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Retention modelling of the bivalent cations in crossflow nanofiltration investigation in the porous models

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Abstract

Our work concerns the feasibility of certain models based on approach of a capillary type, and applied before in ultrafiltration process, for the prediction of the divalent salts retention by a nanofiltration membrane. The model solutions that we chose are those of cadmium and copper salts – whose cations constitute toxic elements introduced into the environment by the effluents coming from industries like those of surface treatment – calcium salt solutions, used within the framework of the nanofiltration softening of the aqueous solutions. The study of the bibliography on the salts retention through a membrane enabled us to formulate some observations: The flow of solvent depends on the membrane permeability; the aqueous solution flow depends on the solvent nature and membrane structure. On this basis, we also could highlight the existence of two mechanisms observed during the filtration of salts: the first, of type solubilization diffusion with the Donnan effect which does not take account of the membrane porosity; the second, electrokinetic who takes account of the membrane porosity. The mathematical models chosen, which seem quite suitable and which derive from this second type of mechanism are: TREMBLAY model; VERNIORY model; NAKAO model. The application of these mathematical models (for the study of the retention evolution of bivalent salts according to volumic flow) requires the development of a data-processing program which finally led to software simulation. We confronted this modeling with experimental results allowing to estimate the principal parameters of transport: the optimal pore radius, reflection coefficient σ and membrane permeability for solute P_S. Apparently, the comparison carried out between the experimental results and numerically results obtained (VERNIORY model in particular) gave a good correspondence for a pore radius close to that evaluated by porosimetry method [1]. Moreover, this confrontation authorized us to underline the essential role of certain parameters influencing

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the retention such as: pH, transmembrane pressure, temperature, concentration of solution treatment and components nature in the solution.

Keywords: Nanofiltration; Porous Models; Bivalent ions retention

1. Introduction

Our work concerns the feasibility of certain phenomenologic models, for the prediction of the retention of divalent salts by a membrane of nanofiltration. The model solutions that we chose are those of calcium salts, coppers and of cadmium, whose cations constitute toxic elements introduced into the environment by industrial effluents and the calcium salts used within the framework of the softening of the aqueous solutions Mehyguene et al (2000), Garba et al. (1998) [1,2].

This contribution lies in the treatment of a specific choice of the mathematical model based on the phenomenologic approach, of which the resolution, carried out using a data-processing program, will allow to model the retention of the divalent ions by a membrane of nanofiltration and its rejection will predict We will be able consequently to determine the electric properties of the membrane. This simulation will be followed of a validation by the experimental results found in our former work Chaabane et al. 2003 [3]. It is within this framework that our study is.

2. Theoretical aspect

2.1. Pore theory and associated modeling

Two mechanisms were established to describe the transfer of matter through the membranes charged:

- solubilization-diffusion with Donnan effect;
- electrokinetic.

With the outlet of these two mechanisms, two types of models were elaborate:

- the first group of models supposes that the membrane is nonporous;
- the second admits that it is microporous.

This model, suggested by Verniory, takes account of the existence of a convective steric embarrassment allowing obtaining the membrane parameters estimated by Kedem [4] and has L, in fact:

- the coefficient of permeability of the membrane to the solution (ω),
- the coefficient of reflexion of the membrane (σ). The flow of the aqueous solution will then be given by the following expression:

$$J_s = D_{2y}\, f(\lambda) F_d \frac{A_k}{\Delta_y}(X_a - Z_2) + J_v Y_2^* g(\lambda) F_c \qquad (1)$$

Where $\lambda = \frac{r_S}{r_P}$

R_s is STOCKS radius defined by $r_S = \frac{K_S T}{6\pi\mu D_s}$ (2)

With $F_d = (1-\lambda)^2$ et $F_c = 2(1-\lambda)^2 - (1-\lambda)^4$

$$f(\lambda) = \frac{1 - 2.1\,\lambda + 2.1\,\lambda^3 - 1.7\,\lambda^5 + 0.73\,\lambda^6}{1 - 0.76\,\lambda^6} \qquad (3)$$

$$g(\lambda) = \frac{1 - 0.66\,\lambda^2 - 0.2\,\lambda^5}{1 - 0.76\,\lambda^6} \qquad (4)$$

$$\sigma = 1 - g(\lambda)\, F_c \qquad (5)$$

$$\omega = D_{2y}\, f(\lambda)\, F_d\, \frac{A_k}{RT\Delta Y} \qquad (6)$$

The $A_k/\Delta y$ ratio is evaluated from the following equations according to two cases [60]:

- taking account of the water radius:

$$\frac{A_k}{\Delta_y}=\frac{8\ \mathrm{Lp}\mu}{{r_p}^2}\left[2\left(1-\frac{r_{eau}}{r_p}\right)^2-\left(1-\frac{r_{eau}}{r_p}\right)^4\right] \quad (7)$$

Where Lp: hydraulic permeability ;

- neglecting the:

$$\frac{A_k}{\Delta_y}=\frac{8L_p\mu}{{r_p}^2} \quad (8)$$

Finally the rate of retention is expressed by the following relation:

$$R=1-\frac{1-\sigma}{1-\sigma\exp\left(\frac{\sigma-1}{\omega}J_v\right)} \quad (9)$$

2. 2. *Model of the steric embarrassment of pore (SHP: Steric hindrance pore)*

In order to consider the parameters structural A_K and R_p starting from the parameters of the membrane σ and P, a model of pore was developed and applied by *Nakao et al.* By combining it with the theory of irreversible thermodynamics, we obtained the following results:

– steric parameters are:

$$H_F=1+\frac{16}{9}\lambda^2 \quad (10)$$

$$H_D=1 \quad (11)$$

−average partition coefficients are expressed by the following equations:

$$S_F=(1-\lambda)^2 \quad (12)$$

$$S_D=(1-\lambda)^2[2-(1-\lambda)^2] \quad (13)$$

2. 3. *VERNIORY model*

This model makes it possible to obtain the membrane parameters of Speigler and Kedem [5], i.e. the coefficient of permeability of the solution (ω) and the coefficient of reflexion (σ) by applying the relations of the theory of the pore: $\sigma=1-g(\lambda)F_c; \omega=D_{2y}f(\lambda)F_d\ \frac{A_k}{\mathrm{RTY}}$

2. 4. *Modèle de Nakao*

Nakao tried to combine the theory of irreversible thermodynamics Nakao et al. (with the theory of the pore. Indeed, it proposes to determine the parameters directly (σ_S) and (P_S) relating to the equation of Speigler and Kedem [5] starting from the structural and physicochemical data of the membrane and the aqueous solution.

The parameter steric are: H_F and H_D

2. 5. *Modèle de tremblay*

Tremblay [6] sought to adapt the model of the fine pore to the membranes of nanofiltration; it used for that an average value of (b), given by:

$$\overline{b^{-1}}=(1-\lambda)^2 b^{-1}$$

Moreover, Tremblay proposes the following equations to calculate the coefficients of division ($P_{y/x}$) and ($P_{z/y}$):

$$P_{y/x}=\frac{1-0.76\ \lambda^5}{1-2.105\ \lambda+2.0865\ \lambda^3-1.7068\ \lambda^5+0.72603\ \lambda^6} \quad (14)$$

$$P_{z/y}=\frac{1-\frac{2}{3}\ \lambda^2-0.20217\ \lambda^5}{1-2.105\ \lambda+2.0865\ \lambda^3-1.7068\ \lambda^5+0.72603\ \lambda^6} \quad (15)$$

Π_1 and Π_2 are calculated starting from the following equations:

$$\Pi_1=R\ T\ C_m \quad (16)$$

$$\Pi_2=R\ T\ C_p\ =R\ T\ C_o(1-R_{exp}) \quad (17)$$

C_m: concentration of the aqueous solution stopped close to the membrane.

C_p: concentration of the aqueous solution in the perméat.

C_0: average concentration of the aqueous solution in the solution.

Thus we end to the expression of the rate of following retention:

$$R = 1 - \frac{\left(\frac{P_{y/x}}{\bar{b}}\right)\exp(\alpha)}{\left(\frac{P_{z/y}}{\bar{b}}\right) + \exp(\alpha) - 1} \qquad (18)$$

3. Results & discussion

The pilot of nanofiltration was of type Millipore Proscale, the membrane used of spiral commercialised by Millipore Proscale (Molsheim, France): Nanomax 50. The polymers using the manufacture of this membrane are of polyamide type/polysulphone. It had a membrane surface of 0.37 m^2 and the cut 400 Da, and a pore radius estimated approximately 0.5 Nm according to manufacturing, of 0.47 Nm according to work's of Jeantet and Maubois (1994) [1]. The isoelectric point of the membrane according to the searcher Jeantet lies between 4.3 and 4.4.

The equations above were used for the prediction of the bivalent ions retention. The model parameters are obtained using a program in language FORTRAN power station which was elaborate while varying the parameters σ and P_S in a suitable interval for a minimal difference between the theoretical and experimental retention.The results are gathered in Tables 1, 2, 3 and 4.

3. 1. *Calculations relating to the method of Verniory*

The physicochemical parameters which enter the calculation of the model of Verniory are gathered below:

T = 293 K; Kboltz = 1.38×10^{-23}; Reau = 0.15 nm; D (Ca^{2+}) = 7.92×10^{-10} m^2/s; D (Cu^{2+}) = 7.14×10^{-10} m^2/s; D (Cd^{2+}) = 7.19×10^{-10} m^2/s

Table 1
Rétentions théoriques et expérimentales des sels de cadmium

$[Cd^{2+}]$ = 5 ppm				
	$Cd(NO_3)_2$		$CdCl_2$	
	R_p = 0.451 nm		R_p = 0.455 nm	
$J_v \times 10^{+6}$ (m/s)	% R_{th}	% R exp	% R_{th}	% R exp
0.00	0.00		0.00	
0.60	30.8919	30.90	28.0969	28.10
2.50	32.0053	32.00	29.7007	29.70
7.50	34.1005	34.10	32.7988	32.80
11.33	35.6035	35.60	34.6004	34.60
14.97	37.0985	37.10	34.8006	34.80
19.73	39.3940	39.40	40.4004	40.40
25.03	40.8001	40.80	42.6012	42.60
27.80	42.4028	42.40	43.9996	44.00
30.00	42.3969	42.40	45.3999	45.40

Table 2
Nakao model parameters for a calcium salt at (pH = 4.5 and T = 20°C) in the case of not neglecting the ionic radius water

$[Ca^{2+}] = 0.5$ mM							
R_p (nm)	λ	H_F	S_D	S_F	$A_k/\Delta Y$ (m^{-1})	σ_S	P_S (m/s)
0.270	1.003	2.789	0.000009	0.000019	2491083.676	0.999945	$1.931*10^{-8}$
0.280	0.967	2.663	0.001069	0.002137	2316326.530	0.994308	$1.961*10^{-6}$
0.300	0.903	2.449	0.009444	0.018800	2017777.777	0.953957	$1.905*10^{-5}$
0.334	0.811	2.169	0.035753	0.070227	1627892.878	0.847673	$4.609*10^{-5}$
0.361	0.749	1.998	0.062869	0.121787	1389765.112	0.756665	$6.920*10^{-5}$
0.368	0.736	1.963	0.069679	0.134503	1341119.691	0.735956	$7.401*10^{-5}$
0.400	0.677	1.815	0.104256	0.197644	1135000.000	0.641260	$9.371*10^{-5}$
0.500	0.542	1.522	0.210048	0.375976	726400.000	0.427895	0.0001208
0.600	0.451	1.362	0.300953	0.511333	504444.444	0.303432	0.0001202

Table 3.
Theoretical and experimental retentions of calcium salts

$[Ca^{2+}] = 0.5$ mM						
	$Ca(NO_3)_2$		$CaCl_2$		$Ca(CH_3COO)_2$	
	$R_p = 0.368$ nm		$R_p = 0.361$ nm		$R_p = 0.334$ nm	
J_v*10^{+6} (m/s)	R_{th}	R_{exp}	R_{th}	R_{exp}	R_{th}	R_{exp}
0.00	0.00	#	0.00	#	0.00	#
1.16	12.7440	12.74	13.4437	13.44	10.8611	10.87
11.46	18.1965	18.20	20.1620	20.17	32.6141	32.62
22.51	20.0165	20.02	21.8444	21.85	36.2414	36.24
30.70	20.0147	20.02	21.8440	21.85	36.2414	36.24

The parameters of the model are:

$$\text{Sigma\_S} = 1 - g(\lambda)F_C \quad \text{et} \quad \text{w} = D\, f(\lambda)F_d\, \frac{A_k}{\Delta y}$$

The rate of retention is then expressed by:

$$\text{TR}_{th} = 1 - \frac{1 - \text{sigma}}{1 - \text{sigma}\exp\left(\frac{\text{sigma}-1}{\text{W}} J_v\right)}$$

3. 2. Calculations relating to the method of Nakao

the model parameters are:

$$\text{Sigma\_}S = 1 - H_f{}^*S_{f_{et}}\ P_S = H_d{}^*S_d{}^*D_S{}^*(RA_k\text{\_}D_y)$$

The rate retention is then expressed by:

$$\text{TR}_{th} = \text{sigma\_}S^* \frac{(1-F)}{(1-\text{sigma\_}S^*F)}$$

3.3.Calculations relating to the method of Tremblay

3. 4. Détermination de la rétention des sels

For the development of the model, it is necessary to take account of the system of operation of the pilot, and the considerations based on the experimental results.

Table 4.
Rétentions théoriques et expérimentales des sels de calcium

		Salt: $CuCl_2$ $[Cu^{2+}]$ = 0.5 mM				
ΔP (bars)	% R Expérimentale	R_p (nm)	λ	$\alpha 10^3$	b	% R
1.5	54.00	0.2972	1.0106	2.2993	33.2694	54.21
		0.3038	0.9888	2.4051	23.4431	53.77
2.5	62.00	0.2967	1.0122	3.8255	34.4448	61.61
		0.2968	1.0121	3.8264	34.3609	62.19
5.0	78.00	0.3043	0.9872	4.0278	23.0062	61.73
		0.2967	1.0124	7.6585	34.6260	77.89
		0.3043	0.9870	8.0701	22.9499	77.93
7.5	78.50	0.3044	0.9869	8.0719	22.9219	77.62
		0.2960	1,0148	11.4382	36.6389	78.63
		0.3052	0.9842	12.1822	22.2562	78.40
10.0	79.00	0.3059	0,9819	16.3265	21.7200	78.71
		0.2954	1.0167	15.1938	38.4997	79.07

In all that follows we will consider that:

- the fluid is Newtonien and the membrane is inert (not reaction with solvent or the aqueous solution);
- the aqueous solutions are rigid spherical molecules with ray rs;
- voluminal flows within the pore obey the law of One tenth of a poise;
- the solutions are diluted and the flow is in tangential mode in order to avoid accumulation continues aqueous solution in the vicinity of the membrane (to avoid the phenomenon of polarization of the concentration),
- the pores are uniform of ray RP and length L much higher at R_P;
- the solution circulates at constant speed and the state of balance is reached.

These results were obtained by weak concentrations. Fig. 1, 2 and 3 show that the density of load evolves/moves with the concentration, and depends on the nature of salt. The same result was found by other researchers.

The possible explanation is that this dependence is due to the interactions between the free ions in the solution and the membrane where each ion individually contributes to the load of the membrane by adsorption Combe et al (1996) [8].

A variation of the coefficient of reflexion causes a variation of the density of load. This can be explained by the relation which binds the coefficient of reflexion to the rate of retention.

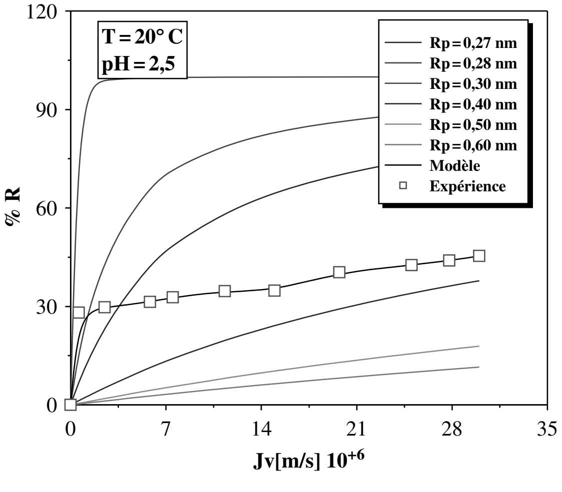

Fig. 1. Evolution de la rétention du sel $CdCl_2$ en fonction du flux du perméat (Cd^{2+}) = 5 ppm – Rp_{moyen} = 0.360 nm.

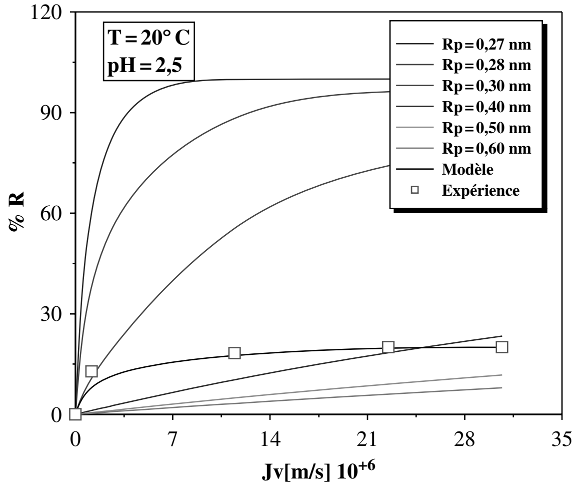

Fig. 2. Evolution de la rétention du sel $Ca(NO_3)_2$ en fonction du flux du perméat $(Ca^{2+}) = 0.5$ mM – $Rp_{moyen} = 0.368$ nm.

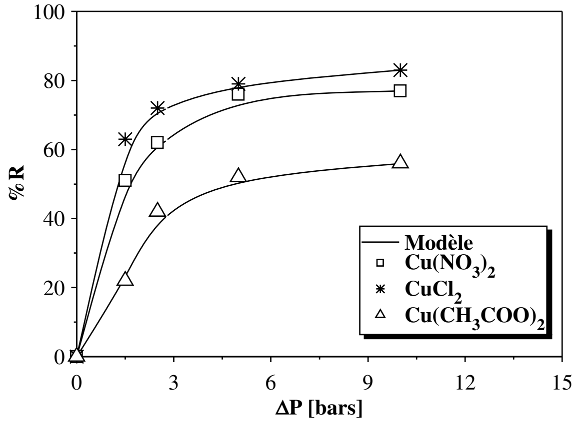

Fig. 3. Evolution du taux de retention des sels de cuivre en fonction de la pression transmembranaire $(Cu^{2+}) = 1$ mM $-$ Rp $= 0.3033$ nm.

4. Conclusion

The study of the bibliography on the retention of salts through a membrane of nanofiltration enables us to formulate some note:

- the flow of solvent depends on the permeability of the membrane;
- the flow of the aqueous solution depends on the nature of solvent and the structure of the membrane.

On this basis, we also could highlight the existence of two mechanisms observed during the filtration of salts:

- the first, of type solubilization diffusion with the effect DONNAN, which does not take account of the porosity of the membrane;
- the second, electrokinetic who takes account of the porosity of the membrane.

The mathematical models chosen, which seem quite suitable and which derive from this second type of mechanism are:

- Tremblay model;
- Verniory model;
- Nakao model.

The application of these mathematical models (for the follow-up of the evolution of the retention of bivalent salts according to voluminal flow) requires the development of a data-processing program (in our case in Language Borland Pascal) which finally led to a software of simulation. This modeling was also confronted with experimental results making it possible to estimate the principal parameters of transport (the ray of the optimal pore, the coefficient of reflexion σ and the permeability of the membrane P_S).

Apparently, the comparison carried out between the experimental results and the results obtained numerically (with the model of VERNIORY in particular) gave a good correspondence for a ray of pore close to that evaluated by Lydie et al., 2004 [9].

Moreover, this confrontation underlines the essential role of certain parameters influencing the retention such as: pH, pressure, the temperature, concentration out of salt and the nature of the aqueous solution.

Lastly, for a better modeling, it would be necessary to introduce corrective factors taking account of the various parameters playing a considerable role into the mechanism of transfer (such as the electric potential of the membrane, the density of density of surface charge and the potential of flow) or to develop other models which take account of these factors in fact those derived from the equation of Nerst Planck.

Symbols

A	permeability of the membrane to solvent (m/s/Pa)
A_k	porosity of the membrane (–)
a_i	activity of component I (kmol/m^3)
B	permeability of the membrane to the aqueous solution (m/s)
b	parameter of friction (–)
C_0	average concentration of the aqueous solution in the solution of food (mol/m^3)
C_m	concentration of the aqueous solution on the surface of the membrane (mol/m^3)
C_p	concentration of the aqueous solution in the perméat (mol/m^3)
C_i	concentration in the pore of component I (mol/m^3)
D_{1y}	coefficient of diffusion of solvent in the membrane (m^2/s)
D_{2y},D_{2x}	coefficient of diffusion of the aqueous solution in the solution upstream (m^2/s)
D_i	coefficient of diffusion in the pore of component I (m^2/s)
D_s	coefficient of diffusion of the aqueous solution in the membrane (m^2/s)
D_m	coefficient of diffusion of the electrolyte in the pore (m^2/s)
F	constant of Faraday (96500 Coulomb)
H	hydrodynamic permeability (m^{-3} s^{-1} kg^{-1})
H_D	steric parameter connected to the factors of correction of the effect of wall in diffusion (–)
H_F	steric parameter connected to the factors of correction of the effect of wall in convection (–)
J_v	flow of the perméat (m/s)
J_s	flow of the aqueous solution (mol m^2/s)
K	Boltzmann constant (1.38*10–23 J/K)
K_{2x}	coefficient of transfer of the aqueous solution in the solution upstream (m/s)
K_{2y}	coefficient of transfer of the aqueous solution in the membrane (m/s)
L	length of the pore (m)
L_p	permeability of the membrane to solvent (m/s/Pa)
M	mass molar aqueous solution (g/mol)
N	a number of pores per unit of area of the membrane (m^{-2})
$P_{y/x}$	coefficient of division of the aqueous solution enters the membrane and the solution upstream (-)
$P_{z/y}$	coefficient of division of the aqueous solution enters the membrane and the solution downstream (-)
P_1	specific hydraulic permeability of the membrane (m^2/s)
P	local permeability of the aqueous solution (m^2/s)
P_s	permeability of the aqueous solution (m/s)
ΔP	difference in pressure on both sides of the membrane (Pa)
q_w	surface density of load (Coulomb/m^2)
R	real rate of retention (%)
R	constant of perfect gas (0.082 l atm K^{-1} mol^{-1}).
R_p	ray of a pore of the membrane (m)
R_s	ray of Stokes of the aqueous solution (m)
R_o	rate of retention observed (%)

S_D partition coefficient of the aqueous solution in diffusion (–)

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