ORIGINAL RESEARCH PAPER

EFFICIENCY OF ULTRAFILTRATION CERAMIC MEMBRANES FOR TOXIC ELEMENTS REMOVAL FROM WASTEWATERS

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Abstract: The preparation and characterization of porous ceramics multilayer ultrafiltration membrane is described. The first step consisted to prepare high-quality macroporous support in Moroccan clay. The choice of this material is based on its natural abundance and thermal stability.
The microporous interlayer was then prepared by slip casting from zirconia commercial powders and finally the active UF toplayers was obtained by sol-gel route using $ZnAl_2O_4$ and TiO_2 mixed sols. The performance of ultrafiltration membrane (TiO_2 (50%) – $ZnAl_2O_4$ (50%)) was evaluated by pores diameter, water flux, thickness and molecular weight cut off (MWCO). The water permeability measured for this composite membrane is 9.42 $L/(m^2 \cdot h \cdot bar)$, the thickness is less than 700 nm, the pore diameter is centered near 5 nm and the MWCO was about 4500 Da.

Keywords: *ultrafiltration membrane, ceramics multilayer, Moroccan clay, heavy metals, colorants, wastewater*

INTRODUCTION

At present, the problem of water purification from toxic elements is very topical. The progress of textiles, leather, surface treatment, mining, automotive and general chemical process industries lead to increase the concentration of colorant and dangerous ions of heavy metals not only in the wastewaters but even in drinking ones [1].

Traditional methods for elimination the toxic elements from wastewaters are flocculation, coagulation, ion exchange, electrodeposition, extraction, crystallization, etc. Some of them have the great disadvantage of using heterogeneous reactions or distribution of substances among different phases, which are phenomena controlled by diffusion, requiring usually large operations times. On the other hand, final metal recovery requires additional treatments, which makes the process more complicated [2].

Membranes are used to obtain effluents without contaminants, to recycle process water, and to recover valuable products, which can be reused in the process itself or in other applications [3].

Actually, most of the scientific workers focus their attention on the application of ultrafiltration membranes in pollution prevention [4 – 6]. The use of organic membranes is actually more developed but inorganic membranes display a number of performance advantages, such as better thermal, chemical resistance and mechanical strength [7].

In this work, asymmetric ceramic ultrafiltration membrane synthesis was performed in order to reduce the contaminants - heavy metals and colorants - from wastewaters.

In the first part, a ceramic UF-membrane is obtained in an asymmetric multilayer configuration. The development of multilayer configuration includes: shaping of an appropriate support from Moroccan clay; formation of microporous interlayer from zirconia "8 m^2"; formation of a thin ultrafiltration separation toplayer from $ZnAl_2O_4$ and TiO_2 mixed sol [8 – 9].

The second part deals with a systematic investigation of the influence of membrane charge on the salt retention behavior. A series of pH dependent filtration experiments is carried out with NaCl, Na_2SO_4, $CaCl_2$ and $CaSO_4$.

The final part of this work consist in a study of the efficiency of TiO_2-$ZnAl_2O_4$ ultrafiltration membrane to remove the heavy metals (as $Pb(NO_2)_3$, $Cr(NO_3)_3$, $Cd(NO_3)_2$) and colorant (methylene blue) from wastewaters.

MEMBRANE PREPARATION [10]

Preparation of the support material

After collection the clay, stones and other heavy particles were removed from the samples, which when crushed, ground and sieved through a 50 μm sieve to remove the larger non-clay fractions for obtaining fine fraction of clay. The sample shaping was performed by extrusion of the mixture of clay and organic additives obtained as follows:

a) Mixing of clay 81.7 wt.%, Amidon 10 wt.% (Amidon de Maïs RG03408, Cerestar), Methocel 4 wt.% (Dow Chemical Company), Amijel 4 wt.% (Cplus 12072, Cerestar) and PEG (1500) 0.3 wt.% (Prolabo),

b) Adding the water (37.2 wt.% of powders) and Zusoplast (126/3) 0.24 wt.% (Zschimmer et Schwartz),

c) Pugging for 30 minutes,
d) Ageing of the paste: the paste is kept in a closed box for 2 days under high humidity to avoid premature drying and to ensure complete diffusion of the water and organic additives,
e) Shaping by extrusion the tubular support,
f) Drying at room temperature the tubular support after extrusion: the wet tubes are set on rollers to ensure homogenous drying and to avoid twisting and bending,
g) Thermal treatment: the samples were heated to 270 °C at a rate of 2 °C.min⁻¹, temperature then increased to 350 °C at 0.5 °C.min⁻¹, finally temperature continued to increase at 5 °C.min⁻¹ to reach 1200 °C. The final temperature was maintained for 1 h.

Preparation of zirconia membrane interlayer

The powder suspension technique was used to prepare the zirconia microfiltration layer. A deflocculated suspension of zirconia was obtained by mixing 10 wt.% of zirconia (Cezus Chimie) powder, 36 wt.% of PVA (12 wt.% aqueous solution) as binder and 54 wt.% of Dolapix CE64 as dispersing agent (0.2 wt.% aqueous solution).
The zirconia layer was deposited on the inner surface of the cordierite support by slip casting. After drying at room temperature the ZrO_2 membrane was sintered at 1100 °C for 2 h, after bonding at 300 °C for 1 h.

Preparation of the membrane top layer

The ultrafiltration layer was prepared using the sol-gel route [16]:
a) $ZnAl_2O_4$ sol preparation: the boehmite suspension was prepared at room temperature according to the method described by Yoldas [20]; 0.9998 g of Al_2O_3, $1H_2O$ (Condea Pural SB) is added to 20 mL of deionized water, 1.145 g of a 1.5 mol.L⁻¹ nitric acid solution is used as a peptizing agent, the molar ratio $[HNO_3]/[Al_2O_3]$ is 4.8. A zinc nitrate solution prepared with 2.028 g of $Zn(NO_3)_2 \cdot 6H_2O$ and 0.248 g of concentrated HNO_3 in 20 mL of deionized water is then added to the former suspension. We obtained a $ZnAl_2O_4$ stable sol which is diluted with 150 mL of water.
b) TiO_2 sol preparation: TiO_2 sol is prepared from the hydrolysis of 35.2 g of $Ti(iOPr)_4$ by 111.6 g of water. After stirring for one hour, 65.2 g of a nitric acid solution 1 mol.L⁻¹ is added. The solution is stirred and heated at 60 °C for 24 hours to obtain the peptization. The sol is sieved at 125 μm and diluted to 250 mL.
c) Mixed sol TiO_2-$ZnAl_2O_4$ preparation: the mixed sol was obtained after mixing together $ZnAl_2O_4$ sol (50% molar ratio), sol TiO_2 (50% molar ratio) and 10g of hydroxyethyl cellulose (2 wt.% aqueous solution) as binder.
d) Ultrafiltration layer preparation: the former sol was deposited in the inner part of the cordierite tubular support by slip casting. The coating time was 2 hours. The coated support was then dried for 24 h at room temperature, then sintered at 400 °C for 2 h, after bonding at 250 °C for 2 h.

MEMBRANE CHARACTERIZATION

Structural characterization

The support and the ultrafiltration membrane were characterized by means of different techniques. The pore size of bulk support and intermediate layer were examined by Hg-porosimetry (Micromeritics Autopore II 9215). For the top layer the pore size distribution was determined by nitrogen sorption (Micromeritics Asap 2010). The pore diameter was calculated by BJH method. The morphology, surface quality and thickness of intermediate and top layer membrane were examined by scanning electron microscopy (Hitachi, S-4500).

Filtration tests

Tangential filtration tests were performed on a laboratory scale filtration plant, using a recycling configuration. It was equipped with an adjustable out-flow pump, a thermostated feed tank and a vertical membrane (length 15 cm) module. The transmembrane pressure (TMP) was regulated by pressure valve and was controlled by two monitored pressure transducers located downstream and upstream the membrane module.

Water permeability
Ultrafiltration membrane (filtration area 19.6 cm^2) was first characterized by its water permeability. Deionized water (15 MΩ.m) filtration was performed under increasing transmembrane pressure in the range of 2-10 bars. The temperature was set to 25 °C and the flow rate to 2.5 m.s^{-1}. The water fluxes through the membrane were measured as a function of time at different transmembrane pressure values. Before these measurements, the membrane was conditioned by immersion in pure deionized water for a minimum of 24 h.

Retention for uncharged solutes-molecular weight cut-off (MWCO)
The retention for uncharged components was studied by filtration experiments using polyethylene glycol (PEG, Fluka) with molecular weight from 600 to 5000. Feed and filtrate streams were analyzed for their PEG concentrations by gel permeation chromatography (GPC, Waters Associates Chromatography) in order to obtain molecular weight distribution curves. From these curves, the percent retention was determined as a function of the molecular weight. The molecular weight of the PEGs retained for 90% is taken as the MWCO of the membrane.

Salts retention

Salt retention was investigated by using four different salts: NaCl, CaCl$_2$, Na$_2$SO$_4$ and CaSO$_4$. Salt retention was determined at different pH and concentration; the pH was adjusted by adding HNO$_3$ for acidification and NaOH for alkalization. Our attention is focused also towards three heavy metals and two colorants. To this end, Cr(NO$_3$)$_3$, Pb(NO$_3$)$_2$, Cd(NO$_3$)$_2$, methylene blue and orange acid were used (Merck products).
The percent salt and colorant retention was determined by comparing samples of feed and permeate solutions. These samples were analyzed for their salts and colorants

concentration by atomic adsorption (Unicam 929 AA Spectrometer) and UV-VIS spectrophotometer (Unicam UV/Vis Spectrometer) respectively. All the experiments were carried out at working pressure fixed at 10 bars.

From the results, the percent retention was calculated with the equation:

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

where C_p and C_f are the salt concentration in the permeate and feed solution, respectively.

RESULTS AND DISCUSSION

Properties of the composite membrane

For the development of high-quality supports, the porosity, the pore size distribution and mechanical strength are important parameters which should be considered. The support prepared from Moroccan clay shows a porosity of ca. 31.6%, pore size of ca. 10.6 µm and mechanical strength of ca. 15 MPa.

The intermediate zirconia microfiltration layer was coated by slip casting on the support. After sintering at 1100 °C for 2 h, the zirconia layer presents a pore diameter of 0.23 µm and an average thickness of the layer above 10µm (Figure 1).

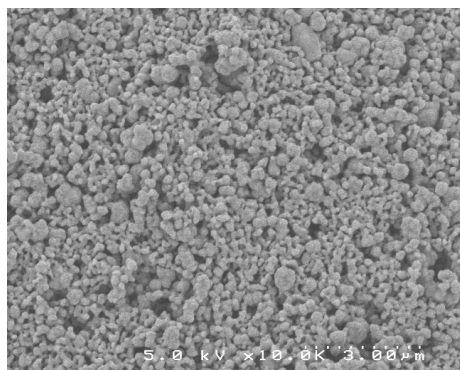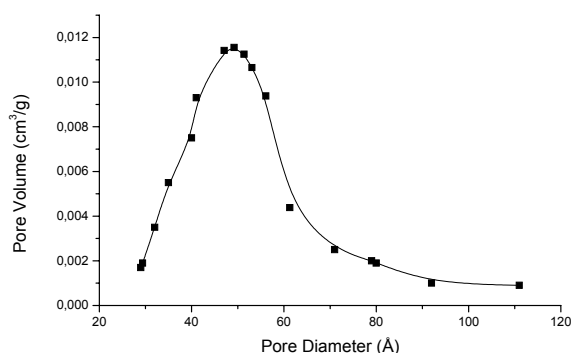**Figure 1.** *Scanning electron micrographs of zirconia interlayer*

Figure 2. *Pore size distribution of ZnAl$_2$O$_4$-TiO$_2$ toplayer*

The final ZnAl$_2$O$_4$-TiO$_2$ ultrafiltration layers obtained by sol-gel process present a pore diameter centered on 5 nm (Figure 2). In Figure 3, the SEM micrograph of ZnAl$_2$O$_4$-TiO$_2$ layers, the thickness homogeneity can be observed. The thickness is less than 700 nm.

The resulting microstructure and the pore size distribution of the layers, which are particularly important for potential ultrafiltration applications, can be adjusted. They depend on a wide range of parameters such as, the particle size of the sol, the type and quantity of the binder, the drying and sintering regime.
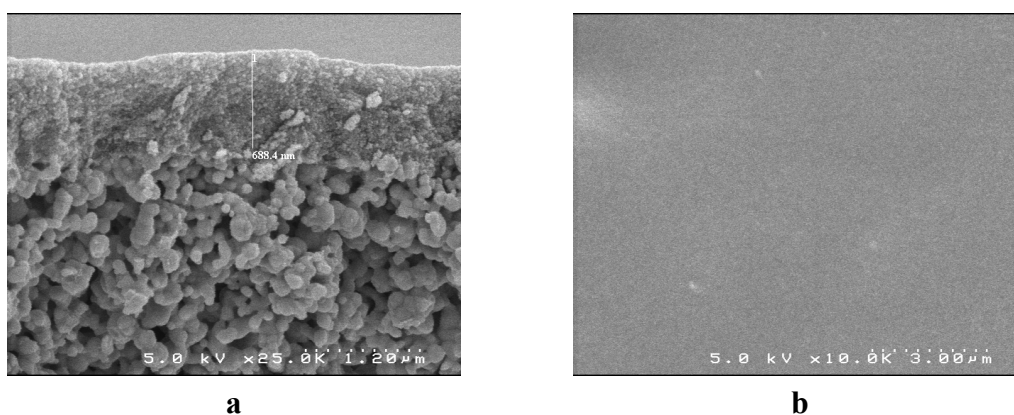
a   **b**

Figure 3. Scanning electron micrographs of TiO$_2$-ZnAl$_2$O$_4$ membrane:
a) cross section view; b) surface view

Filtration results

Water permeability
Ultrafiltration membrane was first characterized by its water permeability. Figure 4 shows that the water flux through the membrane depends on the applied pressure. The water flux increases linearly with pressure and permeability is on average 9.42 L/(h.m^2.bar).
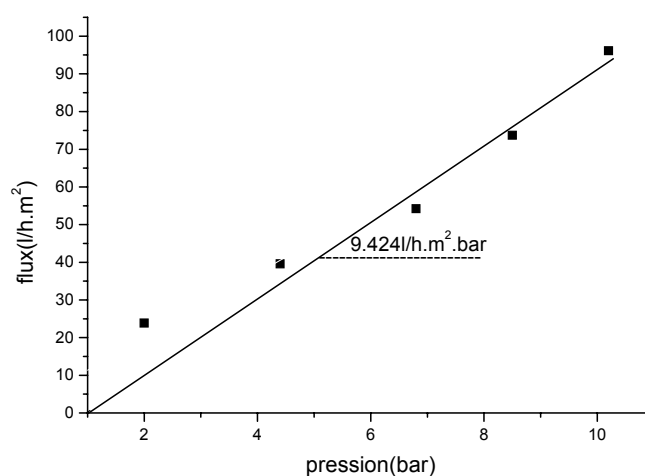
Figure 4. Water flux as a function of transmembrane pressure

Molecular Weight Cut Off (MWCO)
The variation of the rejection rates for increasing molecular weight polymer (PEG) is plotted in Figure 5. The cut off of the membrane is approximately 4500 Da.
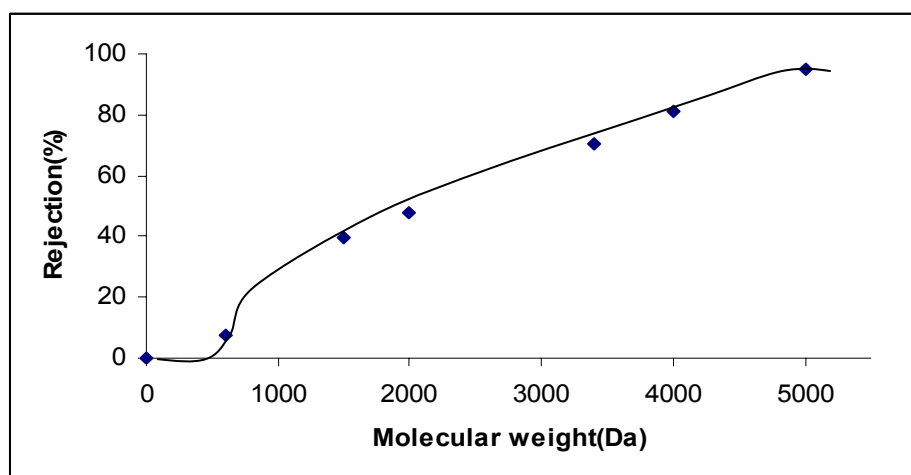
248

Figure 5. *Rejection rates of PEG at different molecular weight*

Salts retention

Filtration of NaCl, Na$_2$SO$_4$, CaCl$_2$, CaSO$_4$

The performance of a low ultrafiltration membrane in term of rejection towards electrolyte solutions, depend at once on the steric and electric interaction between the surface of the membrane and the ions. In our case, due to the compared size of the ions and the pore size of the membrane, the main parameters which must be considered are the electric interactions. In the goal to control this, classical electrolyte (NaCl, Na$_2$SO$_4$, CaCl$_2$, CaSO$_4$) solutions were filtered (Table 1).

Table 1. *Rejection of the different salts*

Salt	Concentration [mol.L^{-1}]	pH	Rejection [%]
NaCl	10^{-3}	6.0	60
CaCl$_2$	10^{-3}	6.1	85
Na$_2$SO$_4$	10^{-3}	6.0	3.2
CaSO$_4$	10^{-3}	6.0	27

The rejection of CaCl$_2$ is higher. The latter value falls only a few percent of the salts which contain SO$_4^{2-}$ anions. Taking into account the pH of the natural solutions, those results are in agreement with positive charge developed in the share plane of the membrane between the Stern layer and the Gouy layer in the dynamic filtration condition [16, 17, 21].

pH effect

The evolution of the rejection rate for the electrolyte at different pH values between 3 and 11 are plotted on Figures 6 and 7. The rejection rate depends strongly on the pH of the filtered solution.

NaCl, CaCl$_2$: At pH < 10, salt retention can be explained as a result of a positive membrane charge which repels the Na$^+$, Ca^{++} co-ions [12]. In order to satisfy electroneutrality condition, an equivalent number of Cl$^-$ counter-ions is retained which results in salt retention.
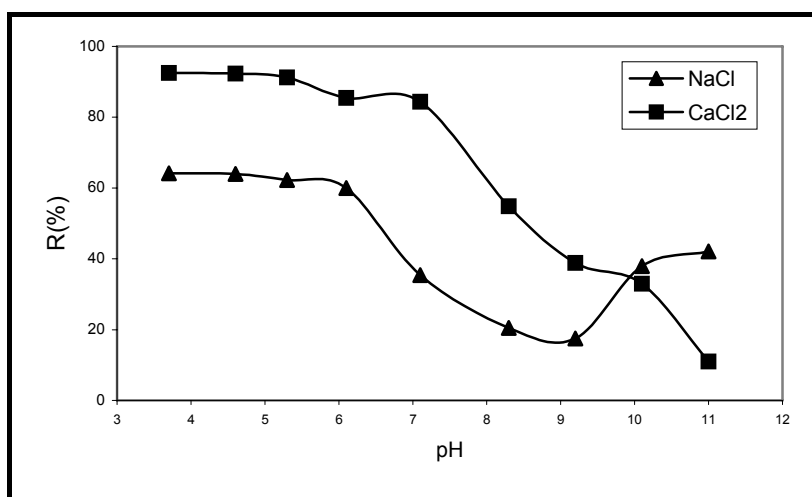
Figure 6. *Salts retention vs. pH for NaCl and CaCl₂*
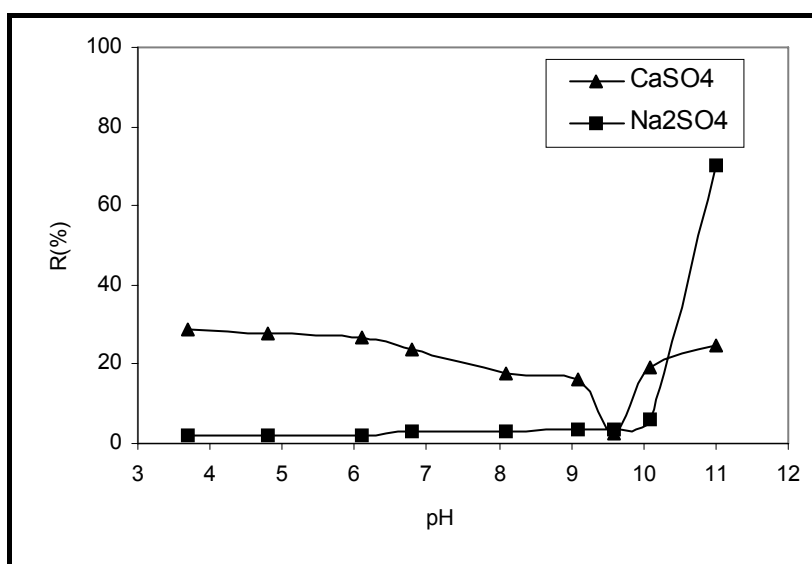

Figure 7. *Salts retention vs. pH for CaSO₄ and Na₂SO₄*

At pH > 10, the membrane exhibits a negative charge, which causes Cl⁻ co-ions repulsion. For $CaCl_2$, the retention reaches a minimal value at higher pH. To explain this behavior, we may take account of electrophoretic mobilities of the powder prepared with the sol 50% TiO_2 and 50% $ZnAl_2O_4$ at the same pH value [16]. The measurement of electrophoretic mobilities in $CaCl_2$ solution shows when the pH increases the mobility decrease. That results correlate with the retention of $CaCl_2$

Around pH ≈ 10, the NaCl retention reaches a low value because the membrane is uncharged. NaCl is indifferent salt.

Na₂SO₄, CaSO₄: The rejection of Na_2SO_4 is 2% from pH 4 to 10 and then increases until 70% at higher pH due to the SO_4^{2-} co-ions repulsion.

For $CaSO_4$, the retention behavior correlates with the membrane charge. At low pH, Ca^{++} co-ions repulsion is caused by the positively charged membrane. At high pH, the strongly negatively charged membrane repels the SO_4^{2-} co-ion. Around pH ≈ 10, the membrane is uncharged and $CaSO_4$ retention is minimal.

Filtration of heavy metals
The treatment of effluents containing heavy metals ions, such as chromium, lead and cadmium will be a challenge in the following years due to new regulations. For this, $ZnAl_2O_4/TiO_2$ ultrafiltration membrane was tested for the filtration of three heavy metals solution ($Cr(NO_3)_3$, $Pb(NO_3)_2$, $Cd(NO_3)_2$) in the goal to evaluate the efficiency of UF layers towards the rejection of toxic metals. The rejections are gathered in Table 2.

Table 2. *Rejection rates of different heavy metals*

Salt	Concentration [mol/L]	pH	Retention [%]
$Cd(NO_3)_2$	10^{-3}	5.1	93
$Pb(NO_3)_2$	10^{-3}	5.2	93.4
$Cr(NO_3)_3$	10^{-3}	3.6	96

The rejection rate is always high whatever the salts. The membrane is positively charged at the natural pH of the solution, which is agreement with the electric behaviour of the powder $ZnAl_2O_4/TiO_2$ suspension [15].

Filtration of colorants
Most of industries like textiles, paper, plastics, leather, food, and cosmetics industries use dyes or pigments to color their product. Such extensive use of color often poses problems in the form of colored wastewaters that require pre-treatment for color prior to disposal into receiving water bodies or publicly owned treatment works. The removal of such compounds at such low levels is a difficult problem. Among the methods employed are the adsorption onto sludge of wastewater treatment plant, as well as other physicochemical techniques as coagulation, flocculation, ozonation and adsorption. Membrane process can be used to obtain effluents without contaminants, to recycle process water and to recover valuable products. In this focus, decolorizing wastewater containing methylene blue and acid orange using $ZnAl_2O_4/TiO_2$ ultrafiltration membrane has been studied.
Ultrafiltration membrane treatment of methylene blue (cationic dye - Figure 8) has been evaluated. The effects of significant parameters such as concentration, pH and pressure were investigated.
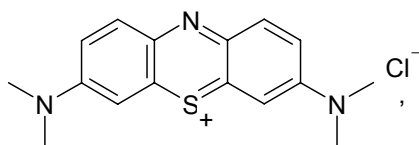
Figure 8. *Methylene blue*

Pressure effect
Figures 9 and 10 are showing the variation of the flux and the retention of methylene blue as a function of time, at different pressures. The flux and retention increase with increasing pressure. This behavior can be explained by the fact that diffusion has a major influence at lower pressures, while convection increases linearly with transmembrane pressure (permeate flux) and becomes dominant at high pressures.
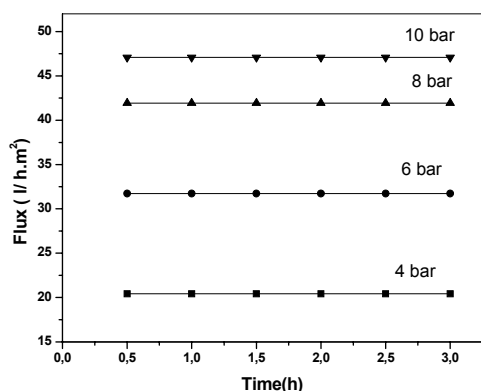
Figure 9. *Variation of flux of methylene blue as a function of time at different pressures (C = 50 ppm, pH = 5.8)*
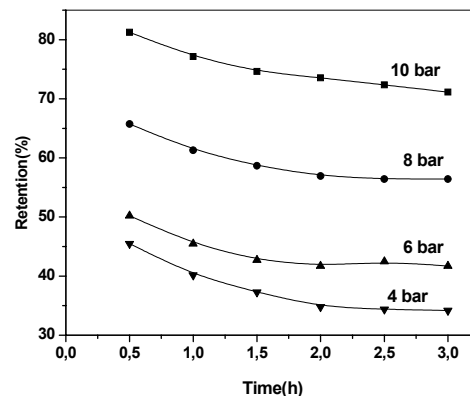
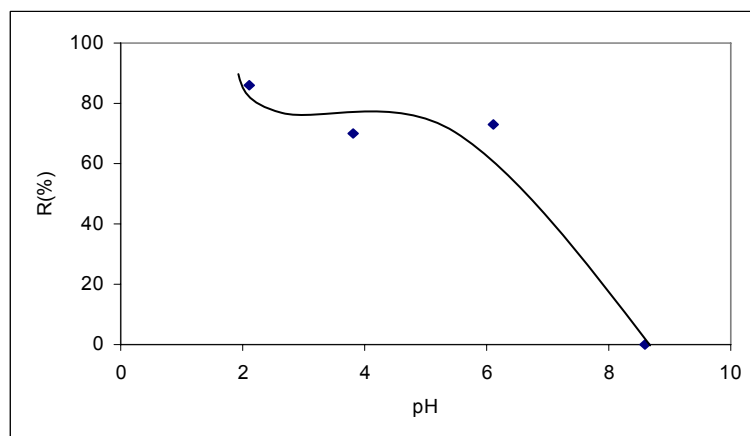**Figure 10.** *Retention of methylene blue as a function of time at different pressures (C = 50 ppm, pH = 5.8)*

Figure 11. *Evolution of methylene blue rejection vs. pH at ΔP = 10 bar (C = 50 ppm)*

pH effect

Figure 11 shows the retention of methylene blue as a function of pH. The rejection rates decreases as the pH value increase, it is about 86% at pH 2 and around 0 at pH 9. Therefore, the decrease of the rejection rate due to decrease of the positive surface charge of the membrane with the pH and to the cationic form methylene blue [18, 25].

Concentration effect

Since the purpose of ultrafiltration membrane is to concentrate the effluent, it was important to have an idea of the influence on the concentration on the performance. In ultrafiltration membrane (diameter of pore less than 10 nm) separation, concentration plays a significant role. In general, the higher the concentration, the higher the osmotic pressure and consequently the lower the permeate flux. For the solution of methylene blue, it can be seen in Figure 12 that the permeate flux decrease with the concentration increase. This may be caused by dye adsorption on the membrane surface observed at the experiment runs, which was indicated by the presence of color on the membrane after filtration, and is in accordance findings in others studies [23].
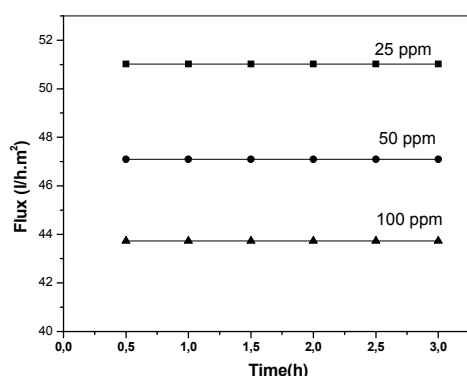
Figure 12. *Variation of flux of methylene blue as a function of time at different concentrations (ΔP = 10 bar, pH = 5.8)*
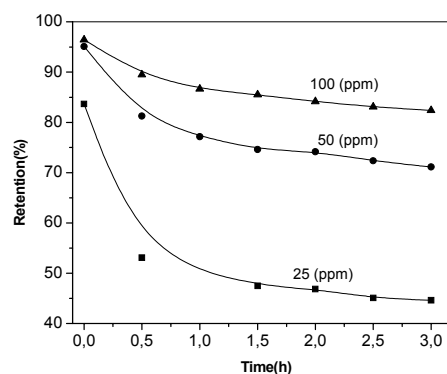
Figure 13. *Retention of methylene blue as a function of time at different concentrations (ΔP = 10 bar, pH = 5.8)*

Figure 13 shows the retention of methylene blue as a function of time at different concentrations. The retention increases with increasing dye concentration. This behaviour can to be explained by formation of a gel layer (lower permeation, Figure 11). A gel layer formed by the rejected dye on membrane surface may operate as an additional resistance to the permeation of dye. Higher dye concentration increased the dye accumulation on membrane surface and color removal became higher than those of the lower dye concentration.

CONCLUSIONS

This study has shown that a multilayer composite membrane which separation properties are in the ultrafiltration range, could be succesfully developed.
The amphoteric structure of the membrane has a strong influence on retention of different salts. A clear pH dependency of salts retention was found. In filtration tests, the membrane shows a standard behavior for conventional UF membranes.
Ultrafiltration membrane separation has been considered as one of the promising methods for the treatment of effluents containing heavy metals and colorants.

ACKNOWLEDGEMENTS

REFERENCES

1.   Mulder, M.: *Basic Principles of Membrane Technology*, 2nd ed., Kluwer, Dordrecht, **1996**;

2. Clever, M., Jordt, F., Knauf, R., Räbiger, N., Rüdebusch, M., Hilker-Scheibel, R.: Process water production from river water by ultrafiltration and reverse osmosis, *Desalination*, **2000**, **131**, 325-336;

3. Shahalam, A.M., Ali-Harthy, A., Al-Zawhry, A.: Feed water pre-treatment in RO systems: unit processes in the Middle East, *Desalination*, **2002**, **150**, 235-245;

4. Alami-Younssi, S., Larbot, A., Persin, M., Sarrazin, J., Cot, L.: Rejection of mineral salt on a gamma alumina nanofiltration membrane: application to environmental processes, *J. Membr. Sci.*, **1995**, **102**, 123-129;

5. Van Gestel, T., Vandecasteele, C, Buekenhoudt, A., Dotremont, C., Luyten, J., Leysen, R., Van der Bruggen, B., Maes, G.: Salt retention in nanofiltration with multilayer ceramic TiO_2 membranes, *J. Membr. Sci.*, **2002**, **209**, 379-389;

6. Blanc, P., Larbot, A., Palmeri, J., Lopez, M., Cot, L.: Hafnia ceramic nanofiltration membranes. Part I : Preparation and characterization, *J. Membr. Sci.*, **1998**, **149**, 151-161;

7. Burggraaf, A.J., Cot, L.: *Fundamentals of inorganic membrane science and technology*, Elsevier Science and Technology Series 4, Elsevier, Amsterdam, **1996**;

8. Laitinen, N., Kulovaara, M., Levänen, E., Luonsi, A., Teilleria, N., Nystrom, M.: Ultrafiltration of stone cutting mine wastewater with ceramic membranes – a case study, *Desalination*, **2002**, **149**, 121-125;

9. Larbot, A., Fabre, J.P., Guizard, C., Gillot, J., Cot, L.: New inorganic ultrafiltration membranes: Titania and Zirconia membranes, *J. Am. Ceram. Soc.*, **1989**, **72**, 257;

10. Saffaj, N., Persin, M., Alami Younnsi, S., Albizane, A., Bouhria, M., Loukili, H., Dach, H., Larbot, A.: *Sep. Purif. Technol.*, **2005**, **47** (1-2), 36-42;

11. Santos, L.R.B., Santilli, C.V., Larbot, A., Persin, M., Pulcinelli, S.H.: Influence of membrane-solution interface on the selectivity of SnO_2 ultrafiltration membranes, *Sep. Purif. Tech.*, **2001**, **22-23**, 17-22;

12. Soulier, S.: *Elaboration and characterization of a new $ZnAl_2O_4$ ultrafiltration membrane*, (Technical report), Montpellier University, September **1997**;

13. Elmarraki, Y., Cretin, M., Persin, M., Sarrazin, J., Larbot, A.: Elaboration and properties of TiO_2-$ZnAl_2O_4$ ultrafiltration membranes, *Mater. Res. Bull.*, **2001**, **36**, 227-237;

14. Elmarraki, Y., Persin, M., Sarrazin, J., Cretin, M., Larbot, A.: Filtration of electrolyte solutions with new TiO_2-$ZnAl_2O_4$ ultrafiltration membranes in relation with the electric surface properties, *Sep. Purif. Technol.*, **2001**, **25**, 493-499;

15. Saffaj, N., Alami-Younssi, S., Albizane, A., Messouadi, A., Bouhria, M., Larbot, A., Persin, M., Cretin, M.: Filtration de solutions ioniques sur des membranes d'ultrafiltration à base d'oxyde de titane et d'aluminate de zinc sur support cordiérite, *Récents progrès en génie des procédés*, **2003**, **89**, 507-514;

16. Yoldas, B.E.: Alumina sol preparation from alkoxides, *Am. Ceram. Soc. Bull.*, **1975**, **54**, 285;

17. Palmeri, J., Blanc, P., Larbot, A., David, P.: Theory of pressure driven transport of neutral solutes and ions in porous ceramic nanofiltration membranes, *J. Membr. Sci.*, **1999**, **160**, 141-170;

18. Koyuncu, I.: Reactive dye removal in dye/salt mixtures by nanofiltration membranes containing vinylsulphone dyes: Effects of feed concentration and crossflow velocity, *Desalination*, **2002**, **143**, 243-253;

19. Saffaj, N., Alami-Younssi, S., Albizane, A., Messouadi, A., Bouhria, M., Persin, M., Larbot, A., Cretin, M.: Elaboration and properties of TiO_2-$ZnAl_2O_4$ ultrafiltration membranes deposited on cordierite support, *Sep. Purif. Technol.*, in press.