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Investigation of performance of a low $ZnAl_2O_4$–TiO_2 ultrafiltration membrane in relation with speciation and membrane solutes interactions

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Abstract

The low ultrafiltration (UF) membranes performances depend mainly on the nature of the interactions between the solutes and the membrane material. This paper reports the filtration tests of different salts: CH_3COONa, Na_2HPO_4 and NaF by means of a TiO_2–$ZnAl_2O_4$ membrane prepared by sol–gel route deposed on a moroccan clay support. The measured rejections depend at once on the pH, on ionic strength of the solution; their interpretation needs to precise the exact speciation of the filtered species.

Keywords: Ceramic membrane; Ultrafiltration; Salt rejection; Solute–membrane interactions

1. Introduction

Low ultrafiltration (UF) membranes are membranes which present a pore diameter between 2 and 10 nm, they are not really nanofiltration membrane [1]. Because their relatively important pore diameter, such membranes are interesting for applications which need high fluxes, this is the case for most of the environmental depolluting processes. Actually the development of new analytical methods more and more efficient for micro pollutant determination leads to straighten the legislation for liquid rejection in the environment [2]. Among the identified source of pollution of aquatic environment, the industrial wastewaters which contain heavy metals and also different micro pollutants with low molecular weight cause serious damages [3]. Some anions such as nitrate, phosphate, sulfide, fluoride are others source of pollution, for example phosphate anions are responsible of the eutrophisation of the river and their rejection is strictly controlled to limit their impact in the environment [4]. Fluoride ions are also known to give damage for human health in the North Africa countries where their concentration in the water source is too important.

In a recent past a lot of authors studied the mechanism of the rejection of chemical species by the low pore size membrane (nanofiltration and low ultrafiltration). Actually it is now well established that the rejection of low UF and NF membranes is ruled by at least a triple mechanism including size exclusion, electric exclusion depending on the compared size of the species and of the pore [5–7] and the so called dielectric exclusion [8–10]. In the case of nanofiltration membranes with pore lower than 2 nm, the size and electric interactions should be considered and it is possible to modify the rejection of a cation after complexation by means of a classical ligand [11]. On the contrary for the low ultrafiltration charged membrane, the size effect is not significant because even after complexation, the size of the formed complex appears to be lower than the pore size, nevertheless relatively high rejections are observed for free metallic cation, this effect is due to the strong electric interactions between the ions and the membrane surface charge. Most of the published works concern the behaviour of salts without acid base properties such as NaCl, Na_2SO_4, $CaCl_2$ ... [12] where the charge of the ion is the same whatever the pH of the filtered solution, in this case for pure salt solutions, the extended Nernst Planck equation was used to predict the rejection [5]. In the case of salts with acid base properties, few works exists and the knowledge of the speciation of the species coupled with the Nernst Planck equation is necessary to explain the results. The

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classical example is the rejection of the carbonate system which is influenced by the change of the charge from 0 (H_2CO_3), to −1 (HCO_3^-) and −2 (CO_3^{2-}) depending on the pH of the solution [13]. Actually the development of new filtration processes for the elimination of low molecular weight complex molecules such as micro pollutants [14], dyes, humic acids which are present at very low concentration among relatively more concentrated salts, needs to precise the role of the speciation of the chemical species on their rejection. In this context, after to have recalled the behaviour of classical neutral salt, our attention was focused on the parameters which governed the rejection of non-neutral salts by means of a low cost ultrafiltration membrane.

2. Experimental

2.1. Membrane preparation

The support used to deposit the ultrafiltration membrane is made of natural moroccan clay, the support preparation was reported in previous papers [15,16]. After preparation of the support, it is dried and sintered at 1250 °C for consolidation, the average pore of the support is 11 μm; its porosity is 43% and its average mechanical strength is 10 MPa.

To prevent the infiltration of the support by the sol used to prepare the ultrafiltration layer, an intermediate layer made of zirconia was coated by slip casting on the clay support using the suspended powder technique according to the method developed in our laboratory [16]. After firing at a temperature of 1100 °C for 2 h, the ZrO_2 microfiltration layer obtained presented a pore diameter of 0.23 μm and an average thickness above 23 μm.

The ultrafiltration top layer was then prepared by sol–gel route using TiO_2 and $ZnAl_2O_4$ mixed sols. The mixture of TiO_2 (50%) and $ZnAl_2O_4$ (50%) sols was deposited on the ZrO_2 microfiltration layer by slip casting. Capillary forces suck the solvent through the support, leaving a layer of concentrated sol on the surface. The coated support was then dried for 24 h at room temperature, kept at 250 °C for 2 h and sintered at 400 °C for 2 h to finally obtained the composite membrane (Fig. 1), more details are reported in Refs. [15,16]. The main characteristics of the prepared membrane are summarized in Table 1.

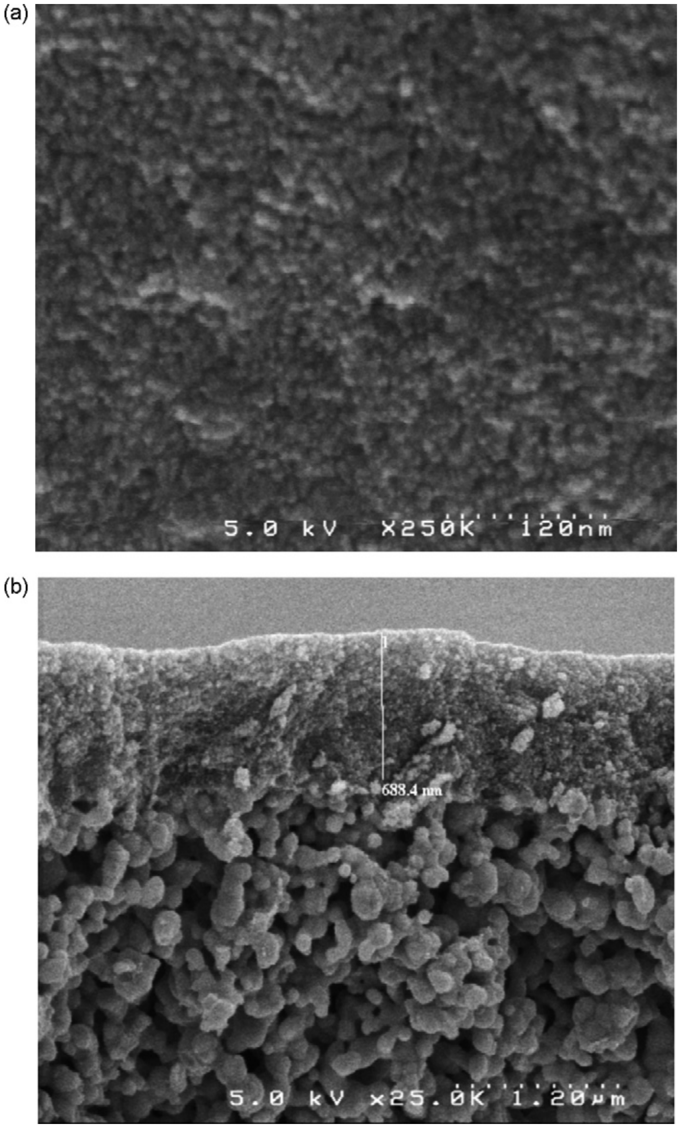

Fig. 1. Scanning electron micrographs of TiO_2–$ZnAl_2O_4$ membrane.

2.2. Filtration pilot

The filtration experiments were carried out on a laboratory pilot scale (Fig. 2). The capacity of the tank was 2 L, the working pressure was fixed between 6 and 10 bars by means of a nitrogen gas bottle. The pilot is equipped with two silver or silver chloride covered wires (depending on the filtered salt) for streaming potential measurements, one is positioned in the axe of the membrane, the other in the permeate compartment close to the membrane wall. The filtered solutions were prepared with analysis grade salts at a concentration between 10^{-3} and 10^{-2} mol L^{-1} or others precised concentrations. The pH of the solution was adjusted with concentrated acid (HCl) or base (NaOH) solutions. The salt rejection R of the different salts was determined by the classical relation: $R\ \% = (1 - C_p/C_f) \times 100$ where C_p is the concentration in the permeate and C_f the concentration in the feed. The feed and permeate concentrations were obtained by atomic adsorption or ionic chromatography measurements (Unicam 929 Atomic Absorption Spectrometer, DX 100 Dionex chromatograph).

Table 1
Main characteristics of the tubular TiO_2–$ZnAl_2O_4$ ultrafiltration membrane

Properties	
Length (cm)	15
Outer diameter (mm)	10
Inner diameter (mm)	7
Pore diameter (nm)	5[a] (±0.2)
Water permeability ($L\,h^{-1}\,bar^{-1}$)	9.4
Working area (cm^2)	26
Cut off (Daltons)	4500

[a] Measured from N_2 adsorption–desorption isotherms.