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New ceramic membranes from natural Moroccan phosphate for microfiltration application

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ABSTRACT

This paper is devoted to preparation of low-cost microfiltration (MF) membranes using lixiviated phosphate powder crushed at 50 μm. The filtering layer was coated on phosphate tubular support with 10 μm pore diameter and 43% porosity. The preparation of this ceramic layer was performed by the slip-casting method. A deflocculated slip was obtained by mixing mineral powder, polyvinyl alcohol, and water with dispersant. After drying at room temperature for 24 h, the MF layer was heated to 800˚C for consolidation. Scanning electron microscopy observation showed homogeneous layers without cracks with an average pore diameter of 0.35 μm for the active layer, the thickness is approximately 10 μm. Water permeability obtained is about 700 L/h m^2 bar. The membranes have been tested to treat wastewater of phosphate industry, to clarify synthetic solutions of lime and aluminum hydroxide, and to remove bacteriological pollution present in water wells. The experiments carried out show that elaborated MF membrane is very efficient for the reduction of turbidity, total phosphorus, and number of bacterial germs with almost the same performances than that obtained with a commercial α-alumina membrane.

Keywords: Phosphate; Ceramic membrane; Microfiltration; Crossflow filtration; Water treatment

1. Introduction

Due to the rapid development in technology and urbanization; industrial, agricultural, and domestic wastes are discharged to several receivers such as rivers, lakes, and seas. The main objective of wastewater treatment is generally to allow human and industrial effluents to be disposed of without danger to human health or unacceptable damage to the natural environment. Several physical, chemical, and biological processes of varying effectiveness can be used to remove pollutants from wastewater.

Compared with conventional water treatments, which operate in discontinuous and produce large

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quantities of sludge, the membrane processes are used to purify water continuously, without creation of by-products and without chemical additives. Therefore, crossflow microfiltration (MF) is widely used as a solid–liquid separation technique in the beverage, food, and biotechnology industries. MF process can also be used as pretreatment for water before reverse osmosis and other membrane systems.

Ceramic membranes can be obtained using asymmetric multilayer configuration where the different layers are coated on a macroporous support which offers a sufficient mechanical resistance. Commonly used materials for ceramic membranes are Al_2O_3, TiO_2, ZrO_2, SiO_2, etc. or a combination of these materials [1]. Significant efforts were accomplished in the last year to produce new inorganic membranes for MF using natural non-expensive raw material [2–4] in order to treat large volumes of effluent at acceptable costs. A lot of materials were used for membrane preparation: natural clay and cordierite were used by Saffaj et al. [5] and Loukili et al. [6] to prepare supports which were coated with ZrO_2 MF layer and then with $ZnAl_2O_4$–TiO_2 ultrafiltration layer. Clay and granitic sand ceramics were used by Rakib et al. [7] as porous supports for tangential ultrafiltration membranes. Due to their abundance, clays are generally among inorganic materials mainly used by researchers to prepare supports or MF membranes [8–10].

The preparation of new monotubular macroporous supports prepared from natural Moroccan phosphates by extrusion process was reported in our previous works [11]. The choice of this material is mostly due to its abundance in Morocco, its low cost than other commercial powders, its mechanical resistance, and its chemical and thermal stability [12,13]. Process parameters for fabrication of ceramic membranes were optimized with choice of treatment process of phosphate, respect to grain size of powder, proportion of binder, concentration of the pore-forming agent, and sintering temperature. The goal of this work is now focused on the use of lixiviated natural phosphate as possible material for the elaboration of MF membrane.

Apatites are a group of phosphate minerals, they are compounds of the general formula $M_{10}(XO_4)_6Y_2$, rather than for specific compounds. Generally, they are known to be able of accommodating a wide variety of modifications and combinations of substitutions of ions and groups within the apatite lattice. However, the term "apatite" has been extensively used to represent the calcium phosphate, $Ca_{10}(PO_4)_6Y_2$ where $Y = F^-$, OH^- or Cl^-. In sedimentary deposits, the major minerals are francolite phosphate (fluoroapatite carbonate). They are associated with a wide variety of minor minerals and impurities [14,15].

In the first part of this work, we will present the elaboration of a MF ceramic membrane, with tubular configuration, made of natural Moroccan phosphate. The novelty of our work is that Moroccan-leached phosphate was used to elaborate support and MF layer. In the second part, the performances of the elaborated membrane were compared with those of a commercial ceramic membrane made from alumina. We evaluate the applicability of these membranes of MF 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. The innovative aspect of this study lies in its direct link with the fundamental principles of sustainable development. The treatment can be economic, since the developed membranes have a low cost compared to commercial membranes.

2. Material and methods

2.1. Phosphate sample

Natural Moroccan phosphates from Khouribga site were used to prepare lixiviated phosphate. The process of leaching or enrichment is the following:

- Debourbage for 15 min in order to disintegrate the grains.
- Wet sieving between 100 and 400 μm in order to separate (i) fractions larger than 400 μm containing the toughest products such as quartz, (ii) intermediate fractions between 160 and 400 μm corresponding to the enriched mineral, and (iii) finer fractions under 160 μm which contain the rich-clay matrix and magnesia (MgO).
- Acid attack by HCl 0.1 N to eliminate free carbonates without attacking fluorapatite.
- Washing with distilled water and drying in an oven at 105°C for 24 h.

The enriched powder was crushed at 50 μm with disk mills Mc call. The chemical composition of phosphate sample is given below (Table 1). The elementary chemical analysis shows essentially the presence of phosphate, calcium, and fluoride elements which can be attributed to fluorapatite mineral. The diameter corresponding to 50% of cumulative undersize (d_x), the mean diameter (d_m), and the median (M) determined from the granulometric analysis of leached phosphate powder milled to 50 μm are, respectively, 13, 9, and 6 μm.

Table 1
Chemical analysis of phosphate sample

Amount (% weight)										
P_2O_5	SO_3	CO_2	SiO_2	CaO	MgO	Fe_2O_3	Al_2O_3	Na_2O	K_2O	F^-
33.40	1.56	4.39	1.40	51.59	0.25	0.12	0.29	1.10	0.06	4.08

2.2. Preparation of support

The preparation of the support from natural phosphate was performed as described in our previous work [11]. Good mechanical properties and a pore size of 10 µm were obtained by the use of natural phosphate after (i) washing, (ii) treatment with diluted HCl (pH 5), (iii) washing, (iv) drying at 105˚C for 24 h, and finally (v) grinding at 160 µm [11].

The elaborated support should be thoroughly cleaned before coating in order to prevent membrane defects. The tubular support has a length of 15 cm. It was washed with distilled water and then sonicated for 15 min in a beaker filled with ethanol. It was finally dried in an oven at 100˚C.

2.3. Development of MF layer

Lixiviated phosphate powder was mixed with water and additives to prepare a deflocculated suspension for coating the tubular support. The MF layer was obtained by slip casting (Fig. 1) by means of a deflocculated suspension which is prepared by mixing 8 wt % of mineral powder (lixiviated phosphate), 40 wt % of polyvinyl alcohol (PVA) (12 wt % aqueous solution), and water with dispersant DOLAPIX PC 67 at 1% (52 wt %). The molecular weight of (PVA) is 80,000 g/mol. Dispersion of the apatite particles was achieved by applying ultrasonic agitation for 10 min. Normally, DOLAPIX PC 67 makes possible the preparation of slips with high solids content. Since the product is liquid and is thus completely dissociated, the deflocculating effect commences immediately after addition to the slip. Here, ultrasonic agitation was applied in order to achieve deflocculating effect of dispersant. The viscosity is an important parameter to determine the slip optimal composition; it was measured just before slip casting by using a rotary viscometer Tve-05 (LAMY). The viscosity of the suspension should be sufficient to prevent the rapid formation of a thick and inhomogeneous layer due to a very rapid absorption of the solvent. This viscosity must also enable the solution to be cast within the support without difficulty.

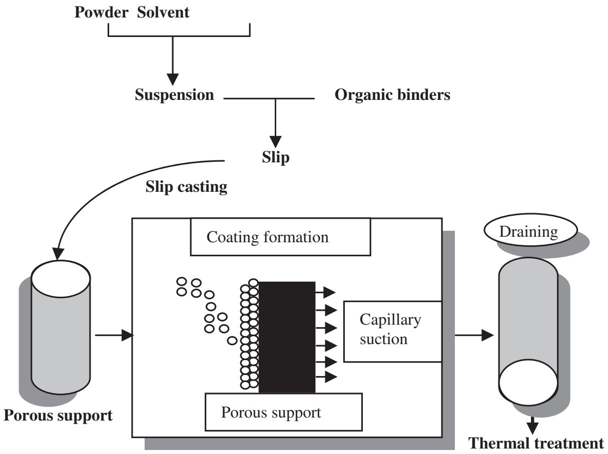


Fig. 1. Slip-casting process.

The composition of the slip is considered to be optimal when the coating allows the production of layers of sufficient thickness to ensure a complete and homogeneous covering of the ceramic support wall. The layers obtained must be free of defects. Furthermore, the quality control of the slip must ensure a perfect reproducibility of the characteristics of the deposit. However, the thickness of the filter layer must be relatively small to not harm the performance of the filtration. The study of the microstructure of the layers in different formulations and at different sintering temperatures allowed us to determine the optimum composition of the slurry.

The slip-casting process was then applied to coat the porous tubular support with 10 µm pore diameter and 43% porosity. The ceramic support was prepared by extrusion method from natural phosphate. To be coated, the support must be used at room temperature to avoid excessive absorption of the suspension due to the difference in temperature. The support was disposed vertically and the lower end of the tube was sealed. The tubular support was then filled with the slip. The deposition time was fixed at 10 min. After the contact time has established, it was drained through the lower part. The deposition is carried out by capillary suction. The support was dried vertically at room temperature for 24 h to allow complete evacuation of the surplus of slip. The MF layer was then sintered at 800˚C for 2 h after debonding at 250˚C for 1 h. The heat treatment allows the elimination of the organic additions and the consolidation of the membrane. The thickness of the MF layer can be controlled by the percentage of the mineral powder added in the suspension and the contact time with the support. The external and internal diameters of the ceramic MF membrane are 5 and 4 mm, respectively.

2.4. Tests of filtration

Crossflow filtration tests were performed using a laboratory scale unit in recirculation mode (Fig. 2). It was equipped with an adjustable pump, a thermostatic feed tank, and a membrane module of 15 cm length. The filtration area developed by the membrane is $1.9 \times 10^{-3}\,\text{m}^2$. A valve on the retentate side was used to control the pressure in the system which varies between 0 and 2 bar. Membranes were conditioned by immersion in pure deionized water for a minimum of 24 h before the filtration tests to obtain a stabilized flux right from the beginning of the experiment.

Elaborated membranes were used to treat (i) washing phosphate effluent supplied by Moroccan CERPHOS Company, (ii) bacteriological (fecal coliforms and streptcoques) contaminated water collected from water wells, and (iii) two synthetic solutions containing, respectively, 1 g of lime per liter and 1 g of Al^{3+} per liter with a few drops of concentrated NaOH.

The performances of the elaborated membrane were compared with those of a commercial ceramic membrane, provided by Pall Corporation, made from alumina and having a pore diameter of 0.2 µm.

2.5. Analysis

The crystal phase composition of the phosphate samples was obtained by X-ray powder diffraction (Siemens) with Cu K_a radiation ($\lambda = 0.154$ nm). Particle size distribution and BET specific area were obtained by means of a particle sizing system Beckman-Coulter and a surface area analyzer type ASAP 2010 Micromeritic, respectively. Surface and cross section of the MF layer were observed by scanning electron microscopy (SEM) (Hitachi, S-4500). Mercury porosimetry device (Micromeritics 9600) equipped with a low and high pressure system was used for material pore size determination.

Oxidizability by $KMnO_4$ was used to estimate organic matter in phosphate industry effluent before and after filtration on MF membrane (NF EN ISO 8467). This test is intended to approximate the content of organic matter in water by measuring the amount of oxygen used for the reduction of potassium permanganate ($KMnO_4$) with the organic substances contained in water. This is a back titration.

The content of suspended matter was determined by filtering a volume of water. The weight of material retained by the filter is then determined by differential weighing after drying at 105°C (NF EN 872). Total phosphorus was analyzed with spectrophotometric method at 430 nm by a coloring reaction with ammonium molybdate vanadate. Turbidity was measured using TN-100/T-100 device. The pH and conductivity of the feed and permeate solution 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. The enumeration of micro-organisms was carried out according to bacterial colony count method described by AFNOR [16].

3. Results and discussion

3.1. Characterization of lixiviated phosphate powder

Purity of the mineral powder was controlled by powder X-ray diffraction (Fig. 3) which confirms the presence of peaks characteristic of fluorapatite mineral (according to ASTM file 15-0876). Fluorapatite is a mineral with the formula $Ca_5(PO_4)_3F$ (calcium

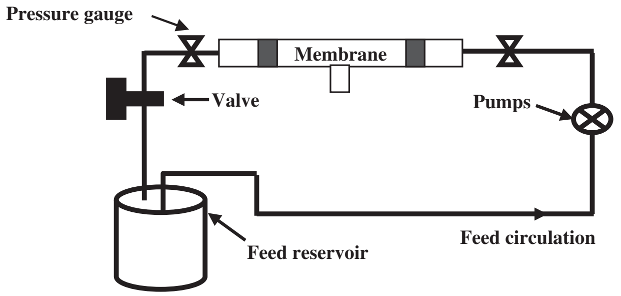


Fig. 2. Scheme of the MF laboratory plant.

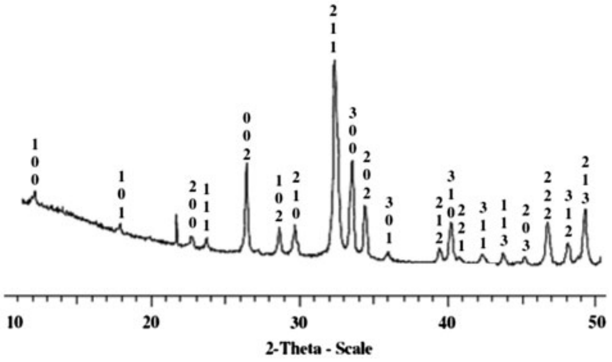


Fig. 3. X-ray diffractogram of the phosphate powder.

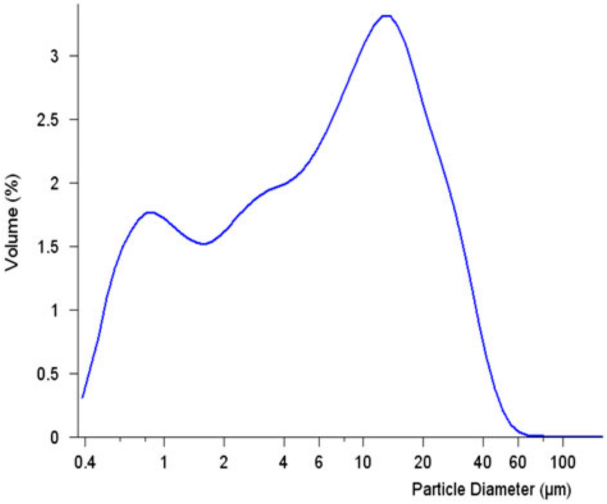


Fig. 4. Distribution of the particle size.

fluorophosphate). No other phase was detected on the XR diffractogram of the sample. The XRD pattern can be indexed in the hexagonal system, the space group is $P6_{3/m}$.

The particle size distribution diagram (Fig. 4) shows that the powder has a mixed particle size, well placed on the side of fine particles. This is confirmed by the high value of surface area measured from nitrogen adsorption/desorption which is about 141 m^2/g.

3.2. Characterization of phosphate powder suspension

The rheological behavior of slip apatite sample shows that the value of the viscosity of 13 mPa s permits to obtain a stable suspension of apatite particles in the slip under study. This viscosity is very stable under magnetic stirring. The rheogram of the slip used revealed a Bingham plastic behavior (Fig. 5). From the linear equation mentioned on Fig. 5, the value 1,963.2 represents the yield shear stress.

3.3. Characterization of the MF layer

The morphology, surface quality, and thickness of top-layer membrane were examined by SEM. Fig. 6 shows the cross section and the surface views of the prepared MF layer, its thickness is uniform with an average value of 10 µm, and moreover the surface of the top layer is homogenous without defects and microcracks. Pore size distribution of the top layer measured by mercury porosimetry is centered on 0.35 µm (Fig. 7); this confirms that we achieved our objective of preparing a MF layer.

3.4. MF tests

Fig. 8 shows that the water flux through the membrane depends on the applied pressure but the stabilization of the flux needs about 1 h. The permeability was determined from the values of flux measured after stabilization for each working pressure. The curve, given the flux vs. pressure, is a straight line with a slope equal to about 700 L/h m^2 bar which corresponds to the permeability of apatite membrane compared with 1,000 L/h m^2 bar for commercial MF membrane used as reference in the next part of this work.

The phosphate mining treatment produces a great amount of wastewater. Several researchers [17–19] showed the negative influence of these effluents on the live conditions of the fauna and flora in ocean due

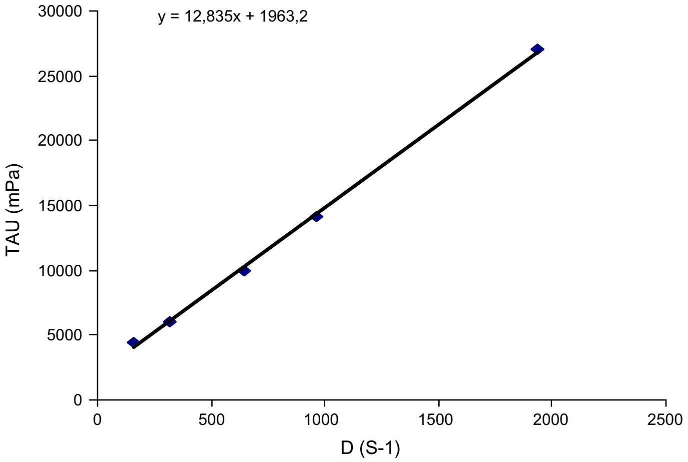
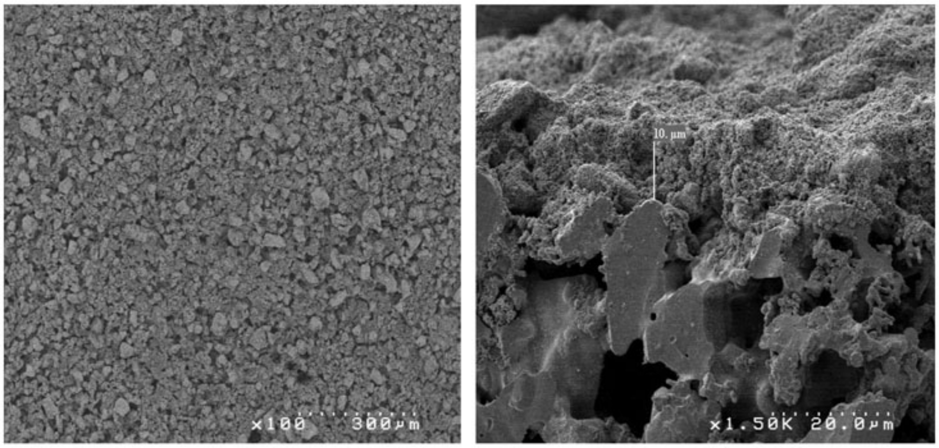


Fig. 5. Rheologic behavior of slip apatite sample.



(a) (b)

Fig. 6. SEM views of surface (a) and cross section (b) of apatite membrane.

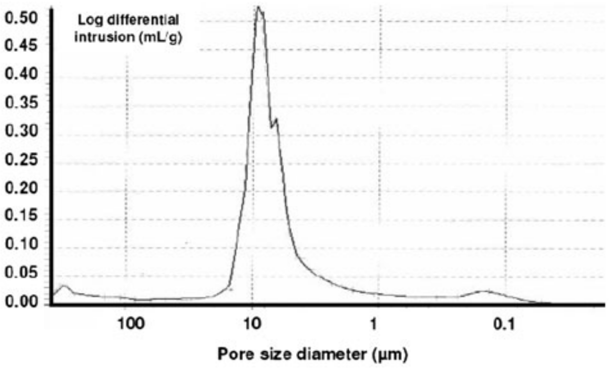


Fig. 7. Pores' diameter distribution for top-layer membrane.

to the contamination by insoluble particles and metallic elements.

Table 2 gathers the main characteristics of phosphate industry effluent before and after treatment by tangential MF process at room temperature and at a low working pressure (1 bar). As it can be seen, the turbidity of effluent decreases from 54 to 0.79 NTU after MF treatment. Results of chemical analysis show also an important reduction of total suspended solid (MLSS) (>97%) and of total phosphorus (64%). The MF treatment with the apatite membrane seems efficient to remove the suspended solid and lead to a clear permeates, the performances compared with commercial alumina membrane are similar.

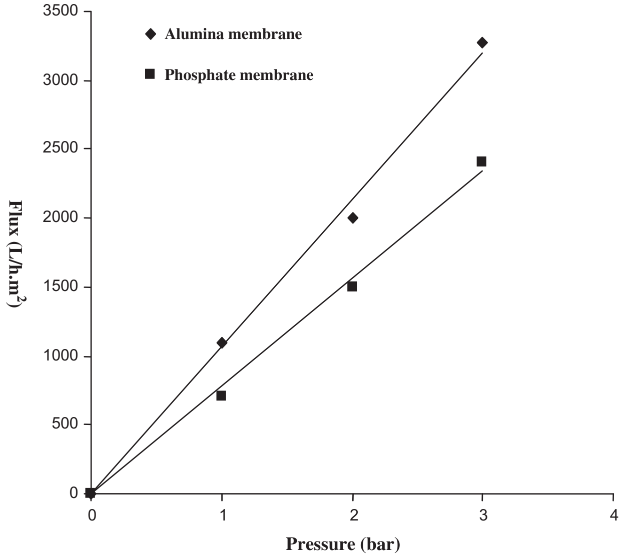


Fig. 8. Water flux vs. pressure for MF membranes.

Efficiency of MF process was also tested for the treatment of two synthetic suspensions: one of lime (408 NTU) and another of aluminum hydroxide (720 NTU). As can be seen, the results presented in Table 3 confirm the possibility to remove completely the turbidity of both effluents by MF treatment.

MF processes are also efficient to stop the pathogens (viruses, bacteria, parasites) because MF membrane is a barrier for these species. Microbial water pollution may be defined by the total pathogenic germs conveyed by the water, by invading part or all of a human organism; these germs are able to induce a more or less serious infectious disease by upsetting the subject's biological equilibrium. For this reason, we have studied in this work the efficiency of apatite

Table 2
Characteristics of phosphate industry effluent before and after filtration on MF membrane

Parameters	Conductivity (µs/cm)	pH	Oxidizability by $KMnO_4$ ($mg\,O_2/L$)	Total phosphorus (mg/L)	Turbidity (NTU)	MLSS (mg/L)	Flux (L/h m^2 bar)
Effluent	2,191	7.92	4.44	2.07	54	85	–
Permeate of PM	2,178	8.47	4.25	0.74	0.79	2	350
Permeate of CAM	2,160	8.2	4.28	0.37	0	0	470

Note: PM: Phosphate membrane; CAM: Commercial α-alumina membrane.

Table 3
Characteristics of synthetic solutions before and after filtration

	Lime			Aluminum hydroxide		
Parameters	Effluent	Permeate PM	Permeate CAM	Effluent	Permeate PM	Permeate CAM
Conductivity (µs/cm)	1976	1,580	1,528	9,730	9,440	9,470
pH	7.62	7.80	7.50	11.44	11.86	12.10
Turbidity (NTU)	408	0	0	720	0	0
Flux (L/h m^2 bar)	–	400	350	–	420	350

Note: PM: Phosphate membrane; CAM: Commercial α-alumina membrane.

Table 4
Characteristics of water wells before and after filtration

Parameters	Fecal coliforms (number of colonies/mL)	Streptococcus (number of colonies/mL)	pH	Turbidity (NTU)	Conductivity (µs/cm)	Flux (L/h m^2 bar)
Effluent	10	10	7.88	1.02	1,475	–
Permeate PM	<1	<1	7.87	0.51	1,459	480
Permeate CAM	<1	<1	7.80	0.21	1,560	540

Note: PM: Phosphate membrane; CAM: Commercial α-alumina membrane.

MF membrane to remove bacteria (fecal coliforms and streptcoques) from water wells. Obtained results from bacteriologic tests demonstrated relatively zero bacteria in the filtered water permeate (Table 4) that means a high rejection of bacterial pollution by the membrane. It is quite normal that there is retention of bacteria (fecal coliforms and streptcoques) by MF because their sizes are between 0.5 and 1 µm and the pore size of MF membrane used is 0.35 µm.

A decrease of turbidity from 1.02 to 0.51 NTU was also observed. Thus, MF membrane can be used successfully for the removal of bacteriological contaminants in water or wastewater.

For all filtration experiments carried out (Tables 2–4), no salt separation can be achieved by MF membrane. The MF membrane allows only the removal of suspended particles; this is why turbidity is considerably decreased for all filtration tests.

Compared with the α-alumina membrane, the performances obtained with the elaborated apatite membrane are quite good and very close to those of the commercial membrane taken as reference.

4. Conclusion

The preparation and characterization of a low-cost ceramic MF membrane, with tubular configuration based on Moroccan phosphate have been described in this work. The membrane support was prepared by the extrusion of ceramic paste made with lixiviated phosphate powder. The MF layer made also from the same material was deposited on the support by slip casting. This membrane has the advantage of having the same composition as that of his support.

The membrane presents interesting retention properties with regard to the suspended matter, turbidity, total phosphorus, and pathogens. Filtration tests conducted using effluent water produced by the washing phosphate process, suspensions of lime or alumina hydroxide, and water wells reveal clearly the performance of the MF membrane elaborated. Its performances are similar to those of the commercial α-alumina membrane.

The ceramic MF membranes elaborated in this work can also be used as a support for diverse ultrafiltration layers. This is the objective of our current study.

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