used to predict the behaviour of four nanofiltration membranes, two were made of polyamide (NF-99 and NF-97) and the other two were made of polypiperazineamide (DL and DK), when used for the removal of atrazine from aqueous solutions. The mass transfer model applied is very simple and its linearization facilitates rapid calculation of the relevant parameters. The two main parameters, permeate concentration and volumetric permeate flux, are obtained from three different coefficients: water permeability, A_w, solute permeability, B_s, and osmotic pressure coefficients, Ψ. Good agreement between the experimental and the predicted atrazine concentrations was obtained for the NF-99, DL and DK membranes when the concentration was low. However, only the NF-99 membrane provided accurate values for the two main parameters in the whole range of concentrations studied, which suggests that the solution-diffusion model can only be applied to this membrane.

Keywords: Atrazine; Membrane process; Nanofiltration; Solution-diffusion model

1. Introduction

Atrazine is used as a herbicide on crops, such as sugar cane, corn, pineapple, sorghum and macadamia nuts, and on evergreen tree farms for regenerating evergreen forest growth. It has also been used to keep weeds from growing on roads and railways. Atrazine can be sprayed on croplands before crops start growing or after they have emerged from the soil. It is a "Restricted Use Pesticide" in the USA, which means that only certified herbicide users may purchase or use it. Permission to use atrazine is obtained through the appropriate governmental office where the herbicide user is licensed [1]. In Europe, atrazine has been considered as a banned herbicide since 1991. Moreover, it is classified as a possible carcinogenic by the International Agency for Research on Cancer. Other chronic effects reported for atrazine include reproductive effects, fetal damage, delayed neurological manifestations and possible immunological disorders [2].

Although, officially banned in Europe, extensive use and discharge of atrazine has ranked it among the most common pesticides found in surface water and groundwater with concentrations frequently far above the European limit for drinking water (0.1 μg/L) and the European alarm level for pesticides in surface waters (1 μg/L) [3,4]. The removal of such organic pollutants in water is usually performed by means of activated carbon [5,6] and oxidation by ozone or ozone and hydrogen peroxide [7]. However, both techniques have disadvantages; for example, activated carbon filtration is effective but expensive since it requires frequent regeneration [6].

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Membrane technology processes, such as ultrafiltration, reverse osmosis and nanofiltration, have increasingly been used for pesticide and micropollutant removal in recent years [4,6,8–12]. Considering that the molecular weights of almost all pesticides range from 200 to 400 Da [3], nanofiltration membranes are potentially useful for their removal. The main advantages of this technique include the absence of any need to use reagents, the simplicity of the apparatus involved, low material consumption and ease of automation.

Several studies have been carried out with nanofiltration membranes. For example, Ahmad et al. [13,14] examined four nanofiltration membranes, NF90, NF200, NF270 and DK, to retain atrazine and dimethoate in aqueous solutions. NF90 showed the highest rejection percentages (above 90%) of all the membranes tested. The same authors found that the NF90 membrane was more resistant to pH changes. Two of these membranes, NF200 and DK, have also been tested [15] to remove pesticide residues, including atrazine, in water. High atrazine rejection percentages (between 80 and 90%) were obtained with both membranes. OPMN-P is another nanofiltration membrane that has been used to remove triazine herbicides, attaining rejection percentages of 97–98% [16]. Kiso et al. [8] used two polyvinyl alcohol polyamide nanofiltration membranes (NTR-729HF, NTR-7250) and two sulfonated polyethersulfone nanofiltration membranes (NTR-7450, NTR-7410) to remove atrazine from water, obtaining rejection percentages of 97.5, 68.4, 14.9 and 10.9, respectively. Van der Bruggen et al. [6] studied the efficacy of four nanofiltration membranes, NF70, NF45, UTC-20 and UTC-60, to remove atrazine. The NF70 membrane obtained the best results with an atrazine rejection percentage of 95%. Apart from the single-pass nanofiltration processes described in the literature, other studies refer to combined treatments such as, for example, the coupling of membrane filtration with subsequent ozone treatment [17] or the combination of hetereogeneous photocatalysis and nanofiltration [18] to improve atrazine removal from surface waters and aqueous solutions, respectively.

Several models to simulate nanofiltration systems have been described in the literature [19–21]. Of these, the solution-diffusion model is one of the simplest since it is easy to use and predicts with an acceptable level of precision the results that can be obtained with reverse osmosis membranes.

The use of models in chemical engineering is very important because they can predict the behaviour of systems and improve interpretation of the results. As an example, our research group successfully applied a typical reverse osmosis model, the solution-diffusion model to predict aniline removal using reverse osmosis membranes [22].

In a previous work [23], atrazine removal was studied using four different nanofiltration membranes, two of them were made of polyamide (NF-99 and NF-97) and the other two were made of polypiperazineamide (DL and DK). As a next step, in this work, the solution-diffusion model is applied to the experimental data obtained in the above-mentioned work to test the extent to which the model predicts the behaviour of the four different nanofiltration membranes used for atrazine removal.

2. Materials and methods

2.1. Reagents

Atrazine with 97.4% purity was purchased from Sigma Aldrich. The properties and the molecular structures of the atrazine are depicted in Table 1.

2.2. Membranes

Two polyamide thin film composite membranes (NF-99, NF-97) manufactured by Dow Chemical and two polypiperazineamide thin film composite membranes (DL and DK) purchased from GE Osmonics were used. The characteristics of the membranes are described in Table 2.

2.3. Membrane test module

All the experiments were performed in an IND-EVEN flat membrane test module, which is designed

Table 1
Atrazine properties [24–26]

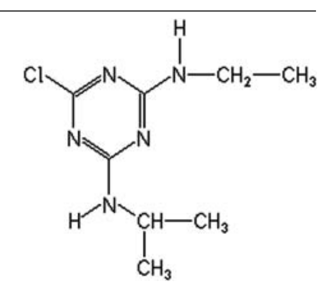
Chemical structure	
Molecular weight (g/mol)	215.69
Solubility in water (mg/L at 20 ℃)	20
Length (*A*)	10.36
Width (*A*)	8.02
Log K_{ow}	2.61
Dipole moment (*D*)	3.44

Table 2
Main characteristics of the membranes used in the experimental INDEVEN test module [23,27]

Provider	Alfa laval	Alfa laval	Indeven	Indeven
Manufacturer	Dow Chemical	Dow Chemical	GE Osmonics	GE Osmonics
Product denomination	NF-97	NF-99	DESAL-5 DL	DESAL-5 DK
Type	Thin-film composite polyester	Thin-film composite polyester	Thin-film composite polysulfone	Thin-film composite polysulfone
Composition	Polyamide	Polyamide	Polypiperazineamide	Polypiperazineamide
Molecular weight cut-off (MWCO) (Da)	≤200	≤200	340	230
Membrane surface area (m^2)	0.003	0.003	0.003	0.003
Maximum pressure (N/m^2)	55×10^5	55×10^5	40×10^5	3.45×10^5
$MgSO_4$ rejection (%)	≥97	≥98	96	98.5
pH range	3–10	3–10	1–11	2–11
Maximum temperature (℃)	50	50	90	50

for a maximum operating pressure of 70×10^5 Pa and which provides data concerning the behaviour of the membranes in cross-flow conditions. The module has a reduced surface area (3×10^{-3} m^2) and low feed flow (13.9×10^{-3}–83.3×10^{-3} m^3/s).

The experimental unit consisted of a closed stainless steel tank with a capacity of 15×10^{-3} m^3 equipped with a coil to provide a constant feed temperature, a flat sheet membrane module that supports the membrane and a high pressure pump which drives the feed solution through the membrane module.

The filtration cell had a rectangular cross section of 10 cm × 3 cm providing an effective filtration area of 30 cm^2. The experiments were carried out in recycling mode, so that the concentrate and permeate streams were returned to the feed tank. Temperature was strictly controlled at 18 ± 0.2 ℃ by circulating feed solutions through a stainless steel coil immersed in the feed tank. The test was run for 120 min. The feed flow was measured with a rotameter. Although the operational pressure was varied, the feed flow was kept constant by a valve after the rotameter, which regulated the flow.

2.4. Experimental procedure

Aqueous atrazine solutions in distilled water of between 3.5×10^{-3} kg/m^3 and 8.0×10^{-3} kg/m^3 were treated in the test module, where the feed stream was separated into two streams: one purified, "permeate" and the other concentrated, "concentrate". Both permeate and concentrate were recycled to keep the feed concentrations practically constant and to simulate a continuous process in a quasi-stationary state. The transmembrane pressures used during experiments were varied from 5×10^5 to 20×10^5 Pa.

2.5. Analytical method

Atrazine concentrations were determined using a Shimadzu UV-160 spectrophotometer. The maximum absorbance was determined at a wavelength of 230 nm. Standards concentrations from 0.1 to 10 mg/L were measured and the equation obtained was $A = 0.112 \times C$, with a correlation coefficient of $r = 0.996$. This method was seen to be adequate to determine atrazine in the range of concentrations used.

Membrane performance was measured in terms of membrane rejection (%R) and permeate flux (J_w). For dilute aqueous mixtures consisting of water and a solute, the selectivity of membrane towards the mixture is usually expressed in terms of the solute rejection coefficient [28]. This parameter, R, is a measure of the membrane 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 [29].

The flow or permeation rate, J_p, is defined as the volume flowing through the membrane per unit area and time, according to the following equation:

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

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

Table 3
Experimental planning

[Atrazine] (kg/m^3)	Pressure (Pa)	pH
Operating pressure variation		
6.5×10^{-3}	5×10^{5}	6.0
	10×10^{5}	
	15×10^{5}	
	20×10^{5}	
Atrazine feed concentration variation		
3.5×10^{-3}	15×10^{5}	6.0
4.5×10^{-3}		
6.5×10^{-3}		
8.0×10^{-3}		
pH variation		
6.5×10^{-3}	15×10^{5}	2.0
		4.0
		6.0
		8.0
		10.0

2.6. Experimental planning

In a previous paper [23], several experiments were carried out to study the influence of pressure, atrazine feed concentration and pH on atrazine rejection and solvent flux. Table 3 summarizes all the experimental conditions tested.

Experiments were allowed to reach the steady-state, as revealed by the constant atrazine concentration value in the permeate stream. The steady-state was considered to have been reached when the difference between the atrazine concentration values in the permeate stream in two consecutive measurements was lower than 3%, which occurred at 120 min. All the experiments were run in duplicate and a standard deviation value of 4.32% was obtained for the whole set of obtained data.

3. Solution-diffusion model

The solution-diffusion models [19,20,30] have been used to depict mass transfer through membranes, after determining the constants of the models experimentally. System mass balances together with solution-diffusion mass transfer models have been used to simulate the separation process. The model equations used in the present work have previously been discussed in other research works [31]. In addition, other authors have applied the same model to the behaviour of different organic compounds in nanofiltration and reverse osmosis membranes [10–12,22]. The equations used to predict the behaviour of the system are the following.

To obtain the solute concentration in the permeate:

$$C_p = \frac{C_a}{1 + \frac{A_w \cdot \Delta P}{B_s \cdot C_w} - \frac{\Psi \cdot C_a \cdot A_w}{B_s \cdot C_w}} \quad (3)$$

and in the permeate flux:

$$Q_p = \frac{J_w \cdot S}{C_{wp}} = \frac{A_w \cdot S}{C_w} \cdot \left(\Delta P - \Psi \cdot C_a + \frac{\Psi \cdot C_a}{1 + \frac{A_w \cdot \Delta P}{B_s \cdot C_w} - \frac{\Psi \cdot C_a \cdot A_w}{B_s \cdot C_w}} \right) \quad (4)$$

From Eqs. (3) and (4) it is possible to determine the solute concentration in the permeate and the volumetric permeate flux as a function of the solute feed concentration, C_f, the operating pressure, P, the osmotic pressure coefficient, Ψ, and the membrane size and characteristics expressed by the constants A_w (water permeability) and B_s (solute permeability). C_w is the solvent permeate concentration.

The solvent flux, J_w, depends on the hydraulic pressure applied across the membrane, ΔP, minus the difference in the osmotic pressures of the solutions on the feed and permeate side of the membrane, $\Delta\pi$, and can be expressed by the following equation:

$$J_w = A_w(\Delta P - \Delta\pi) \quad (5)$$

where A_w is the solvent permeability parameter, which can be determined as the slope of the representation of J_w vs. ΔP.

The solute flux depends on the solute concentration gradient across the membrane.

$$J_s = B_s(C_f - C_p) \quad (6)$$

where B_s is the solute permeability.
Taking into account that:

$$J_s S = Q_p C_p \quad (7)$$

$$J_w S = Q_p C_w \quad (8)$$

and dividing the previous expressions gives the following equation:

$$J_s = \frac{J_w C_p}{C_w} \quad (9)$$

Eq. (9) can be written as follows:

$$\frac{J_w C_p}{C_w} = B_s(C_f - C_p) \quad (10)$$

From the slope of Eq. (10), the values of B_s can be obtained.

Finally, for the osmotic pressure, the Van't Hoff equation, which relates osmotic pressure with concentration, can be used. Assuming constant temperature and introducing an osmotic pressure coefficient, ψ, considered to be constant for low to moderate solute concentrations [32], the Van't Hoff equation can be written as follows:

$$\Delta\pi = \psi(C_f - C_p) \tag{11}$$

Introducing the osmotic pressure coefficient into Eq. (5) and reorganizing the terms, the following equation is obtained:

$$\left(\Delta P - \frac{J_w}{A_w}\right) = \psi\,(C_f - C_p) \tag{12}$$

The osmotic pressure coefficient, ψ, can be determined from the slope of Eq. (12).

4. Results and discussion

4.1. Fitting the model: parameter determination

For the determination of A_w, distilled water was used as feed and fluxes were measured at pressures of 5×10^5, 10×10^5, 15×10^5 and 20×10^5 Pa. The initial feed flow for all membranes was 5.56×10^{-5} m^3/s. The fitting of the experimental data to Eq. (5), for the four membranes, is depicted in Fig. 1.

For the determination of B_s, from the slope of Eq. (10), and operating the experimental system with aqueous atrazine solutions at concentrations of 6.2×10^{-3}, 3.8×10^{-3}, 4.6×10^{-3} and 7.4×10^{-3} kg/m^3 and a feed flow of 5.56×10^{-5} m^3/s, it is possible to obtain the values of B_s for three of the membranes.

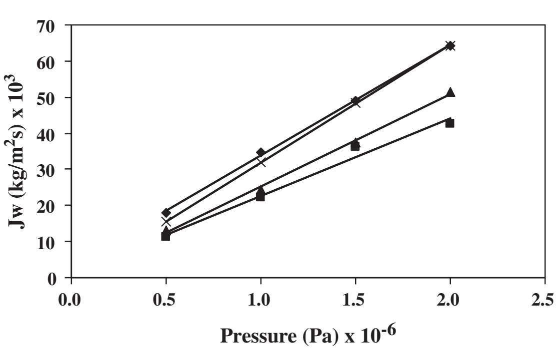


Fig. 1. Variation of solvent flux with operation pressure for the different membranes and feed flow of 5.56×10^{-5} m^3/s. Membranes: (■) NF-97, (◆) NF-99, (▲) DL and (×) DK.

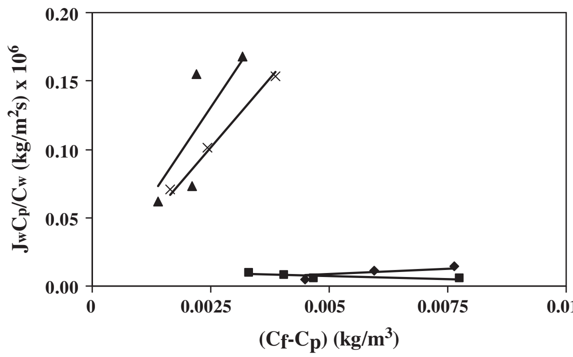


Fig. 2. Determination of B_s for the four membranes; operation pressure = 15×10^5 Pa. Membranes: (■) NF-97, (◆) NF-99, (▲) DL and (×) DK membrane.

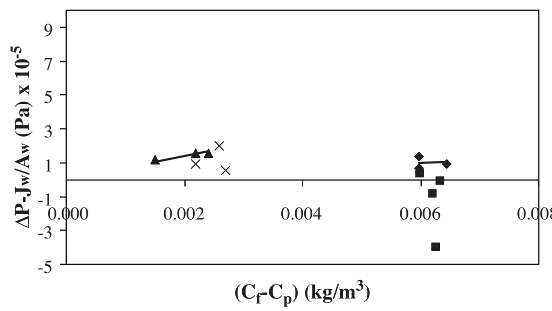


Fig. 3. Determination of ψ for the four membranes, aqueous atrazine feed solution = 0.0065 kg/m^3 and feed flow = 5.56×10^{-5} m^3/s. Membranes: (■) NF-97, (◆) NF-99, (▲) DL and (×) DK membrane.

Fig. 2 shows the fitting of Eq. (10) for the four membranes, C_w, C_p and C_f being the solvent, permeate and feed concentration, respectively.

For the determination of Ψ, experiments were carried out with an aqueous atrazine feed solution of 6.5×10^{-3} kg/m^3 and fluxes were measured at pressures of 5×10^5, 10×10^5, 15×10^5 and 20×10^5 Pa. The feed flow was fixed in all the experiments at 5.56×10^{-5} m^3/s. Fig. 3 shows the fitting of Eq. (12) for the four membranes.

The experimentally determined model constants (solvent permeability parameter, A_w, solute permeability parameter, B_s, and osmotic pressure coefficient, ψ)

Table 4
Solvent and solute permeability for all the membranes tested

Membrane	A_w (s/m)	B_s (m/s)	Ψ (m^2/s^2)
NF-97	2.23×10^{-8}	–	–
NF-99	3.28×10^{-8}	1.71×10^{-6}	1.82×10^{7}
DL	2.53×10^{-8}	5.24×10^{-5}	7.00×10^{7}
DK	3.21×10^{-8}	4.06×10^{-5}	1.34×10^{8}

are shown in Table 4 for all the membranes. It was not possible to obtain coefficient B_s for membrane NF-97 because the slope of the fitting was a negative value. For the same reason, it was not possible to calculate coefficient ψ for membrane NF-97.

Related to the obtained values for the permeability parameters from the results shown in Table 4, it can be observed that the highest water permeability was obtained for the NF-99 membrane. This behaviour can be explained from the data provided by the manufacturers, which are summarized in Table 1.

The corresponding statistical analysis, carried out using the software Sigma Plot V 10.0, is depicted in Table 5. In the case of the model parameter A_w, coefficients a and b from the linear regression showed a good linear fit for the four membranes. Both parameters have a good level of significance according to the values of the determination coefficient, R^2, the Student t-value and the probability p. The statistical analysis results for B_s were acceptable for all the membranes except NF-97. Finally, the NF-99 and DL membranes were the only ones that allowed a good fit to Eq. (12), which was used to determine parameter ψ. This suggests that the solution-diffusion model might not be appropriate to explain the behaviour of membranes NF-97 and DK. This assumption will be checked in Section 4.2.

In Table 4, it can be observed that the highest values of water permeability were obtained for membranes

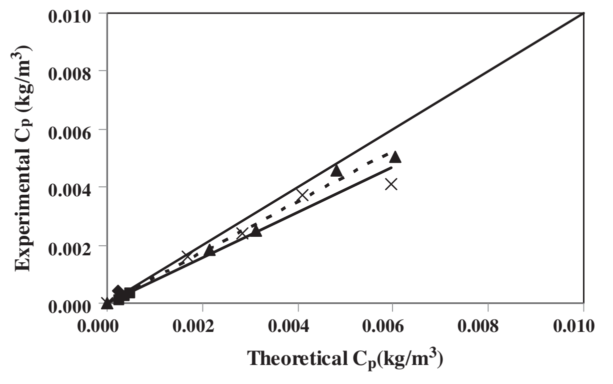


Fig. 4. Experimental and model permeate concentrations at different atrazine feed concentrations. Membranes: (◆) NF-99, (▲) DL and (×) DK.

Table 5
Statistical analysis for parameters A_w, B_s and ψ for the four membranes

Membrane	Model parameters	Linear regression to equation $y = a + bx$					Anova analysis	
		Coefficient	Value	R^2	t	p	F	p
NF-97	A_w	a	0.0004	0.9911	0.2510	0.8180	334.51	0.0004
		b	2.204E−8		18.2897	0.0004		
	B_s	a	1.13E−8	0.6461	–	–	–	–
		b	−8.30E−7		–	–		
	ψ	a	0	0.0909	0.0000	1.0000	0.2998	0.6221
		b	−1.8E+7		−1.1698	0.3266		
NF-99	A_w	a	0.0012	0.9981	1.2728	0.2928	1596.7018	<0.0001
		b	3.20E−8		39.9588	<0.0001		
	B_s	a	−2.66E−10	0.9996	–	–	–	–
		b	1.72E−6		–	–		
	ψ	a	0	0.8713	0.0000	1.0000	6.7716	0.2336
		b	1.82E+7		4.5781	0.1369		
DL	A_w	a	−0.0002	0.9990	−0.2729	0.8026	2987.1303	<0.0001
		b	2.544E−8		54.6546	<0.0001		
	B_s	a	−4.90E−9	0.8408	−0.1739	0.8730	15.8500	0.0284
		b	5.45E−5		3.9812	0.0284		
	ψ	a	0	0.9743	0.0000	1.0000	75.6880	0.0130
		b	7.00E+7		17.2118	0.0034		
DK	A_w	a	−0.0003	0.9999	−1.1831	0.3220	28422.21	<0.0001
		b	3.232E−8		168.5887	<0.0001		
	B_s	a	2.48E−9	0.9979	–	–	–	–
		b	3.97E−5		–	–		
	ψ	a	0	0.1068	0.0000	1.0000	0.3587	0.5914
		b	1.34E+8		1.4593	0.2406		

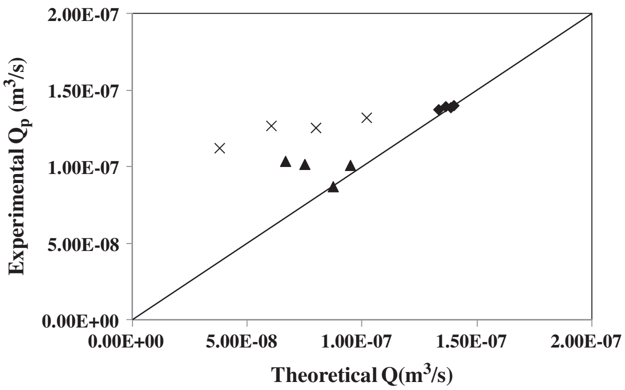


Fig. 5. Experimental and model volumetric permeate flux. Membranes: (◆) NF-99, (▲) DL and (×) DK membrane.

NF-99 and DK. This behaviour can be attributed to the intrinsic properties of these membranes (hydrophilicity, smaller active layer thickness, etc.) according to the data provided by the manufacturers, which are summarized in Table 2. For this reason, in the following, the applicability of the solution-diffusion model to the three membranes considered (NF-97 membrane is eliminated) will be discussed based on the statistical analysis of the experimental results and those predicted by the model and not on the nature of the membranes.

4.2. Checking the model: system simulation

With the estimated parameters of the model it is possible to obtain the solute concentration in the permeate stream and the volumetric permeate flux by means of Eqs. (3) and (4). The experimental and calculated values of these variables are represented in Figs. 4 and 5. The diagonal that appears in these figures represents the ideal level of accuracy between the experimental and the calculated values.

It can be observed from Fig. 4 that the model only accurately predicts the permeate concentrations for DL and DK membranes for low atrazine concentrations. Other authors [22,31], too, have demonstrated that the solution-diffusion model predicts the permeate concentrations when these concentrations are low. Membrane NF-99 shows good agreement between the experimental and the predicted atrazine concentrations in the permeate stream for the whole concentration range studied.

Using the above-mentioned software (Sigma Plot V 10.0), the above qualitative affirmations were checked by means of a statistical analysis. The calculated and experimental C_p values were fitted to the linear equation $y = a + bx$. Coefficients a and b from the linear regression are shown in Table 6, where the good linear fit for membranes NF-99, DL and DK can be seen.

Table 6
Statistical analysis for the permeate concentration

Membrane	Linear regression to equation $y = a + bx$					Anova analysis	
	Coefficient	Value	R^2	t	p	F	p
NF-99	a	−1.77E−5	0.9452	−0.4865	0.6747	34.5009	0.0278
	b	0.6417		5.8737	0.0278		
DL	a	−2.29E−5	0.9819	−0.1003	0.9264	217.5965	0.0007
	b	0.8761		14.7512	0.0007		
DK	a	0.0003	0.9504	0.8747	0.4461	57.5066	0.0048
	b	0.7133		7.5833	0.0048		

Table 7
Statistical analysis for the volumetric permeate flux

Membrane	Linear regression to equation $y = a + bx$					Anova analysis	
	Coefficient	Value	R^2	t	p	F	p
NF-99	a	1.25E−10	0.9992	–	–	–	–
	b	1.0116		–	–		
DL	a	7.98E−9	0.8613	0.4323	0.6947	18.6232	0.0229
	b	1.0907		4.3155	0.0229		
DK	a	3.03E−8	0.7444	1.1035	0.3504	8.7360	0.0598
	b	1.2295		2.9557	0.0598		

Besides, both parameters have a good level of significance according to the values of the determination coefficient, R^2, the Student t-value and the probability p. Furthermore, the values of the coefficients a and b for DK membrane are the closest to 0 and 1, respectively, and very close to the diagonal.

Fig. 5 depicts the experimental and theoretical volumetric permeate flux values. The results from the statistical test are shown in Table 7, where it is seen that the solution-diffusion model only correctly fits the results obtained with membrane NF-99.

5. Conclusions

The solution-diffusion model was applied to predict the behaviour of four nanofiltration membranes (two polyamide, NF99 and NF97, and two polypiperazideamide, DK and DL) using atrazine solutions. Linearization of the mass transfer equations permitted the different parameters of the model to be obtained and there was good agreemet between the experimental and the predicted atrazine concentrations for NF-99, DL and DK membranes when the atrazine concentration was low. Only membrane NF-99 provided accurate values for the different parameters in the range studied, which suggests that the solution-diffusion model can be applied to this membrane.

Based on these promising results, more studies are being carried out with the NF-99 membrane using different models in an attempt to improve the results.

Nomenclature

a	—	coefficient (intercept) in a linear regression
A_w	—	water permeability, s/m
b	—	coefficient (slope) in a linear regression
B_s	—	solute permeability, m/s
C_f	—	solute concentration in the feed stream, kg/m^3
C_p	—	solute concentration in the permeate stream, kg/m^3
C_w	—	solvent concentration in the permeate stream, kg/m^3
F	—	statistic F of Snedecor
J_p	—	permeate flux, m^3/m^2 s
J_s	—	solute flux, kg/m^2 s
J_w	—	solvent flux, kg/m^2 s
P	—	operation pressure, Pa
p	—	probability in the ANOVA analysis
Q_p	—	volumetric permeate flux, m^3/s
R	—	membrane rejection, %
R^2	—	coefficient of determination in a regression
S	—	membrane active area, m^2
t	—	statistic t of student
ΔP	—	hydraulic pressure applied across the membrane, Pa
$\Delta\Pi$	—	difference in the osmotic pressure of the solutions on the feed and permeate side of the membrane, Pa
Ψ	—	osmotic pressure coefficient, m^2/s^2

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