REMOVAL OF INDIGO CARMINE AND HEAVY METALS BY ULTRAFILTRATION CERAMIC MEMBRANE

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ABSTRACT

This article describes the preparation and characterization of a porous ceramic multilayer ultrafiltration membrane and its performance on indigo carmine and heavy metals removal. The first step of elaboration consists in preparing a high quality macroporous support from Moroccan clay. The microporous interlayer is prepared by slip casting from zirconia commercial powder suspension. The active ultrafiltration toplayers are obtained by sol-gel route using ZnAl2O4 and TiO2 mixed sols. The performance of the ultrafiltration membrane (TiO2 (50 %)-ZnAl2O4 (50 %)) was evaluated by water permeability, thickness, pore diameter and molecular weight cut off (MWCO). The water permeability measured for this composite membrane is 9.42 l/(m2·h·bar), the thickness is less than 700 nm, the pore diameter is centred near 5nm and the MWCO was about 4500 Da. The final part of this study consists in studying the efficiency to remove Cr(NO3)3, Ni(NO3)2, Cd(NO3)2 and indigo carmine colorant from wastewater.

I. INTRODUCTION

At present, the problem of removing toxic elements during water purification is very topical. The progress of textiles, leather, surface treatment, mining, automotive and general chemical process industries lead to increasing concentrations of colorants and dangerous ions of heavy metals not only in wastewaters but even in drinking water (Mulder, 1996). Traditional methods to eliminate the toxic elements from wastewaters include flocculation, coagulation, ion exchange, electrodeposition, extraction and crystallization. Some of these have the great disadvantage of using heterogeneous reactions or distributing substances among different phases. These are phenomena controlled by diffusion, which require usually large operations times. Moreover, final metal recovery requires additional treatments, which makes the process even more complicated (Clever et al., 2000).

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 (Shahalam et al., 2002). Actually, most research focuses on the application of ultrafiltration membranes for pollution prevention (Alami-Youssi et al., 1995; Van Gestel et al., 2002; Blanc et al., 1998). The use of organic membranes is actually more developed but inorganic membranes display a number of performance advantages, such as higher thermal and chemical resistance and better mechanical strength (Burggraaf & Cot, 1996; Soulier, 1997).

In this study, in order to remove heavy metals and colorant contaminants from wastewater, an asymmetric ceramic ultrafiltration membrane was developed. First, the ceramic UF-membrane is obtained in an asymmetric multilayer configuration. The development of the multilayer configuration includes: shaping of an appropriate support from Moroccan clay; realization of a microporous interlayer from zirconia “Bm”; and elaboration of a thin ultrafiltration separation toplayer from ZnAl2O4 and TiO2 mixed sol (Laitinen et al., 2002; Larbot et al., 1989). The performance of the ultrafiltration membrane was then evaluated by thickness, pores diameter, water permeability and molecular weight cut off (MWCO). The final part of this work consists in studying the efficiency of the TiO2-ZnAl2O4 ultrafiltration membranes to remove the heavy metals Cr(NO3)3, Ni(NO3)2 and Cd(NO3)2 and indigo carmine colorant from wastewater.

II. MATERIALS AND METHODS

II.1 Membrane preparation

II.1.1 Preparation of the support material

The choice of Moroccan clay as support material is based on its natural abundance and thermal stability. After collection of the clay, stones and other heavy particles were removed. The clay was then crushed, ground and sieved through a 50 µm sieve to remove the larger non-clay fractions in order to obtain only the fine clay fraction. 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.%, starch 10 wt.% (corn starch RG03408, Cerestar), Methocel 4 wt.% (The Dow Chemical Company), Amigel 4 wt.% (Cplus 12072, Cerestar) and PEG(1500) 0.3 wt.% (Prolabo);
b) Adding 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 the tubular support by extrusion (outside diameter=10 mm; inside diameter=5 mm; length=12 cm)
f) Drying the tubular support at room temperature 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 was then increased up to 350 °C at 0.5 °C.min⁻¹, finally temperature continued to increase by 5 °C.min⁻¹ until reaching a final temperature of 1200 °C, which was maintained for 1 hour.

II.1.2 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 clay support by slip casting. After drying at room temperature the ZrO₂ membrane was sintered at 1100 °C for 2 hours, after bonding at 300 °C for 1 hour.

II.1.3. Preparation of the membrane top layer

The ultrafiltration layer was prepared using sol-gel route [15]:

a) ZnAl₂O₄ sol preparation: the boehmite suspension was prepared at room temperature according to the method described by Yoldas [19]: 0.9998 g of Al₂O₃·1H₂O (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 [HNO₃]/[Al₂O₃] is 4.8. A zinc nitrate solution prepared with 2.028 g of Zn(NO₃)₂·6H₂O and 0.248 g of concentrated HNO₃ in 20 ml of deionized water is then added to the former suspension. A stable ZnAl₂O₄ sol is obtained which is then diluted with 150 ml of water.

b) TiO₂ sol preparation: TiO₂ sol is prepared by hydrolysis of 35.2 g Ti(OPr)₄ and 111.6 g water. After stirring for one hour, 65.2 g of a nitric acid solution 1mol.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) TiO₂-ZnAl₂O₄ mixed sol preparation: obtained by mixing ZnAl₂O₄ sol (50 % molar ratio), TiO₂ sol (50 % molar ratio) and 10 g of hydroxyethyl cellulose (2 wt.% aqueous solution) as a binder.

d) Ultrafiltration layer preparation: the former sol was disposed in the inner part of the cordierite tubular support by slip casting. The coating time was 2 hours. The coated support was first dried for 24 hours at room temperature and then sintered at 400 °C for 2 h.

II.2. Membrane characterization

II.2.1. Structural characterization

The support and the ultrafiltration membrane were characterized by means of different techniques. The pore size of the support and intermediate layer were examined by use of H₂-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 the BJH method. The morphology, surface quality and thickness of the intermediate and top layer membranes were examined by scanning under an electron microscopy (Hitachi, S-4500).

II.2.2. 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 a pressure valve and was controlled by two monitored pressure transducers located downstream and upstream the membrane module.

Water permeability

The ultrafiltration membrane (filtration area 19.6 cm²) was first characterized by its water permeability. Deionized water (15MΩ.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 during at least 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 a molecular weight from 600 to 5000 Da. Feed and filtrate streams were analysed for their PEG concentrations by gel permeation chromatography (GPC) (Waters Associates Chromatography) in order to obtain molecular weight distribution curves. From these curves, the retention percentage 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.
II.2.3. Retention of salts, heavy metals and Indigo Carmine

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 concentrations; the pH was adjusted by adding HNO$_3$ for acidification and NaOH for alkalisation. Also the retention efficiency of three heavy metals and a colorant was studied. For this purpose, Cr(NO$_3$)$_3$, Ni(NO$_3$)$_2$, Cd(NO$_3$)$_2$, and indigo carmine were used (Merck products). The percentage of salts and colorant retention was determined by comparing samples of feed and permeate solutions. These samples were analysed for their salts and colorant concentration by atomic adsorption (Unicam 929 AA Spectrometer) and UV-VIS spectrophotometry (Unicam UV/Vis Spectrometer) respectively. All the experiments were carried out at fixed working pressures of 10 bars. From the results, the retention percentage was calculated as follows:

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

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

III. RESULTS AND DISCUSSION

III.1. Properties of the composite membrane

For the development of high-quality supports, the porosity, the pore size distribution and the mechanical strength are important parameters which should be considered. The support prepared from Moroccan clay shows a porosity of ca. 41%, a pore size of ca. 11 µm and a mechanical strength of ca. 15 MPa.

The intermediate zirconia microfiltration layer was coated on the support by slip casting. 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 10 µm (figure 1).

![Figure 1. Scanning electron micrograph of zirconia interlayer](image1)

The final ZnAl$_2$O$_4$-TiO$_2$ ultrafiltration layer, obtained by sol-gel process, presents a pore diameter centred of 5 nm (figure 2). In figure 3, the SEM micrograph of the ZnAl$_2$O$_4$-TiO$_2$ layer, its thickness and 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 kind and quantity of the binder, the drying and sintering regime.

![Figure 2. Pore size distribution of ZnAl$_2$O$_4$-TiO$_2$ toplayer](image2)
III.2. Filtration results

III.2.1. Water permeability

The ultrafiltration membrane was first characterized by its water permeability. Figure 4 shows how the water flux through the membrane depends on the applied pressure. The water flux increases linearly with pressure and the average permeability is 9.42 l/(h.m².bar).

![Figure 4. Water flux as a function of transmembrane pressure](image)

### III.2.2. Molecular Weight Cut Off

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.

![Figure 5. Rejection rates of PEG at different molecular weights](image)
III.3. Salts Filtration

III.3.1 Filtration of NaCl, Na2SO4, CaCl2, CaSO4

Figure 6. Rejection of several salts vs. pH ([C=10^{-3} mol L^{-1}, working pressure=10 bar] (●) CaCl2 (□) NaCl, (△) CaSO4, (▲) Na2SO4)

At pH<10, NaCl and CaCl2 salt retention can be explained as a result of a positive membrane charge which repels the Na+, Ca2+ co-ions (Abrabri et al., 1998; Blanc et al., 1997; Soulier, 1997; Elmarraki et al., 2001a and 2001b). In order to satisfy electroneutrality condition, an equivalent number of Cl- counter-ions is retained which results in salt retention.

At pH>10, the membrane exhibits a negative charge, which causes Cl- co-ions repulsion. For CaCl2, the retention reaches a minimal value at higher pH. To explain this behaviour, electrophoretic mobilities of the powder prepared with the 50%TiO2 and 50%ZnAl2O3 sols at the same pH value must be taken into account (Elmarraki et al., 2001a)

Around pH 10, the NaCl retention reaches a low value, as the membrane is uncharged. NaCl is an indifferent salt (Saffaj et al., 2003 and 2004; Yoldas, 1975; Palmeri et al., 1999).

The rejection of Na2SO4 is 2 % from pH 4 to 10 and then increases until 70 % at higher pH caused by SO4^{2-} co-ions repulsion. For CaSO4, the retention behaviour correlates with the membrane charge. At low pH, Ca2+ co-ions repulsion is caused by the positively charged membrane. At high pH, the strongly negatively charged membrane repels the SO4^{2-} co-ion. Around pH 10, the membrane is uncharged and CaSO4 retention is minimal (Elmarraki et al., 2001b; Saffaj et al., 2003 and 2004; Yoldas, 1975; Palmeri et al., 1999).

III.3.2 Heavy Metals Filtration

The treatment of effluents containing heavy metals ions, such as chromium, nickel and cadmium will be a challenge in the following years due to new regulations. For this, the ZnAl2O4/TiO2 ultrafiltration membrane was tested for the filtration of three heavy metals ([Cr(NO3)3], Ni(NO3)2, Cd(NO3)2) in the goal to evaluate the efficiency of the UF layers towards the rejection of toxic metals. The rejections are gathered in table 1.

The rejection rate is high for all tested salts. The membrane is positively charged at neutral pH of the solution, which agrees with the electric behaviour of the powder ZnAl2O4/TiO2 suspension (Elmarraki et al., 2001a).

<table>
<thead>
<tr>
<th>Table 1. Rejection rates of different heavy metals</th>
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<tbody>
<tr>
<td>Salt</td>
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<tr>
<td>Cd(NO3)2</td>
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<tr>
<td>Ni(NO3)2</td>
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<tr>
<td>Cr(NO3)3</td>
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III.3.3 Filtration of colorants

Textile, paper, plastic, leather, food, and cosmetic industries use dyes or pigments to colour their products. Such extensive use of colorants often poses problems in the form of coloured wastewaters that require pre-treatment prior to disposal into receiving water bodies or public treatment plants. The removal of such compounds at such low levels consists of a difficult problem. Among the methods employed are the adsorption onto sludge of wastewater treatment plants, as well as other physicochemical techniques such as coagulation, flocculation, ozonation and adsorption. Membrane processes can be used to obtain effluents without contaminants, to recycle process water and to recover valuable products (Koyuncu, 2002; Akbari et al., 2002). In this focus, decolourising wastewater containing indigo carmine using ZnAl2O4/TiO2 ultrafiltration membrane has been studied.

Pressure effect

Figures 7 and 8 show the variation of flux and retention of indigo carmine as a function of time at different pressures. The flux and retention increase with increasing pressure. This behaviour can be explained as follows: diffusion has a major influence at low pressures while convection increases linearly with transmembrane pressure (permeate flux) and becomes dominant at high pressures.
Figure 7. Variation of flux of Indigo Carmine as a function of time at different pressures (C=50 ppm, pH=6)

Figure 8. Retention of Indigo Carmine as a function of time at different pressures (C=50 ppm, pH=6)

pH effect
Figure 9 shows the retention of Indigo Carmine in function of the pH.

The retention can be explained by the strong interaction between the membrane surface (positive charge) and the solute (anionic dye) between pH 2 and 10

\[ \text{MOH}^+ + \text{Dye SO}_3^- \rightarrow \text{DyeSO}_3^- \cdot \text{H}_2\text{OM} \quad \text{(ionic bond)} \]

The rejection rates increase as the pH value increases, with about 65% at pH 2 and about 80% at pH 10. Therefore, the increase of the rejection rate is due to the decrease of the positive surface charge of the membrane with increasing pH because of the anionic form of Indigo Carmine (Saffaj et al., 2003 and 2004; Akbari et al., 2002).

Concentration effect
Since the purpose of using the ultrafiltration membrane is to concentrate the effluent, it is important to have an idea about the influence of the concentration on the performance. In ultrafiltration membrane (pore diameter 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. Figure 4 shows how the permeate flux decreases with increasing concentration of methylene blue solution. This may be caused by dye adsorption on the membrane surface. As observed at the experimental runs, colour exposure occurs on the membrane during filtration, which is in accordance with findings in other studies (Koyuncu, 2002).
Figure 5 shows the retention of Indigo Carmine as a function of time at different concentrations. The retention increases with increasing dye concentrations. This behaviour can be explained by the formation of a gel layer (lower permeation, figure 4). A gel layer formed by the rejected dye on the membrane surface may operate as an additional resistance to the dye permeation. Higher dye concentration increases the dye accumulation on the membrane surface and the colour removal becomes higher than in solutions with lower dye concentration.

**Figure 10.** Variation of flux of Indigo Carmine as a function of time at different concentrations (∆P=10 bar, pH=6)

**Figure 11.** Retention of Indigo Carmine as a function of time at different concentrations (∆P=10 bar, pH=6)

4. CONCLUSION

This study shows that a multilayer composite membrane which separation properties are in the ultrafiltration range, can be successfully developed. The amphoteric character of the membrane has a strong influence on salts retention and a clear pH dependency of salt retention was found. In filtration tests of ions concentration, the membrane shows a standard for conventional UF membranes. Ultrafiltration membrane separation has been considered as one of the promising methods for the treatment of heavy metals and colorant effluents.

REFERENCES


