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Wastewater Treatment by $ZnAl_2O_4$ Ultrafiltration Ceramic Membrane

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Abstract

In this study, $ZnAl_2O_4$ ultrafiltration membranes was tested for removing the Heavy Metals and Carmoisine from water. The water permeability measured for this membrane is 11.53 l/(m^2.h.bar), the pore diameter is centered near 7nm and the MWCO was about 6000Da. For the heavy metals, the electrical interactions between solution and surface material is responsible for the rejections of heavy metals. For carmoisine, the membrane shows a good rejection; the membrane suffered from flux decline due to its sensitivity to fouling when the concentration increases.

Keywords - Ceramic Membrane, Ultrafiltration, Environment, Carmoisine.

I. INTRODUCTION

At present, the problem of water purification from toxics elements is very topical. The progress of food, 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 drinking ones [1].

Traditional methods for elimination the toxics elements from wastewaters is flocculation, coagulation, ion exchange, electrodeposition, extraction, crystallization, ect…. Some of them have the great disadvantage of using heterogeneous reactions or distribution of substances among different phases, which are phenomena controlled by diffusion, requires usually large operations times. In other one, final metal recovery requires additional treatments, which make 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 application [3].

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

In this work, in order to reduce the contaminants from wastewater, asymmetric ceramic ultrafiltration membrane synthesis was made for heavy metals and colorant removal of wastewater.

The first part, 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 "8m2"; formation of a thin ultrafiltration separation toplayer from $ZnAl_2O_4$ sol [8-9].

The second part in this work consist a study the efficiency of $ZnAl_2O_4$ ultrafiltration membrane to remove the heavy metals ($Pb(NO_2)_3$, $Cd(NO_3)_2$, $Cu(NO_3)_2$) and colorant (carmoisine) from wastewater.

II. MATERIALS AND METHODS

The support used during these experiments was prepared from Moroccan Sahara clay. The chemical analysis reveals that clay powder is essentially formed with a large amount of silica (50%) and alumina (11%). The particle size analysis shows that clay has a higher percentage of fraction less than 5 µm.

Plastic paste is prepared from ceramic powder mixed with organic additives and water [8-10]. The paste must have rheological properties allowing shaping by extrusion. The paste is then forced through a die under pressure. After drying and sintering at 1250°C, the support shows a mean pore diameter of ca. 11µm, porosity of ca. 43% and the mechanical strength of ca. 10Mpa.

It’s necessary to coat an intermediate layer on to the supports before coating the sol-gel layer. This microfiltration layer allows the ultrafiltration membrane to be maintained without infiltration into the support. Using the suspended powder technique, a ZrO_2 membrane has been elaborated [9-10]. At firing temperature of 1100°C for 2 hours, a ZrO_2 membrane with pore diameters equal to 0.23µm was obtained and an average thickness of the layer above 10µm.

Using the sol-gel techniques, the ultrafiltration membrane was prepared by deposing of $ZnAl_2O_4$ sol and 10g of hydroxyethyl cellulose in the inner of the clay tubular support [8,9,11]. The coating time was 2 hours. The coated support was then dried for 24 h at room temperature, then sintered at 500°C for 2 h, after bonding at 250°C for 2 h.

The pore diameters measured by nitrogen adsorption-desorption are centered near 7nm.

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.

The water flux through the membrane depends on the applied pressure. A stable flux as a function of pressure was obtained, giving a permeability of 11.53 $l/h.m^2.bar$.

The molecular weight cut off (MWCO) of this membrane was determined by using a solution containing polyethylene glycol of different molecular weight from 600 to 7000. The concentration of each solution is 10-3 $mol.l^{-1}$. The MWCO was about 6000 Da.

III. RESULTS AND DISCUSSION

1.1 FILTRATION OF HEAVY METALS

The use of ceramic membrane in pollution prevention is increasing due to their excellent mechanical strength and tolerance to solvent, as well as pH, oxidation and temperature extremes. For this, $ZnAl_2O_4$ ultrafiltration membrane was tested for the filtration of tree heavy metals solution $Pb(NO_2)_3$, $Cd(NO_3)_2$ and $Cu(NO_3)_2$ in the goal to evaluate the efficiency of UF layers towards the rejection of toxics metals. The rejections are gathered in table 1.

Table 1. Rejection rates of different heavy metals

Salt	Concentration (mol/l)	pH	Retention (%)
$Pb(NO_3)_2$	10^{-3}	5	93
$Cd(NO_3)_2$	10^{-3}	5.3	92
$Cu(NO_3)_2$	10^{-3}	4.2	94

Whatever the salts, the rejection rates are always high. 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 [8, 9, 11].

1.2 FILTRATION OF CARMOISINE

Ultrafiltration membrane treatment of carmoisine (anionic dye) has been evaluated. The effects of significant parameters such as concentration, pH and pressure were investigated.

Pressure effect

Fig. 1 and 2 show the variation of flux and retention as a function of time of carmoisine at different pressure. The flux and retention increase with increasing pressure. This behaviour can be explained that diffusion has a major influence at lower pressure while convection increase linearly with transmembrane pressure (permeate flux) and become dominant at high pressures.

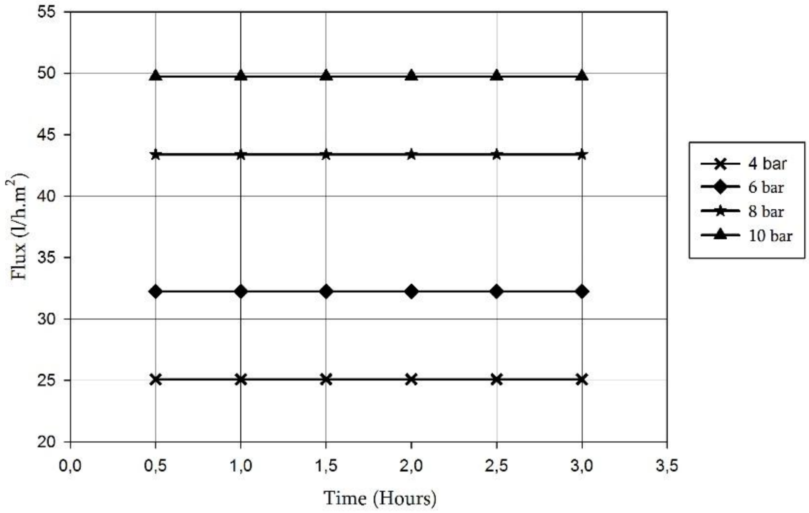

Fig.1. Variation of flux of carmoisine as a function of time at different pressure (C=50 ppm, pH=6)

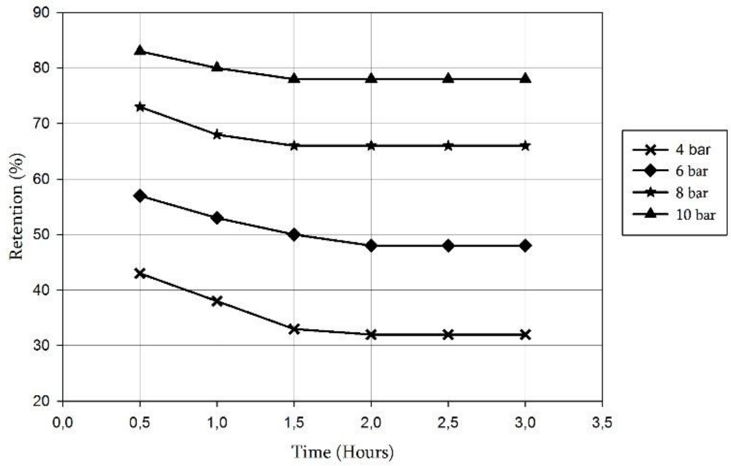

Fig.2. Retention of carmoisine as a function of time at different pressure (C=50 ppm, pH=6)

<u>pH effect</u>

Fig. 3 shows the retention of carmoisine as a function of pH.

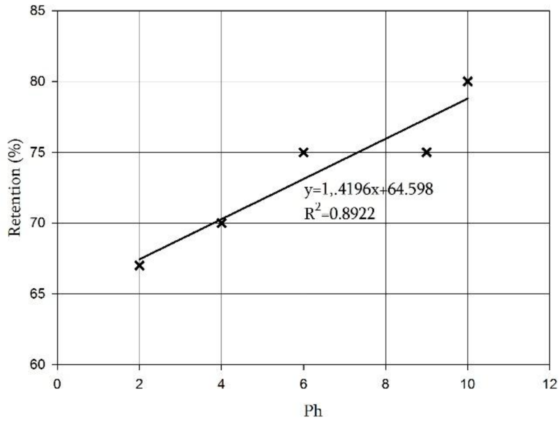

Fig.3. Evolution of carmoisine rejection versus pH at ΔP=10 bar (C= 50 ppm)

The retention can be explained by the strong interaction between the membrane surface (positive charge) and the solute (anionic dye) between pH 2 and 9.

$$\mathbf{MOH_2^+ + Dye\ SO_3^- \rightarrow DyeSO_3^{-}\ {}^{+}H_2OM}$$

(Ionic bond)

The rejection rates increase as the pH value increase, it is about 67% at pH 2 and around 80 at pH 9. Therefore, the increase of the rejection rate due to decrease of the positive surface charge of the membrane with the pH because the anionic form of carmoisine [8-9].

<u>Concentration effect</u>

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 carmoisine, it can be seen in fig. 4 that 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 [12].

Fig.5 shows the retention of carmoisine as a function of time at different concentration. The retention increases with increasing dye concentration. This behaviour can to be explained by formation of a gel layer (lower permeation, fig. 4). 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.

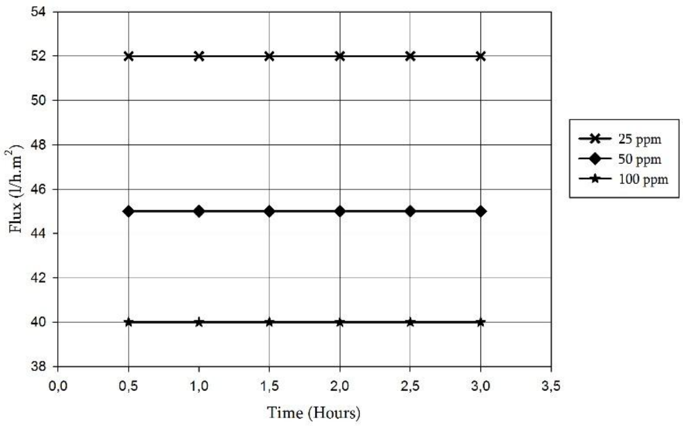

Fig.4. Variation of flux of carmoisine as a function of time at different concentration (ΔP= 10 bar, pH=6)

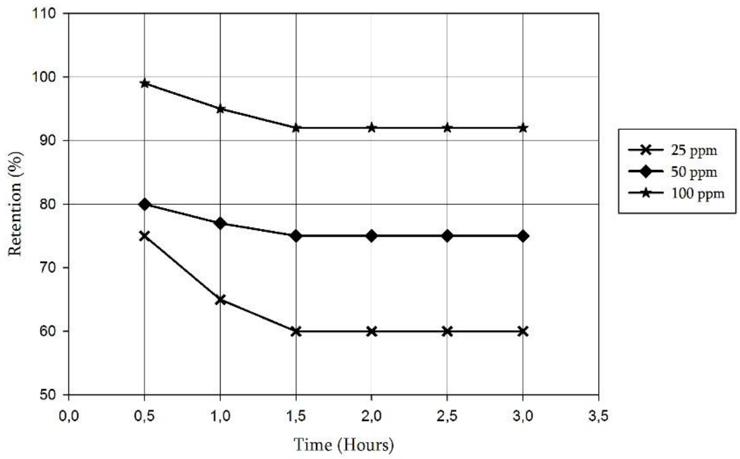

Fig.5. Retention of carmoisine as a function of time at different concentration (ΔP= 10 bar, pH=6)

IV. CONCLUSION

In this work, we investigate the performance of a low composite ultrafiltration membrane in treating of heavy metals and colorants.

A good retention has been obtained for heavy metals; it's can be interpreted by electric interaction mechanism.

For colorant, the membrane shows a good retention but it suffered from flux decline due to its sensitivity to fouling.

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