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Treatment of Aqueous Solutions Containing Chromium - Experimental Study and Modeling

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Ultrafiltration is an important technique in the recovery of metal cations from aqueous solutions, this technique is in most cases associated with a complexation reaction, it increases the size of the cations in solution to be retained by the ultrafiltration membrane; in this first part of the work, we are interested only to the effect of pH on the complexation reaction of trivalent chromium by the complexing agent (ethylene diamine tetra-acetate: EDTA), knowing that it is the important parameter in this type of reaction, it can give the percentage of the different species in solution. The second part is devoted to the experimental study of the ultrafiltration of Cr-EDTA complex, carried out in a pilot of ultrafiltration, in order to determine the total transfer resistance of the liquid through the ultrafiltration membrane, this resistance is used for modeling the tangential flow of the Cr-EDTA solution in a tubular membrane for understanding the effect of some parameters (Reynolds and Peclet numbers) on membrane fouling in the treatment of water solutions containing Cr-EDTA complex, using transport equations, Navier-Stokes and continuity; resolution is carried out by the finite volume method, and the results showed that the deposition of solute on the membrane is more important for small Reynolds number values range of 200 to 400 and for large Peclet number values in the range of 10^4 to 10^5.

1. Introduction

Membrane processes are among the reliable technologies, effective in the treatment of wastewater and economically with low energy consumption. The basic idea of complexation-ultrafiltration is a fixation of metallic ions on macromolecular species, which is performed to increase their molecular weight. These compounds become larger than the membrane pore sizes, they can be recovered after filtration, at the same time water is purified (Trivunac et al., 2006). The membrane is characterized by a coefficient of hydraulic permeability depending on its thickness, the number of pores and their dimensions (Lutz et al., 2013). In practice, the filtration of solutions is provided inside the hollow fibers and tangentially to the membrane to minimize the accumulation of species that may be retained (Chikhi et al., 2008). In the present work, an experimental study of a solution containing Cr-EDTA complex is performed on an ultrafiltration apparatus; the resistance in series model coupled with transport, continuity and Navier-Stokes equations are used for modeling the flow in the tubular module.

2. Materials and method

After preparing solutions of chromium from the compound $CrCl_3$, $6H_2O$ and EDTA from Fluka Chemika, the complexation reaction is carried out according to the optimum conditions (agitation = 600 rpm, $[Cr^{3+}]_0$=0.003mol/L, $[EDTA]_0$=0.095mol/L, T=20°C) (Balaska et al., 2012), in the first part the influence of pH on the reaction kinetic is shown; and in the second one the resulting solution (containing Cr-EDTA) is introduced into a feed tank ultrafiltration apparatus. The feed solution is circulated by a pump with a variable speed motor (PCM R0.4H12, Moineau, France), the permeate is collected in a test tube, while the

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concentrate is recycled to the feed vessel. The solution volume used is 3L, the tubular membrane (D=10^{-2} m, L=1.2m) was made of ZrO_2 and the solvent is distilled water. The transmembrane pressure (TMP) is being controlled between 1 and 2.5 bars by the adjustment of the pump and by the introduction of compressed air to the feed tank. The permeate samples are analyzed by a UV-Visible spectrophotometer at a wavelength of 540nm to determine different concentrations of the solute. From these concentrations, the rejection efficiency of the membrane is determined by the following expression (Paulo et al., 2011):

$$R.E. = \left(1 - C_i / C_0\right) 100 \tag{1}$$

with *R.E* the rejection efficiency; C_i and C_0 are the permeate and initial concentrations.

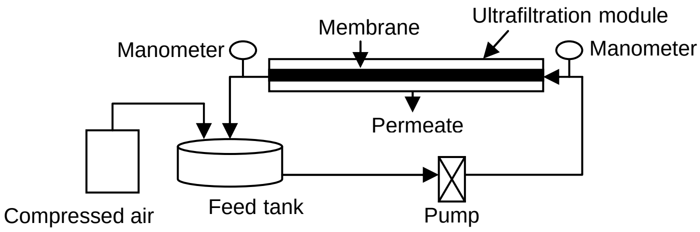


Figure 1: Ultrafiltration apparatus

3. Mathematical model

The liquid, flows tangentially in the tubular membrane, is modeled by transport, continuity and Navier-Stokes equations. In addition, the flow is considered axisymmetric, only the half of the membrane is considered.

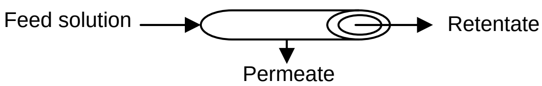


Figure 2: Tubular membrane of ultrafiltration (cylindrical module)

3.1 Equations of transport, continuity and Navier-Stokes

In a fluid where concentration is not uniform, the mass fluxes obey to the equations of balance expressing the conservation of the mass in an element of fluid (Bird et al., 2002).

$$\frac{\partial C}{\partial t} + \frac{\partial}{\partial z}\left(C\, u_z - Diff\, \frac{\partial C}{\partial z}\right) + \frac{1}{r}\frac{\partial}{\partial r}\left(C\, r\, u_r - Diff\, r\, \frac{\partial C}{\partial r}\right) = 0 \tag{2}$$

The mass balance of the fluid which crosses a unit volume is expressed by :

$$\frac{1}{r}\frac{\partial(r\, u_r)}{\partial r} + \frac{\partial(u_z)}{\partial z} = 0 \tag{3}$$

A mathematical description of fluid motion is given by Navier-Stokes equations :

$$\rho\left(\frac{\partial u_r}{\partial t} + u_r\frac{\partial u_r}{\partial r} + u_z\frac{\partial u_r}{\partial z}\right) = \mu\left(\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial}{\partial r}(r\, u_r)\right) + \frac{\partial^2 u_r}{\partial z^2}\right) - \frac{\partial P}{\partial r} + \rho\, g_r \tag{4}$$

$$\rho\left(\frac{\partial u_z}{\partial t} + u_r\frac{\partial u_z}{\partial r} + u_z\frac{\partial u_z}{\partial z}\right) = \mu\left(\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial u_z}{\partial r}\right) + \frac{\partial^2 u_z}{\partial z^2}\right) - \frac{\partial P}{\partial z} + \rho\, g_z \tag{5}$$

u_z , u_r : dimensional velocities, axial and radial.
ρ, μ : density and viscosity of fluid.
P, *g*, *Diff* : pressure, gravity and diffusion coefficient .
The dimensionless general transport equation of a variable for an incompressible fluid in cylindrical coordinates, is written as follows:

$$\frac{\partial C}{\partial t^*}+\frac{1}{R}\frac{\partial(RV\,C)}{\partial R}+\frac{\partial(U\,C)}{\partial Z}=\frac{1}{R}\frac{\partial}{\partial R}\left(R\frac{1}{Pe}\frac{\partial C}{\partial R}\right)+\frac{\partial}{\partial Z}\left(\frac{1}{Pe}\frac{\partial C}{\partial Z}\right) \quad (6)$$

U,V, R, Z, P and t^* are dimensionless variables. With:

$$U=\frac{u_z}{u_0}\ ;\ V=\frac{u_r}{u_0}\ ;\ Z=\frac{z}{D}\ ;\ R=\frac{r}{D}\ ;\ P=\frac{p}{\rho\, u_0^2}\ ;\ t^*=\frac{t\, u_0}{D}$$

With: D is the diameter of the membrane(m).
The equations (solute transport, continuity and Navier-Stokes) are discretized to obtain linear algebraic equations of the general form of the equation (7), with Φ the considered variable:

$$A_P\,\Phi_P^{(t+\Delta t)}=A_E\,\Phi_E^{(t+\Delta t)}+A_W\,\Phi_W^{(t+\Delta t)}+A_N\,\Phi_P^{(t+\Delta t)}+A_S\,\Phi_S^{(t+\Delta t)}+b \quad (7)$$

3.2 Application of the model to the ultrafiltration of Cr-EDTA solution in a cylindrical module
The resulting model is the transport phenomena occurring in a cylindrical membrane (tubular) with radius R and length L, for laminar flow. However, the following assumptions were adopted (Paris et al., 2002):
- The liquid density is constant, and considered equal to that of pure solvent;
- The fluid is incompressible;
- The axial diffusion is neglected;
- The radial diffusion and convection are taken into account.

The surface of the membrane is permeable, so the boundary condition reflects equality between the diffusive and the convective fluxes, the latter is function of the permeate flow which is presented by the resistance in series model.

- Initial and boundary conditions
Initial and boundary conditions (dimensional) are as follows:

$$C(0,r)=C_0\,;\ \frac{\partial C(z,0)}{\partial r}=0\,;\ \frac{\partial C(L,r)}{\partial z}=0\,;\ C(z,R))\,J=Diff\,\frac{\partial C(z,R)}{\partial r} \quad (8)$$

$$u_z(0,r)=u_0\ ;\ u_r(z,0)=0\,;\ \frac{\partial u_z(z,0)}{\partial z}=0\,;\ u_r(z,R)=J\ ;\ u_r(L,r)=0\ ; \quad (9)$$

The solution of the model was obtained by the use of finite volume method in non-uniform mesh in radial direction and uniform in the axial direction, with the parameters values specified in the corresponding figure captions; taking account initial and boundary conditions, using FORTRAN language. The resistance in series model is used to determine the permeate flux.

4. Results

4.1 Influence of pH on complexation kinetics of Cr (III) by EDTA
The complexation reaction of chromium by EDTA is presented in the following equation:

Cr^{3+} + EDTA $\leftrightarrow$ Cr-EDTA (10)

For a pseudo first order reaction, we obtain (Balaska et al., 2012):

$$\ln((A_{\inf}-A)/(A_{\inf}-A_0))=-k_{app}\,t \quad (11)$$

Where k_{app} is the apparent rate constant; A_0, A, $A_{\inf}$ the absorbance initially, at time t and at infinite time, respectively; and t is the time.
In this part, we try to study the influence of pH on the complexation reaction because it's an important parameter which can give the necessary information to avoid the precipitation of any cation in the form of hydroxides.

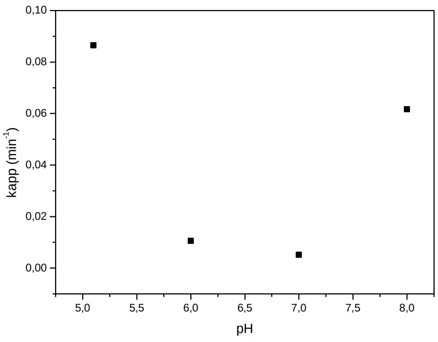


Figure 3: Influence of pH on kinetic complexation reaction

The figure 3 shows that a pH of 5.1 is favourable for the complexation reaction of chromium by the EDTA, for this value of pH the EDTA is in the form of H_2Y^{2-}. However, a less significant elimination of chromium is observed when the pH of the solution incresaes to neutral value. According to this figure, an important reduction in the cation concentration corresponding to a high value of k_{app} is obtained for a further increase of the pH to 8. This may be due to a competition between the precipitation and the complexation reactions, where most of chromium was precipitated in the form of hydroxides $Cr(OH)_3$.

4.2 Determination of total resistance by ultrafiltration of Cr-EDTA

The ultrafiltration of the feed solution containing mainly the Cr-EDTA, was undertaken. It is known that ultrafiltration of a solution containing a solute causes accumulation near the membrane, resulting in a concentration gradient in the boundary layer. This phenomenon is called concentration polarization leads to a decrease in the flow in the separation diverges then the relationship of Darcy becomes (resistance in series model) (Benbrahim et al., 1998):

$$J = \frac{\Delta P}{\mu(R_m + R_c + R_p)} = \frac{\Delta P}{\mu R_T} \qquad (12)$$

where: R_m: hydraulic resistance of the membrane (m^{-1}), R_c: clogging resistance (m^{-1}), R_p: polarization resistance (m^{-1}), R_T: total resistance (m^{-1}), μ : dynamic viscosity of the solution (Pa.s).

Therefore the variation of the permeate flux according to the transmembrane pressure using the Cr-EDTA solution (Figure 4) can determine graphically the total resistance to the transfer of liquid through the ultrafiltration membrane. The slope of this line is equal to:

$$\frac{\Delta P}{\mu R_T} \qquad (13)$$

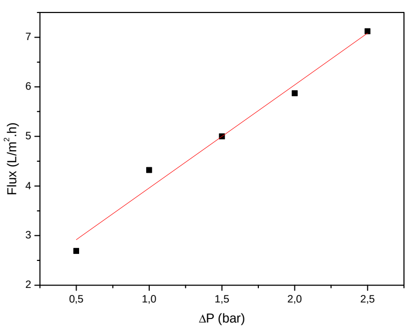


Figure 4: Graphical determination of the total resistance

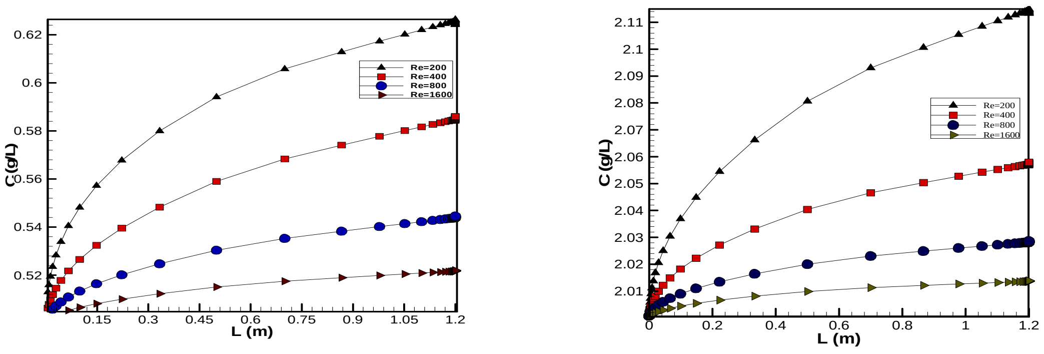
The value of the total resistance (R_T= 1.729.10^{14} m^{-1}), is used in the computer code for the hydrodynamic study of the complex solution in Cr-EDTA in tubular ultrafiltration module.

4.3 Numerical Simulation of the flow of the feed solution into a tubular module ultrafiltration

In this part, the study of the flow by numerical simulation of a solution containing Cr-EDTA in a tubular ultrafiltration module is carried out. The flow is tangential and the influence of Reynolds and Peclet numbers on the solute concentration is presented in this section.

4.3.1 Influence of the Reynolds number

Figures 5 ((a) and (b)) show the variation of the concentration of solute at the membrane surface as a function of its length (L) for different Reynolds numbers. Concentrations of the solute: 0.5 and 2 g/L.



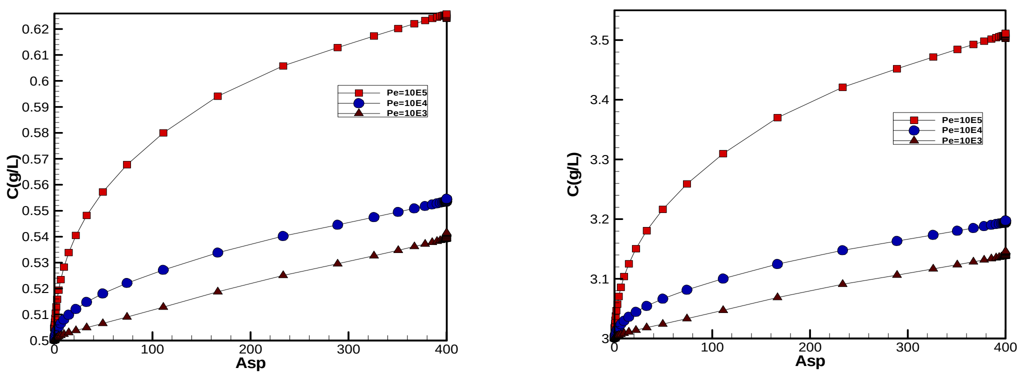
(a) (b)

Figure 5 ((a) and (b)): variation of the Cr-EDTA concentration at the membrane surface as a function of its length for different values of the Reynolds number: (a) $C_0 = 0.5$ g / L , (b) $C_0 = 2$ g / L.

According to Figure 5 ((a) and (b)), the solute concentration increases with the length of the membrane and decreases with the Reynolds number. When this latter increases, the solute concentration decreases thereby preventing the formation of solute deposition on the surface of the membrane, we can say that the increase in the velocity of liquid promotes membrane filtration, because the great problem of this technique is the polarization concentration of the membranes which reduces their efficiency. At a certain length of the membrane, the solute concentration at the surface becomes more and more constant.

4.3.2 Influence of the Peclet number

Figures 6 ((a) and (b)) show the variation of the concentration of solute at the surface of the membrane as a function of dimensionless length (L/D = Asp) for different Peclet numbers. Concentrations of the solute: 0.5 to 3 g/L.



(a) (b)

Figure 6 ((a) and (b)): variation of the concentration of solute at the surface of the membrane depending on its length dimensionless (Asp) for different values of Peclet number (a) $C_0 = 0.5$ g / L , (b) = $C_0 = 3$ g / L.

The Peclet number represents the ratio of convective and diffusive fluxes. Its variation along the membrane (depending on the Asp) is shown in Figure 6 ((a) and (b)). The increase of the Peclet number promotes clearly convection relatively to diffusion, thus leading to an increase in concentration at the surface of the membrane.

5. Conclusion

This work summarizes two major parts:

- The experimental study of the complexation reaction of Cr^{3+} with Cr-EDTA, and ultrafiltration of a solution containing Cr-EDTA complex was carried out by determining the total resistance, by plotting the permeate flux of Cr-EDTA solution with the transmembrane pressure, the value of total resistance R_T is used in the model for the simulation of the flow inside the tubular membrane.
- A study by numerical simulation of the flow of Cr-EDTA (complex) was undertaken to better understand the phenomenon of polarization of the membrane, the Reynolds and Peclet numbers have a great influence on the concentration of Cr-EDTA on the membrane surface, these numbers have opposite effect; the increase of the solute concentration in the membrane surface leading to clogging of the latter, corresponding to small values of the Reynolds and large values of Peclet numbers.

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