J. Mater. Environ. Sci. 6 (8) (2015) 2190-2197
ISSN : 2028-2508
CODEN: JMESCN

Elaboration and characterization of ceramic membranes made from natural and synthetic phosphates and their application in filtration of chemical pre-treated textile effluent

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Received March 2015, Revised 24 Aug 2015, Accepted 24 Aug 2015
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Abstract
This study is related to the development of microfiltration and ultrafiltration ceramic membranes using natural and synthetic phosphates. Macroporous support was formed by extrusion of a ceramic paste derived from natural Moroccan apatite coming from the mine of Khouribga. The preparation and characterization of support and membranes layers were described in this work. Microfiltration MF membrane from natural Moroccan phosphate and ultrafiltration UF membrane from PTP (Potassium Titanyl Phosphate) were performed respectively by slip casting process and sol-gel route. The support fired at 1000 °C showed a pore diameters centered near 10 µm and a porosity of about 43%. The pore diameters are 0.35 µm and 10 nm for microfiltration and ultrafiltration layers, respectively. The measured water permeability is about 778.6 $L.h^{-1}.m^{-2}.bar^{-1}$ and 80 $L.h^{-1}.m^{-2}.bar^{-1}$ for MF and UF membranes, respectively. Elaborated membranes were successfully applied as a complementary process for decolorizing concentrated textile effluent pretreated by coagulation-flocculation. These membranes present interesting retention properties with regard to residual turbidity and dye remained in the effluent after the chemical pre-treatment.

Keywords: Natural phosphates; PTP; Ceramic membranes; MF and UF; Textile effluent.

1. Introduction
The aim of ceramic membrane production is to obtain defect-free layers with homogeneous thickness and a narrow pore size distribution [1]. An inorganic membrane can be obtained in an asymmetric multilayer configuration formed by a macroporous support with successive thin layers deposited on it. The support provides mechanical resistance to the medium. The successive layers are active in microfiltration or ultrafiltration, depending on their pore diameters [2]. Ceramic inorganic membranes have several key performance advantages over its organic counterpart such as thermal and chemical resistances and better mechanical strength under high pressure. However, higher cost of ceramic inorganic membranes has probably restricted their widespread use for different commercial applications [3]. In these last years a significant effort was provided in order to develop new types of low cost inorganic membranes by using cheaper raw materials. Elmarraki et al. [4] described a method for the elaboration of a new ultrafiltration membrane prepared with two different ceramic materials (TiO_2 and $ZnAl_2O_4$) deposited on alumina support. Rakib et al. [5] elaborated porous supports for tangential ultrafiltration membranes by the use of clay and granitic sand ceramics. Saffaj et al. [6,7] described the elaboration of microfiltration and ultrafiltration membranes deposited on cordierite support and on a raw support prepared from natural Moroccan clay. Majouli et al. [8] described the elaboration of new tubular ceramic membrane from local Moroccan perlite for microfiltration process. Jo et al. [9] prepared stainless steel/fly ash and stainless steel/fly ash/TiO_2 membranes for hot gas cleaning. Dong et al. [10] investigated the development of mullite membrane by sintering fly ash with the addition of chemically pure titania. Fang et al.

[11] elaborated new ceramic membrane from spherical fly ash for microfiltration of rigid particle suspension and oil-in-water emulsion, etc.
In this present work, we have developed an ultrafiltration monotubular membrane prepared from natural and synthetic phosphate PTP (Potassium Titanyl Phosphate). The choice of natural phosphate is mostly due to its abundance in Morocco, and on the other hand to its low cost than other commercial powders, to its mechanical resistance, and to its chemical and thermal stability [12,13]. The support was elaborated by extrusion process, the microfiltration layer was elaborated by classical ceramic technique "slip-casting process" and the top ultrafiltration layer was deposited using the sol-gel route emerged as an extremely versatile technique for preparation of high-purity microporous materials with well-controlled physical and chemical properties [14]. Several parameters were considered and optimised, during the fabrication process of the ceramic membranes, such as treatment process of phosphate, powder granulometry, proportion of binder, concentration of the pore forming agent and sintering temperature.
Pressure-driven membrane separation processes such as microfiltration (MF) and ultrafiltration (UF) has emerged as a feasible alternative to conventional treatment processes of water and wastewater. They has proven to save the operation costs and water consumptions by water recycling [15,16]. In our previous works [17], we have evaluated the applicability of phosphate MF membranes in treating wastewater generated by the phosphate industry, in clarification of synthetic solutions of lime and aluminum hydroxide, and in bacteriological purification of water wells. In this study, the application of the elaborated phosphate membranes will be tested in order to evaluate their efficiency in term of dye removal.

2. Materials and methods

2.1 Sample of phosphate schlamms

The raw material used in this study is the phosphate schlamms coming from the mine of Khouribga (Morocco). The powder granulometry is an important parameter because pore sizes and porosity of membranes are dependent on particles diameter. The natural phosphate was crushed to an average size inferior to 160 µm and 50 µm to prepare support and microfiltration layer, respectively. The mineralogy characterization of phosphate schlamms shows the presence of the principal constitute of phosphates, the apatite with a high amount (95.8%). The content of quartz and clay is about 1.3% and 2.1%, respectively. The particle-size distribution, presented in Table 1, shows the diameter corresponding to x% of cumulative undersize x = 50 (d_x), the mean diameter (d_m) and the median (M).

Table 1: Particle-size distribution of phosphate schlamms.

Particles	d_x	d_m	M
<160 µm	31.50	26.73	13.24
<50 µm	13	9	6

2.2 Elaboration of the support

Plastic pastes were prepared from ceramic powder, mixed homogeneously with organic additives and water. A porous tubular support was obtained by the extrusion process. The optimal composition of this paste is as follow: 10 wt % of Amidon, 2 wt % of Polyethylene glycol 1500 (Prolabo) as a binder, 3 wt % of Amijel derived from starch (Cplus 12072, Cerestar) as a binder and 3 wt % of methocel (The Dow Chemical Company) as a plasticizer. The addition of these products gives a plastic character to the pastes and facilitates their shaping. The extruded pieces were kept at room temperature during 24 h and two steps for firing treatment were carried out in air atmosphere in a programmable furnace; the first one for the decomposition of organic additives and the second one for sintering [18]. The pieces were then treated at 300 °C for 2 hours and at 1000°C for 3 hours at a rate of temperature rise of 1°C/min and 2°C/min, respectively. This allowed the removal of organic additives without causing defects in the ceramic structure. The prepared substrates are placed inside a ceramic tube during the heat treatment so as to have a homogeneous sintering and to avoid deformations.

2.3 Elaboration of the microfiltration layer

The slip casting process was used to elaborate microfiltration layer. For a good adhesion on the macroporous support, viscosity (wt % of PVA) must be sufficient and the casting time should be optimized too. A deflocculated slip was obtained by mixing 8 wt % of natural apatite powder (specific area 140 m^2/g), 52 wt % of an solution containing dispersant at 1 % wt (DOLAPIX CE 64 from Zschimmer and Schwartz) and 40 wt % of aqueous solution of PVA at 12 wt % as a binder. The final mixture was maintained under continuous stirring for 24 hours. The microfiltration layer was deposited on the inner surface of the support by slip casting. The tubular support is filled with the obtained mixture and the coating was carried by capillary suction during 10 min. After coating vertically the tubular support with the suspension, it was dried at room temperature and then fired. The program of sintering is reported in Figure 1.

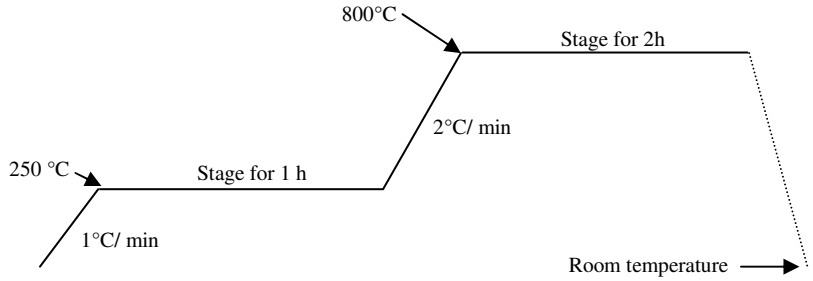

Figure 1: Sintering temperature program used for microfiltration layer.

2.4 Elaboration of the ultrafiltration membrane

The ultrafiltration membrane was prepared by the process of sol-gel [19-21]. A sol was obtained from a composition of 0.4 wt % KTP ($KTiOPO_4$) (specific area 200 m^2/g at 550 °C) and 5.6 wt % of PVA at 12 %. The coated support was dried for 24 h at room temperature and then fired following the thermal program reported in Figure 2. The temperature rate relatively slow (2°C/min) is needed in order to avoid the formation of cracks on the layer.

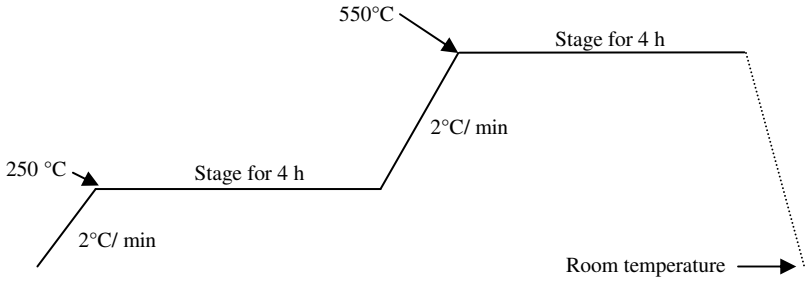

Figure 2: Scheme of the thermal treatment program used for UF membranes.

2.5 Mechanical strength and structural analysis

The mechanical resistance of the material was evaluated using the destructive three-point bending flexural method to assess the flexural properties of the specimens. A universal testing machine (model LRX, Lloyd Instruments) was employed. The characterization of the supports (surface quality, thickness) was done by scanning electron microscopy SEM (Hitachi, S-4500). The pore size distribution of the support and MF layer was evaluated by the use of a mercury porosimetry (Micromeritics Autopore II 9220 V3. 05). The pore size distribution of the ultrafiltration layer was determined by nitrogen adsorption/desorption (BET method-Micromeritics Asap 2010).

2.6 Dynamic permeability of membranes

The membranes elaborated present tubular configuration with a length of 150 mm and an internal diameter of about 5 mm. The water permeation measurements were carried out on a filtration pilot plant in the laboratory (see Figure 3) using distilled water. The membranes were conditioned by immersion in pure deionized water for a minimum of 24 h before filtration tests to obtain a stabilized flux right from the beginning of the experiment. Fluxes are measured at different transmembrane pressures values.

2.7. Characterization of pre-treated textile effluent and membranes permeates

Elaborated membranes were applied as a complementary process for decolorizing concentrated textile effluent pretreated by coagulation-flocculation. The pH and conductivity were measured directly by the use of a Fisher Scientific Accumet Basic AB15 pH Meter (USA) and a Conductivity Meter Model 101 (Orion Research, Cambridge, MA, USA), respectively. Turbidity was measured using a device (TN-100/T-100, Eutech Instruments). Residual concentration of dye was analyzed at λ_{max} = 620 nm using ATI Unicam UV2 UV/vis Spectrometer (Cambridge, UK). The calibration curve was prepared with the pure dye (Blue Bezaktiv S-GLD) present in the studied textile wastewater. The percent of rejection rate was calculated by the classical relation:

$$R(\%) = \left(\frac{1 - C_p}{C_f} \right) x100$$

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

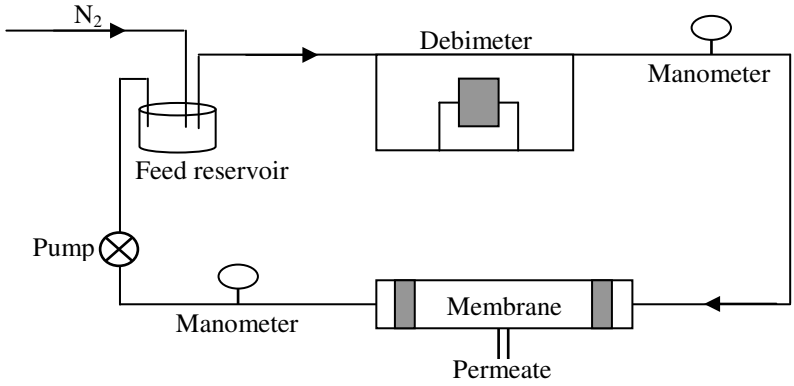

Figure 3: Scheme of pilot plant used for filtration.

3. Results and discussion

3.1 Characterization of the support

The observation by scanning electron microscopy, of the morphology of surface and cross section of support fired at 1000 °C, do not show any macro defects (see Figure 4). The obtained tubular supports (Φ_{int} = 4 mm and Φ_{ext} = 7 mm) present good final characteristics, the mean pore diameter is equal to 10 µm (Figure 5) and the porosity is 43%.

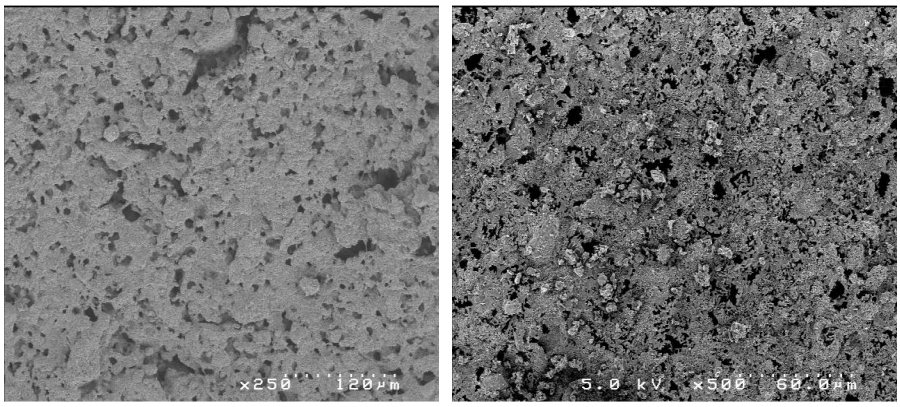

Figure 4: SEM images of the surface of the elaborated porous support.

The mechanical resistance test was performed using the three points bending strength to control the resistance of the material fired at different temperatures. The mechanical resistance of the ceramic material was evaluated on specimens with the following dimensions: length 4 cm, thickness 2 mm and width 10 mm. Specimens were elaborated using the formulation and the thermal program adopted previously for supports elaboration. The mechanical strength reported in Figure 6 increases with increasing sintering temperature. Each value given on the curve is the arithmetic average of at least 10 determinations. The margin of error calculated in this case for each measure is 3%. The Flexural strength, also known as modulus of rupture (σ), is about 30 MPa at the firing temperature adopted in this work (1000°C) and reflects good strength of the elaborated support. Indeed, the ceramic consolidates by densification and becomes more rigid. The grain boundaries expand due to the absorption of small grains by the largest. This gives great rigidity to the ceramic and ensures to it good mechanical strength.

3.2 Characterization of MF and UF layers

Microfiltration layer, made from natural apatite powder and deposited on the porous tubular support, shows homogenous surface without cracks (see Figure 7a). The pore diameter of MF layer is equal to 0.35 µm (Figure not shown). The thickness of the MF layer is about 10 µm (see Figure 7b). On the other hand, the observation by SEM reveals that the surface of ultrafiltration layer, made from Potassium titanyl phosphate $KTiOPO_4$, is homogeneous (see Figure 7c) and presents a good adhesion with the support. It doesn't present any cracks, the membrane thickness has a value of 1.5-1.7 µm (see Figure 7d). The characterization of UF layer by nitrogen adsorption-desorption (see Figure 8) shows a pore diameter centred near 10 nm.

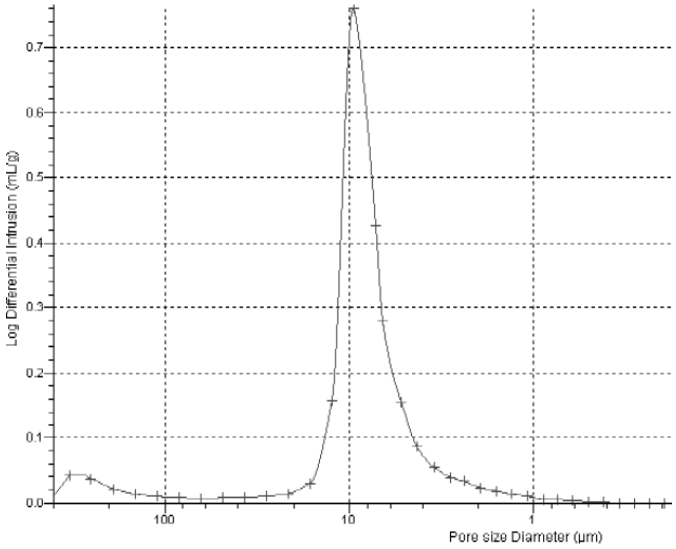

Figure 5: Pore diameter distribution for support. .

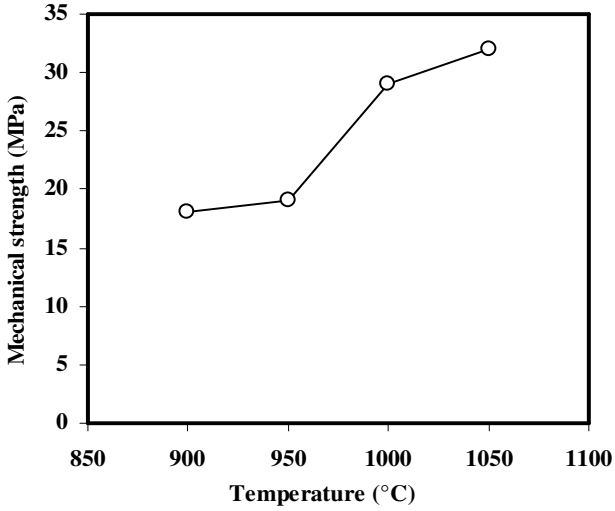

Figure 6: Mechanical strength versus firing temperature of the support

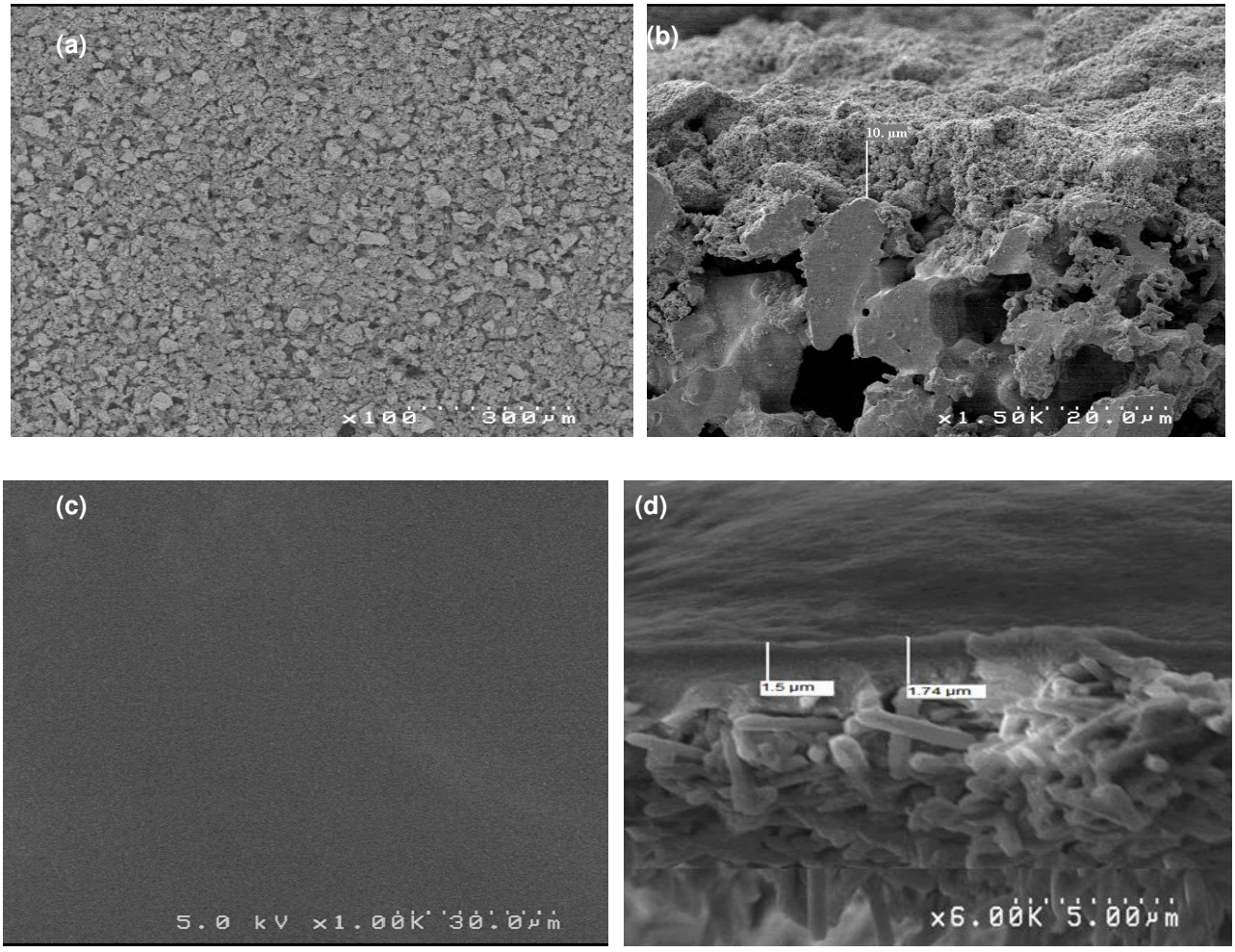

Figure 7: SEM images of the microfiltration and ultrafiltration membranes: surface of MF membrane (a), cross-section of MF membrane (b), surface of UF membrane (c), and cross-section of UF membrane (d).

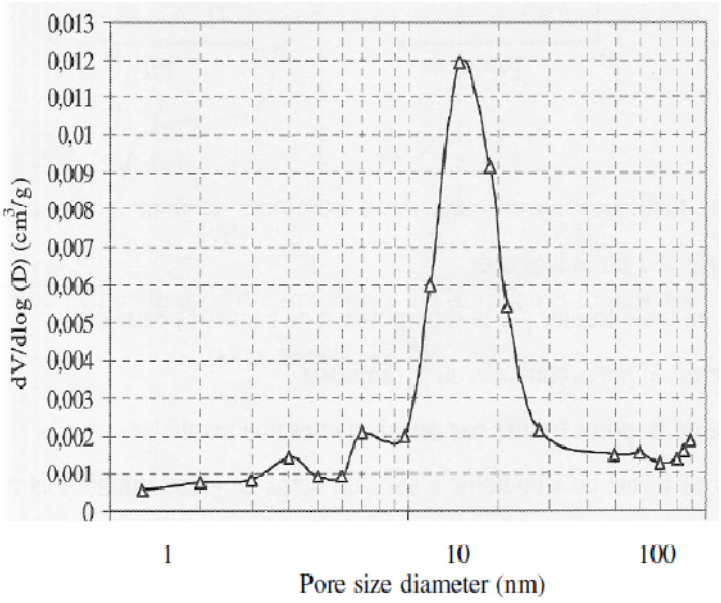

Figure 8: Pore diameter distribution for top ultrafiltration layer.

3.3 Membrane permeability

Tangential filtration tests were performed on a laboratory scale filtration pilot, using a recycling configuration. Microfiltration and ultrafiltration membranes were first characterized by their water permeability using pure distilled water. For each membrane, fluxes are measured at different transmembrane pressures (1, 2 and 3 bar). It was observed that the stabilization of the water flux through the membranes takes approximately 30 min. Experiments show also that the water flux through the membrane depends on the applied pressure. The average permeability was determined from the values of flux measured after stabilisation for each working pressure. From the curves given the flux vs. pressure (see Figure 9), the average permeability of MF and UF membranes is about 778.6 L/h.m^2.bar and 80 L/h.m^2.bar, respectively. Permeability is a function of the nature of membrane and of its porosity. It also depends on the pore size and thickness of the membrane [8].

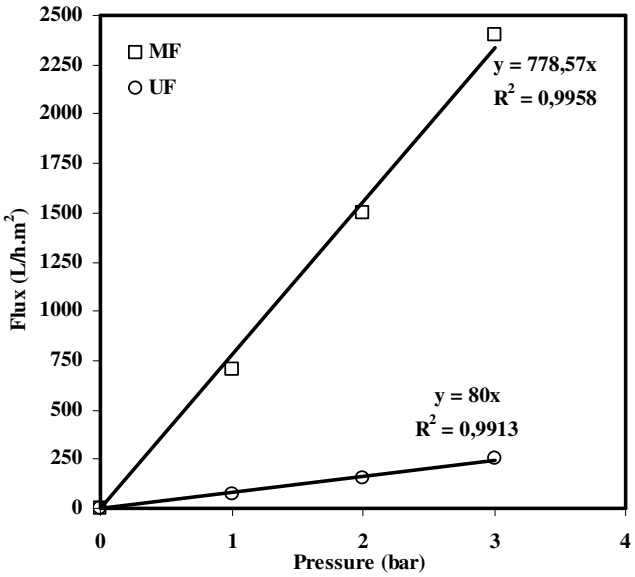

Figure 9: Water flux through microfiltration and ultrafiltration membranes as a function of pressure.

3.4 Filtration of a pre-treated textile effluent

Most dyes used in textile industries are stable to light and are not biologically degradable. Furthermore, they are resistant to aerobic digestion. In order to reduce the risk of environmental pollution from such wastes, it is necessary to accurately treat them before discharging to the receiving environments.

Wastewaters pre-treated by coagulation-flocculation were obtained from a textile industry. The objective of our work was the removal of the residual amount of dye, remaining in the pre-treated effluent, by the use of the elaborated membranes of MF and UF. The effluent was first analyzed for pH, turbidity, conductivity and concentration of dye. The results of this characterization are shown in Table 2. The high conductivity (5.6 ms/cm) can be explained by the use of chemical salts in the textile processes. The turbidity and the concentration of the residual dying matter are about 58 NTU and 38 mg/L, respectively. The characteristics of the permeates from microfiltration and ultrafiltration process, obtained under a pressure of 1 bar for MF and 2 bar for UF (velocity of 6 m/s), show that coupling pressure-driven membrane technology and chemical treatment has proved effective in the treatment of textile wastewater with quasi-complete removal of dyed matter, reduction of conductivity and total rejection of turbidity. The rejection of residual dye can achieve 96% and 99% by the use of MF and UF membranes, respectively. Microfiltration and ultrafiltration lead to a decrease of turbidity of about 97% and 100%, respectively. On the other hand, we note that UF membrane leads to a decrease of conductivity of about 70%.
All of these results show the potential application of the membranes elaborated and the possibility of their use as a complementary process for pre-treated concentrated textile effluents. The use of hybrid treatment processes based on coagulation-flocculation combined with membrane processes MF and UF show relatively identical performance in terms of quality of treated water. However, the permeate flux of MF membrane is higher than that of UF membrane. This highlights the effect of the mineral composition and the pore diameters of filtration layers.

Table 2: Characteristics of pre-treated textile wastewaters and permeate of MF and UF.

Pre-treated effluent and permeates	Concentration of dye (mg/L)	pH	Conductivity (ms/cm)	Turbidity (NTU)	Flux ($L/h.m^2$)
Pre-treated effluent	38	6.8	5.6	57.7	-
Permeate of MF	1.49	7.5	4.5	1.5	94
Permeate of UF	0.3	8.4	2.4	0.002	38

Figure 10 shows the appearance of raw textile wastewater, effluent obtained after chemical pre-treatment, by coagulation-flocculation, and permeate of ultrafiltration process. As it can be seen, filtration on ceramic membranes improves considerably the appearance and quality of the effluent.

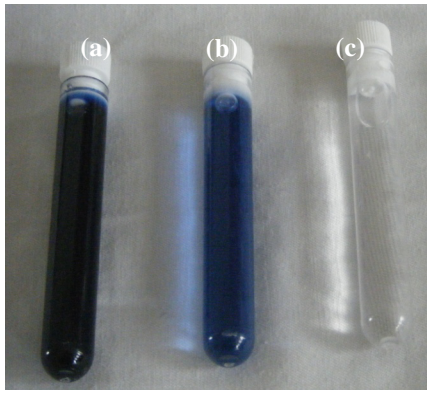

Figure 10: Raw textile effluent (a), Effluent pre-treated by coagulation- flocculation (b), and Permeate of UF membrane (c).

Conclusion

In this work, we successfully prepared microfiltration and ultrafiltration membranes from natural and synthetic phosphate, respectively. The bulk ceramic support was formed by extrusion of a ceramic paste derived from natural Moroccan apatite. The microfiltration layer made from natural apatite was obtained by using slip-casting process and the ultrafiltration layer made from PTP was obtained by sol-gel route.
Both membranes MF and UF present good characteristics. The microfiltration and ultrafiltration layers have a pore diameter of 0.35 µm and 10 nm, respectively. The water permeability of microfiltration and ultrafiltration

membranes is about 700 L/h.m^2.bar and 80 L/h.m^2.bar, respectively. The filtration tests confirm the ability of the prepared low cost membranes in removing residual dye from chemical pre-treated textile wastewaters. In general, microfiltration and ultrafiltration treatment technologies showed to be promising in removing pollution from textile wastewaters. The use of these processes, as complementary treatment, offers the possibility to remove the dye species from pre-treated industrial textile effluents and comply with the principle of sustainable development.
Attempts to elaborate support from other natural mineral powders and deposit different microfiltration and ultrafiltration layers made of various ceramic materials are now in progress to extend the filtering properties and to modify the selectivity of the membranes.

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