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Removal of salts and dyes by low $ZnAl_2O_4$–TiO_2 ultrafiltration membrane deposited on support made from raw clay

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Abstract

This paper reports the dynamic characterizations of a $ZnAl_2O_4$–TiO_2 membrane deposited on a macroporous support prepared from Moroccan clay coated with a zirconia microfiltration interlayer. The water permeability of the membrane is $0.26 \times 10^{-10}\,m\,s^{-1}\,Pa^{-1}$, its thickness is less than 700 nm with an average pore diameter of 5 nm, and a cut off about 4500 Da. The investigations of filtrations performed with different salts (NaCl, $CaCl_2$, Na_2SO_4, $CaSO_4$) prove the rejection mechanism is governed by a Donnan exclusion of the coion. Results obtained with solutions charged in heavy metal ions such as Cr^{III} and synthetic dyes are very promising to consider the use of this membrane in depolluting filtration processes.

Keywords: Multilayer; Ultrafiltration; Electrical interactions; Colour removal; Heavy metals

1. Introduction

Membrane processes are now widely used for the removal of salts to produce drinking water from sea water. Usually in the Gulf countries, reverse osmosis (RO) membranes are used [1–3] and the salts are mainly removed by a mechanism of exclusion outside of the membrane matrix. Unfortunately, reverse osmosis processes need high working pressure (up to 100 bars) due to the osmotic pressure of sea water. For removal of low concentration of salt, nanofiltration membranes which need lower working pressure will be interesting to consider, moreover nanofiltration membranes with a pore size near 2 nm have a more open structure than reverse osmosis membrane. With nanofiltration membranes the rejection of electrolyte is governed at once by the steric hindrance and the electric interactions between the ions and the charged membrane surface. A lot of works described the mechanism of the ions rejection from theoretical considerations based on thermodynamic of irreversible processes [4,5]. The main conclusions of these works are the possibility to obtain strong electric interactions even for membranes with relatively large pore lower than 10 nm, which correspond to the use of low ultrafiltration membranes [6,7]. Although actually most of the applications are developed with organic nanofiltration membranes, the growing of the market for specific applications in drastic conditions need to use ceramic membranes which present best mechanical and chemical resistance than organic membranes but are also more expensive. Beside the classical oxides materials used to elaborate these membranes (ZrO_2, Al_2O_3, ...) [8–10], a lot of research works were devoted to the preparation of original filtering materials such as SnO_2 [11], KTP (potassium titanyl phosphate) [12], HfO_2 [13] and spinel [14]. Elmarraki et al. [15,16] described a method for the elaboration of new ultrafiltration membranes prepared with two different ceramic materials (TiO_2, $ZnAl_2O_4$) deposited on α alumina support and reported the rejections of some electrolytes which depend strongly on the pH of the salt solution. Recently, in our group, we reported also the behaviour of a TiO_2–$ZnAl_2O_4$ membrane deposited on artificial cordierite

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support [17]. Rejection measurements for NaCl and Na_2SO_4 solutions were in agreement with previous data given by Elmarraki et al. [16]. In the goal to develop the use of low cost membranes for potential environmental application, we present here the characterization of a Zn–Al_2O_4–TiO_2 membrane deposited on a raw support prepared from Morrocan natural clay. The first part of the work will be devoted to recall the main steps of the membrane preparation [18]. In the second part, we will present the performance of the prepared membrane for the filtration of solutions which contains metallic cations and dyes, the results will be correlated with the membrane surface charge by means of streaming potential coefficient (SP) measurements in different conditions of salts, concentrations and pH of the filtered solution.

2. Experimental

2.1. Membrane preparation

2.1.1. Preparation of the membrane support

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

(a) Mixing of 81.7% (w/w) clay, 10% (w/w) Amidon (Amidon de Maïs RG03408, Cerestar), 4% (w/w) Methocel (The Dow Chemical Company), 4% (w/w) Amijel (Cplus 12072, Cerestar) and 0.3% (w/w) PEG1500 (Prolabo).
(b) Adding of 37.2% (w/w) water and 0.24% (w/w) Zusoplast 126/3 (Zschimmer et Schwartz) to the solid mixture obtain in step a.
(c) Pugging for 30 min.
(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 of the tubular support.
(f) Drying at room temperature of 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 1250 °C, the final temperature was maintained for 1 h.

2.1.2. 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% (w/w) of zirconia (Cezus Chimie) powder, 36% (w/w) of PVA (12% w/w aqueous solution) as binder and 54% (w/w) of Dolapix CE64 as dispersing agent (0.2%, w/w, 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 unbinding at 300 °C for 1 h.

2.1.3. Preparation of membrane top layer

The ultrafiltration layer was prepared using sol–gel route according to [15,18]:

(a) $ZnAl_2O_4$ sol preparation: the boehmite suspension was prepared at room temperature according to the method described by Yoldas [19]; 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 $Zn(NO_3)_2$, $6H_2O$ 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 1 h, 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 h 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 10 g of hydroxyethyl cellulose (2%, w/w, 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 h. The coated support was then dried for 24 h at room temperature, and then sintered at 400 °C for 2 h, after unbinding at 250 °C for 2 h.

2.2. Membrane properties

The $ZnAl_2O_4$–TiO_2 ultrafiltration layers obtained by sol–gel process presents a pore diameter centred on 5 nm measured by nitrogen adsorption desorption. The scanning micrography shows that the average layer thickness is about 700 nm (Fig. 1). The water permeability of the membrane is 0.26×10^{-10} m s^{-1} Pa^{-1}. The cut off given for the 90% rejection of calibrated polyethylene glycol polymers (MW from 600 to 10^5 Da) is about 4500 Da, this is in agreement with the mentioned pore size (Table 1).

2.3. Filtration tests

2.3.1. Filtration pilot

Tangential filtration tests were performed on a handmade laboratory filtration pilot, using a recycling configuration.