

## Fabrication of flat ceramic microfiltration membrane from natural kaolinite for seawater pretreatment for desalination and wastewater clarification

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### ABSTRACT

The aim of this work is the manufacturing of flat microfiltration membrane made from Moroccan natural kaolinite clay and corn starch as porosity agent. The membrane was prepared by uniaxial pressing technique and sintering at 1,100°C. The effect of starch on membrane features was investigated from 0 to 15 wt.%. The membrane has a diameter of 37.8 mm and a thickness of 2.3 mm. In order to optimize its properties, prepared membrane was characterized in terms of apparent porosity, water absorption, apparent density, mechanical strength, pore size, microstructure, and water permeability measurements. Experimental results showed that the membrane prepared with 10 wt.% of starch is considered as an optimized membrane which has an average pore size of 2.3 μm, the mechanical strength of 20.2 MPa, and permeability of 2,129 L h<sup>-1</sup> m<sup>-2</sup> bar<sup>-1</sup>. The optimized membrane was applied for pretreatment of raw seawater for desalination and clarification of agro-food effluent using dead-end filtration under pressure of 0.12 bar. Filtration results showed that turbidity rejection achieves 73% and 99%, respectively for raw seawater and agro-food model effluent.

*Keywords:* Clay; Porosity; Microfiltration; Corn starch; Wastewater; Kaolinite

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### 1. Introduction

As well-known, oceans, seas, lakes, and rivers cover approximately two-thirds of the surface of the earth however only 3% of water is fresh that is not equally distributed across the globe. On the other hand, water demand rapidly increases due to development of industrial activities and eruption of human population [1]. Desalination of seawater could contribute to solve water issues. The main desalination technologies used are multi-effect distillation, thermal distillation, and reverse osmosis. Nowadays, the most dominant

technique is reverse osmosis due to its energy efficiency compared to the other technologies [2,3]. Desalination using reverse osmosis technology requires pretreatment of seawater in the upstream of reverse osmosis unit. It is critical for system life because the thin-film reverse osmosis membranes are subject to fouling by suspended matters presented in raw seawater that has a negative impact on the performance of reverse osmosis [4]. Microfiltration process could be suitable for pretreatment of seawater at low cost. Recently, several studies have been investigated microfiltration process for pretreatment of seawater desalination. Polysulfone

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microfiltration membrane was used for the removal of toxic micro-algae [5]. Yang and Kim [6] found that the microfiltration process is effective for the enhancement of turbidity removal and filtration flux of seawater by applying coagulation. In another work, Corral et al. [7] found that reverse osmosis performance was more stable when microfiltration pretreatment was used.

In the past few years, significant efforts have been made to fabricate new ceramic membranes using cheaper materials instead of common industrial oxides ( $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ , etc.) because these industrial oxides are expensive and they also need high sintering temperature. This makes commercial ceramic membranes more expensive. In order to reduce their cost, ceramic microfiltration membranes were manufactured using local geomaterials. For instance, natural pozzolan was used for fabrication microfiltration membrane which was used to treat textile effluent [8], bentonite clay was employed for the preparation of microfiltration membrane and applied for industrial effluents treatment [9], natural perlite was used to fabricate ceramic membrane that was applied for the treatment of industrial wastewater [10], and clay/phosphate mixture were employed for manufacturing microfiltration membrane for pretreatment of seawater desalination and industrial wastewater treatment [11]. Therefore, it was proved that using local and natural resources in preparation of low-cost membranes, is a promising approach.

Kaolinite has unique physical properties such as high refractory and low plasticity [12]. In addition, kaolinite membrane has a hydrophilic behavior which is desired to enhance the permeability [13]. Kaolin, quartz, and calcium carbonate were used for the preparation of microfiltration membranes for the separation of oil and bacteria from aqueous solutions [14]. Kaolin, quartz, sodium carbonate, calcium carbonate, boric acid, and sodium metasilicate were used to manufacture microfiltration membranes by wet route for application in chemical and biochemical processes [15]. Kaolin and starch were used to elaborate the microfiltration membrane by extrusion for a solution containing dextran [16].

In order to improve the permeability, several pore-forming agents such as starch and carbon were used to control membranes properties [17]. Starch generates pores during the thermal treatment between 300°C and 600°C and it is considered as an appropriate porosity agent because it is cheap, environmentally friendly [18,19]. Referring to literature, some works were carried out using starch as porosity agent. For instance, 10 wt.% of starch was added to kaolin and phosphoric acid, and sintered at 1,100°C to elaborate membrane with 36.81% in porosity [20]. Alumina was mixed with 8 wt.% corn starch, and sintered at 1,400°C to elaborate membrane with a porosity of 46% [21]. In other work, clay mixed with corn starch at 15 wt.% was sintered at 1,200°C to prepare membrane with 24% of porosity [22]. Furthermore, clay and 10 wt.% of corn starch was used and sintered at 950°C to elaborate microfiltration membrane with 35.8% of porosity [23].

Moroccan kaolinite was used to elaborate tubular support for microfiltration and ultrafiltration composite membrane. Saffaj et al. [24] used kaolinite to manufacture tubular support by extrusion and sintering at 1,225°C.

The obtained support could not be directly used for microfiltration without deposition of supplementary membrane layer since its pore diameter appears relatively high (10.25  $\mu\text{m}$ ). To elaborate the microfiltration ceramic membrane many processes can be used such as tape casting, slip casting, extrusion, freeze casting, and pressing [25]. From these techniques, dry pressing is easier and faster method to elaborate ceramic membranes beside the fact that dry pressing is environmentally friendly since the process does not require water (the energetic benefit as there is no drying step) [10]. Furthermore, applying high pressure leads to obtain denser structure [26] and the increase of grains contact effectively contributes to the reduction of sintering temperature which is economically favorable [27].

The main purpose of this work is the elaboration of flat microfiltration membrane made from Moroccan natural kaolinite and starch. Flat membrane was obtained by uniaxial pressing method followed by sintering at 1,100°C. The effect of starch addition on properties of kaolinite membrane was investigated. The optimized membrane was applied for pretreatment of raw seawater for desalination and also for clarification of agro-food model effluent.

## 2. Experimental

### 2.1. Raw materials

Raw kaolinite was collected from Rabat region, Morocco. It should be mentioned that kaolinite used in this work was characterized in detail in previous study [24]. Chemical composition analysis showed that the sample is essentially constituted of 80.00 wt.% of silica and 12.09 wt.% of alumina beside of low amount of other oxides such as  $\text{K}_2\text{O}$ ,  $\text{TiO}_2$ ,  $\text{CaO}$ , and  $\text{Fe}_2\text{O}_3$  (Table 1). Corn starch ( $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ , Merck KGaA, Germany) was used as porosity agent.

### 2.2. Preparation of kaolinite membrane

Kaolinite microfiltration membrane was obtained by dry route using a hydraulic press and sintering. The preparation process is illustrated in Fig. 1. As shown in the figure, kaolinite rock was crushed using ball mill to obtain small grains. The obtained powder was sieved through a sieve of 50  $\mu\text{m}$ . Thereafter, clay powder was mixed with corn starch at different contents from 0 to 15 wt.%. The homogenized mixture was poured in cylindrical stainless steel mold and pressed up to 954 bar for 10 min. Finally, the flat disk obtained was sintered in a programmable oven (Nabertherm L9/13/P320, Germany). Table 2 shows the composition of the prepared membranes.

Differential thermal analysis (DTA) and thermogravimetric analyses (TGA) were performed in a SDT 2960 TA instrument. The sample was heated to 1,100°C in a Pt crucible in  $\text{N}_2$  flowing (3 L  $\text{h}^{-1}$ ) at heating rate of 10°C  $\text{min}^{-1}$ . The thermal analysis was used to establish adequate program for thermal treatment of green membranes (Fig. 2). The first plateau at 100°C corresponds to removal of residual moisture, this plateau is important to avoid cracks formation during the process [27]. The second plateau at 520°C is to ensure the transformation of kaolinite structure to metakaolin, also for corn starch removal. Finally, the last plateau at 1,100°C is for the consolidation of ceramic membranes.

Table 1  
Chemical composition of raw kaolinite

Oxides	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	CaO	MgO	TiO <sub>2</sub>	SO <sub>2</sub>
wt.%	80.00	12.09	1.00	0.50	3.73	1.21	0.06	1.21	<0.2

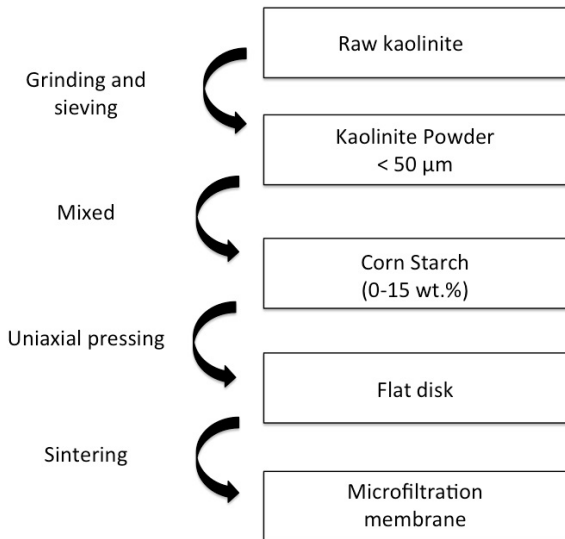


Fig. 1. Membrane preparation process.

Table 2  
Composition of the elaborated membranes

Membrane	Kaolinite (wt.%)	Amount of starch (wt.%)
M1	100	0
M2	95	5
M3	90	10
M4	85	15

2.3 Membrane characterization

A scanning electron microscopy (SEM) JEOL IT 300, (Japan) was used to study the morphology of membranes surface, the structure of pores, and possible defects on prepared membranes. ImageJ software (v.1.44e) was used to estimate the average pore size using SEM images.

The average pore size of the membranes was also estimated using Hagen–Poiseuille equation [28] (Eq. (1)):

$$d = 2 \sqrt{8 \cdot J_w \cdot \delta \cdot \frac{\tau}{P} \cdot \frac{\Delta X}{\Delta P}} \quad (1)$$

where  $d$  is the pore diameter (m),  $J_w$  (m s<sup>-1</sup>) is the water flux,  $\delta$  (Pa s) represents the water viscosity,  $\tau$  is the tortuosity factor,  $P$  (%) is the porosity of the membranes,  $\Delta P$  (Pa) is the transmembrane pressure, and  $\Delta X$  (m) is the thickness of the membranes.

Mechanical strength of the membranes was carried out using a three-point bending according to the American Society for Testing and Materials (ASTM) C674–88 methods.

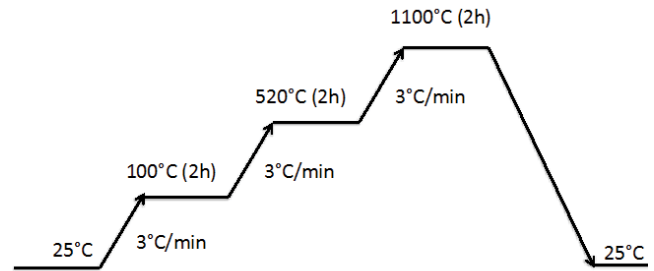


Fig. 2. Thermal treatment applied for kaolinite membranes synthesis.

The samples are rectangular (60 mm in length and 20 mm in width) with the same thickness as flat membrane. Three samples were used to measure the mechanical strength for each membrane.

Chemical resistance of the membranes was evaluated by weight loss in acidic and alkaline solutions using respectively HCl solution at pH 1.5 and NaOH solution at pH 13.0 for a period of 7 d under atmospheric conditions. Membrane shrinkage was calculated using the following equation (Eq. (2)):

$$S = \frac{D_b - D_a}{D_b} \times 100 \quad (2)$$

where  $D_b$  and  $D_a$  are the diameter of the membrane before and after sintering, respectively. Diameter was measured by Vernier Caliper. Apparent density, water absorption, and apparent porosity were all measured according to ASTM C373-88 method.

2.4 Filtration tests

Filtration experiments were performed using microfiltration pilot in dead-end filtration mode at low pressure from 0 to 0.12 bar at room temperature (Fig. 3). The filtration area of the membrane is 5.3 cm<sup>2</sup>. The membrane was soaked in bidistilled water for 24 h before any filtration experiment.

The permeability  $L_p$  (L h<sup>-1</sup> m<sup>-2</sup> bar<sup>-1</sup>) at room temperature of the membranes was determined using bidistilled water. Besides, membrane performance was evaluated by clarification of two feed solutions:

- Raw seawater that was collected from Atlantic Ocean near Mohammedia city, Morocco. The sample was pre-filtered through a sieve of 50 μm to remove the larger particles,
- Agro-food model effluent with high turbidity that was prepared by dispersing corn starch in water (0.5 g L<sup>-1</sup>).

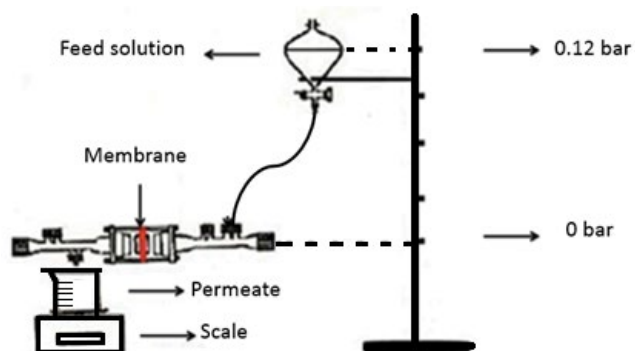


Fig. 3. Microfiltration setup.

Further characteristics of the two feed solutions are summarized in Table 3. Feed (A) is characterized by a high conductivity of  $51 \text{ mS cm}^{-1}$  due to the seawater salts, while the solution (B) is characterized by a high turbidity of 444 NTU due to the presence of suspended corn starch.

Filtration experiments were made at 0.12 bar for 2 h. Turbidity, chemical oxygen demand (COD), pH, and conductivity of the permeate were measured every 20 min. A portable turbidimeter (HACH 2100Q, USA) was used to measure the turbidity. The accuracy on turbidity measurement is  $\pm 2\%$ . Rejection (%) of turbidity was calculated by following equation (Eq. (3)):

$$R = \left(1 - \frac{T_p}{T_f}\right) \times 100 \quad (3)$$

where  $T_p$  and  $T_f$  are the turbidity of permeate and feed solutions, respectively. pH was measured using a Fisher Scientific Accumet Basic AB15 pH meter (USA) and conductivity was measured with Meter Model 101 (Orion Research, Cambridge, Ma, USA). COD was determined according to Fujimori et al. [29] method.

After the filtration experiments of the two feed solutions, the membranes were washed with bidistilled water for 20 min, after that water flux was performed. The flux recovery ratio (FRR) was calculated by following equation (Eq. (4)):

$$\text{FRR} = \left(\frac{J_{p,b}}{J_{p,a}}\right) \times 100 \quad (4)$$

Table 3  
Characteristics of the feed solutions

Parameters	Raw sea-water (A)	Agro-food model effluent (B)
pH	7.7	5.53
Conductivity ( $\text{mS cm}^{-1}$ )	51	0.0096
Turbidity (NTU)	$6.3 \pm 0.1$	$444 \pm 6$
COD ( $\text{mg L}^{-1}$ )	5.9	–

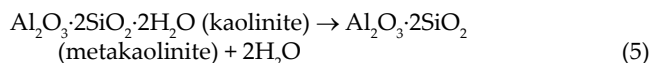
where  $J_{p,a}$   $J_{p,b}$  are the water flux before and after the experiment, respectively.

### 3. Results and discussion

#### 3.1. Thermal analysis of kaolinite

The thermal analysis profiles (TGA and DTA) are shown in Fig. 4. The total weight loss of the raw material was approximately 3 wt.% from  $25^\circ\text{C}$  to  $1,100^\circ\text{C}$ . TGA shows that there are basically two-weight losses. The first weight loss begins from  $25^\circ\text{C}$  to  $250^\circ\text{C}$ , it is mainly due to the physisorbed water. The second begins from  $400^\circ\text{C}$  to  $620^\circ\text{C}$ . It is corresponded to dehydroxylation of kaolinite [30].

DTA shows thermal behavior of kaolinite. The peak at  $570^\circ\text{C}$  is endothermic and it is corresponded to dehydroxylation reaction in which the kaolin is turned to amorphous metakaolin phase according to Eq. (5) [31]. The peak located between  $900^\circ\text{C}$  and  $950^\circ\text{C}$  is exothermic, that is corresponded to spinel crystallization [32].



#### 3.2. Characterization of kaolinite membrane

##### 3.2.1. Visual inspection and shrinkage

As shown in Fig. 5, the membranes color had changed during the thermal process from grey to brown. It is highly probable that  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  are responsible for this color change. During the thermal process, their oxidation led to darker color. After sintering at  $1,100^\circ\text{C}$ , shrinkage increased weakly from 6.9% to 7.0% as the added amount of starch increased from 0 to 15 wt.% due to densification phenomenon.

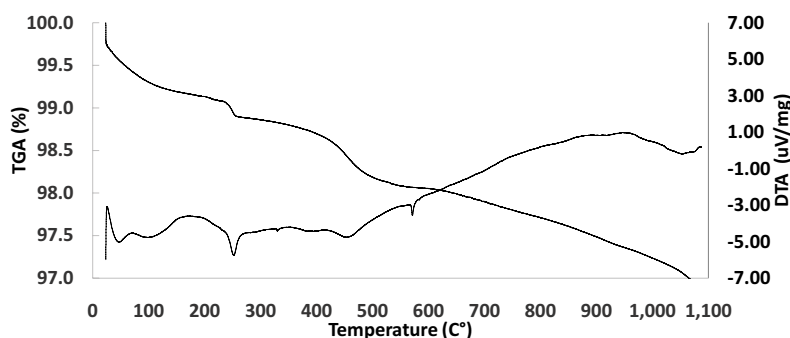


Fig. 4. TGA and DTA analyses.



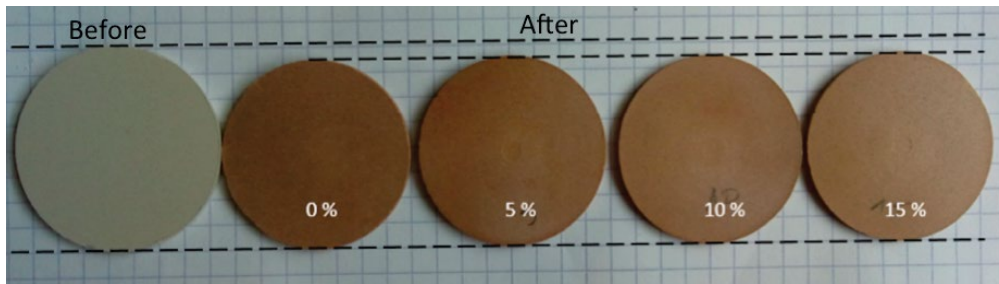


Fig. 5. Views of obtained membranes before and after sintering.

### 3.2.2. Surface characterization

SEM characterization was used to evaluate the densification and surface morphology of kaolinite membranes prepared with different starch contents (0–15 wt.%). As shown in Fig. 6, prepared membranes present good consolidation. In addition, the surface of the membranes seems homogeneous and it is free of cracks. Therefore, the addition of starch affected the surface morphology of the membrane, when the starch was added which contributes in the enhancement of porous microstructure of prepared membranes. A progressive increase of pore size and pores number can be seen when the percentage of starch increases. When the percentage of starch increased the

connectivity between pores increased as well and led to an open porosity to reach its maximum at 15 wt.%. Similar results were found by other researchers using starch in the preparation of porous ceramics [33,34].

### 3.2.3. Pore size

#### 3.2.3.1. Average pore size measured from SEM characterizations

SEM pictures were used to estimate the average pore diameter of prepared membranes using ImageJ software. Fig. 7 shows the pore size diameter of the prepared membranes. The estimated pore size was  $2.2 \pm 0.1 \mu\text{m}$  and

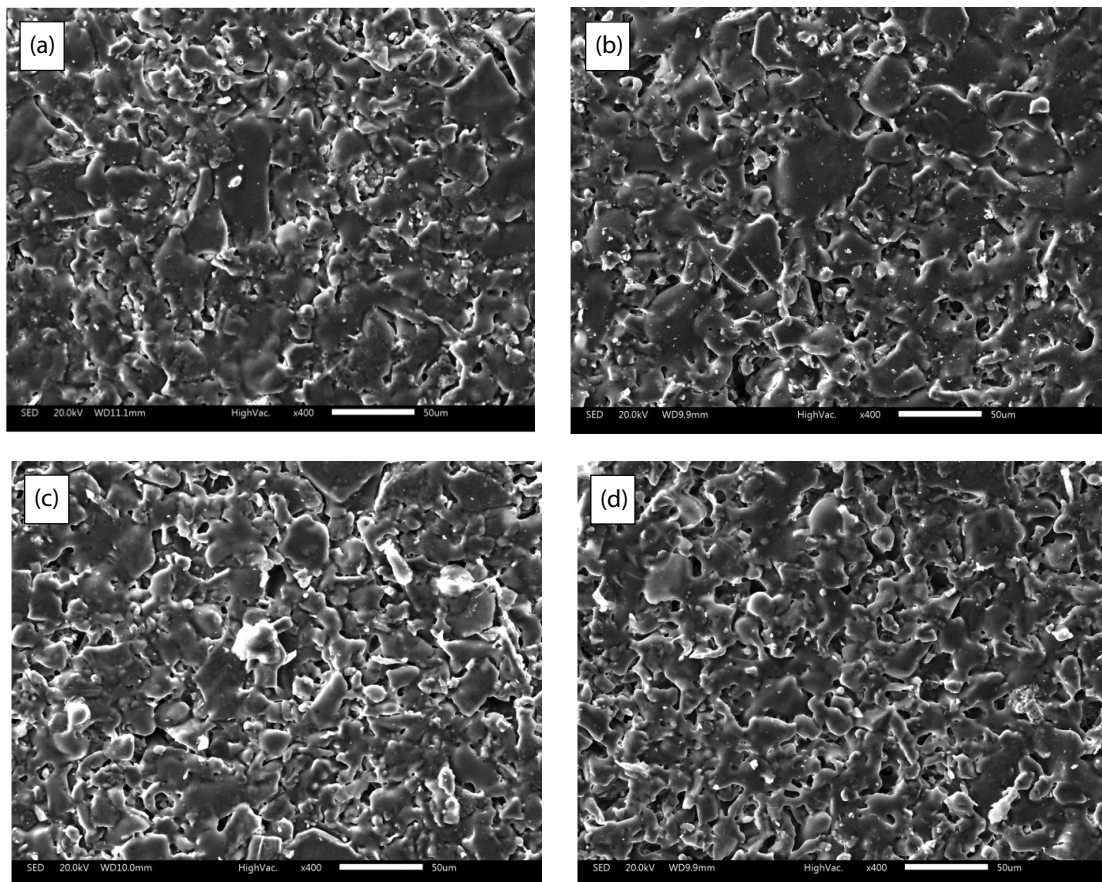


Fig. 6. SEM images of kaolinite membranes containing (a) 0 wt.%, (b) 5 wt.%, (c) 10 wt.%, and (d) 15 wt.% of starch.

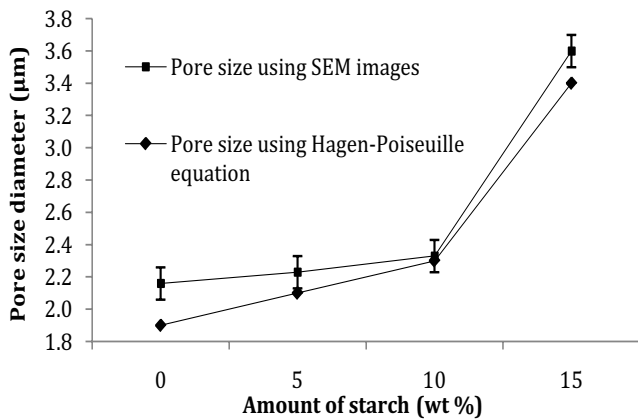


Fig. 7. Average pore size of kaolinite membranes vs. starch addition.

remained fix when the amount of starch increased from 0 to 10 wt.%. However, the pore size increased to 3.6 µm when the maximum of corn starch (15 wt.%) was used.

#### 3.2.3.2. Pore size estimation using Hagen–Poiseuille method

The average pore size of the membrane was also estimated using the Hagen–Poiseuille method. As it can be seen in Fig. 7, the pore size of the membranes increased when the amount of the added starch increased. The pore size of the membranes prepared with 0, 5, 10, and 15 wt.% of starch are, respectively, 1.9, 2.1, 2.3, and 3.4 µm. The average pore size slightly increased from 1.9 to 2.3 µm when the amount of starch increased from 0 to 10 wt.% and it exponentially increased to 3.4 µm when the amount of the added starch increased to 15 wt.%. The average pore size obtained from the Hagen–Poiseuille method shows a slight increase when the amount of the added starch increased from 0 to 10 wt.% unlike that obtained by ImageJ method.

During the sintering process the clay fills in the open space of the material by moving through the contact points. When the corn starch is added it manages to leave more open spaces inside the material, this phenomenon leads to larger pore size and higher porosity in the sintered material. When the percentage of starch was 15 wt.%, the amount of starch became important in the mixture, and it leads to a higher connectivity between pores. During the sintering process, starch leaves more open spaces leading to the exponential increase of pore size. A similar result was found by other authors [35,36].

#### 3.2.4. Apparent porosity and water absorption

As shown in Table 4, the apparent porosity increased from 12.3% ± 0.9% to 58.6% ± 3.4% when starch percentage increased from 0 to 15 wt.%. This important rise implies the fact that starch is pore former. When membranes were sintered, the combustion of starch leads to pores creation. From Table 4, we can observe that water absorption also increased from 5.8% ± 0.4% to 32.4% ± 1.9% when the percentage of starch increased from 0 to 15 wt.%. The increase of apparent porosity is linked to the increase of water absorption when starch is added. Apparent density barely decreased with the addition of starch from 2.12 ± 0.03 to 1.81 ± 0.02. This decrease is due to pore creation when starch is burned. Similar results were found by other authors using different clays with starch [23,37].

#### 3.2.5. Mechanical resistance

From Fig. 8, it can be seen that the increase of starch percentage leads to lower mechanical strength. Mechanical strength decreased from 23.3 ± 0.6 to 18.4 ± 0.5 MPa as the amount of starch increased from 0 to 15 wt.%. The addition of a porosity agent leads to reduce mechanical strength due to the increase of apparent porosity and pore volume of the material. Mechanical resistance and apparent porosity are inversely linked. In the case of starch addition, mechanical strength decreases when apparent porosity increases.

#### 3.2.6. Water permeability

Water permeability  $L_p$  (L h<sup>-1</sup> m<sup>-2</sup> bar<sup>-1</sup>) of prepared membranes were measured at room temperature using bidistilled water in dead-end filtration in the range 0–0.12 bar. Fig. 9 presents permeate flux as a function of transmembrane pressure. The permeability of kaolinite membranes prepared with 0, 5, 10, and 15 wt.% of starch are respectively 153; 1,151; 2,129; and 3,589 L h<sup>-1</sup> m<sup>-2</sup> bar<sup>-1</sup> with an accuracy of ±5%. As shown in Fig. 9, the addition of starch has a direct impact on permeability since starch addition expands pores and increases the flux of the membrane.

During the sintering process, the combustion of starch leads to pores creation. Higher amount of added starch causes higher the interconnection between pores. The interconnection between pores becomes accessible to fluid leading to higher permeability. The permeability of commercial ceramic membranes are reported to be higher than 50 L h<sup>-1</sup> m<sup>-2</sup> bar<sup>-1</sup> [38]. Generally, the permeability depends on the pore size of the membranes. Commercial ceramic microfiltration

Table 4  
Starch effect on apparent porosity, water absorption and apparent density

Amount of starch (wt.%)	Apparent porosity (%)	Water absorption (%)	Apparent density
0	12.3 ± 0.9	5.8 ± 0.4	2.12 ± 0.03
5	25.3 ± 2.7	12.1 ± 1.4	2.10 ± 0.04
10	40.0 ± 2.5	20.3 ± 2.0	1.98 ± 0.09
15	58.6 ± 3.4	32.4 ± 1.9	1.81 ± 0.02

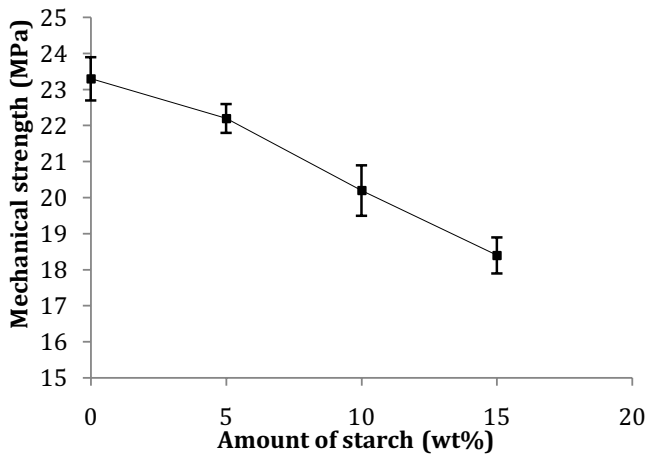


Fig. 8. Mechanical strength of the elaborated membranes.

membranes with pore size range from 0.5 to 10.0  $\mu\text{m}$  have permeability between 300 and 50,000  $\text{L h}^{-1} \text{m}^{-2} \text{bar}^{-1}$  [39].

Water permeability, mechanical strength, and pore size diameter are the effective characteristics to take in consideration in order to choose the optimized membrane. The chosen membrane should not have the highest pore size otherwise it will have the lowest selectivity. The optimized membrane should also have high water permeability and high mechanical strength. The membrane with 15 wt.% has the highest value of permeability. On the other hand, membranes prepared with 0 and 5 wt.% of starch have good mechanical resistance and small pore size diameter but their water permeability is low compared to the membrane prepared with 10 wt.% of starch. Thus, the membrane with 10 wt.% is considered as the optimized membrane and selected for further characterization such as chemical resistance and filtration experiments. Table 5 reports characteristics of optimized membrane and other ceramic membranes reported in literature. The amount of added porosity agent and sintering temperature are strongly affected by mechanical resistance, porosity, and pore size of the ceramic membrane. The porosity of optimized

membrane (40%) is in concordance with a porosity of the reported works that is between 24% and 46%. The mechanical strength is also relatively in a good agreement with the other works, only one work has been reported a better mechanical strength (27 MPa) but the membrane has lower porosity (24%). As mentioned earlier, mechanical strength and apparent porosity are inversely linked. In other words, the more mechanical strength is higher the more porosity is lower. Furthermore, the water permeability of the optimized kaolinite membrane is so promising in comparison with other membranes reported in Table 5.

### 3.2.7. Chemical resistance

During filtration, membrane fouling can be a serious problem, which it requires periodical cleaning. Generally, chemical cleaning is carried out using alkaline and/or acid solutions. Therefore, the membrane must have good chemical stability to avoid its degradation when cleaning or disinfecting solutions are applied. To evaluate its chemical resistance, the optimized membrane was dipped in acidic (HCl at  $\text{pH} = 1.5$ ) and basic (NaOH at  $\text{pH} = 13$ ) solutions for 7 d under atmospheric conditions. Fig. 10 shows weight loss as a function of time. In the alkaline solution, the weight loss after 7 d is 0.23 wt.% while it is only 0.06 wt.% in an acidic solution for the same period of time. It can be concluded that the membrane is relatively more stable in acid solution than an alkaline solution. However, weight loss of 0.23 wt.% observed in acidic medium is insignificant. Therefore, the kaolinite membrane shows an excellent chemical resistance that is typical for commercial ceramic membranes [32].

### 3.3. Filtration experiment

The performance of the kaolinite membrane was evaluated by dead-end filtration at 0.12 bar during 2 h at room temperature. Fig. 11 shows the flux vs. filtration time during three steps of filtration: (i) filtration of water during 30 min, (ii) filtration of effluents A and B during 120 min, and (iii) filtration of water during 30 min after membrane cleaning using bidistilled water. For feed (A), the

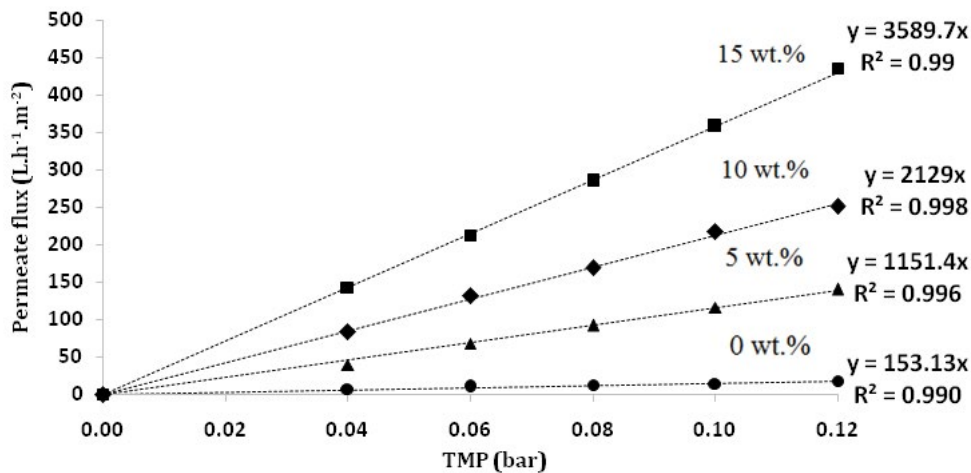


Fig. 9. Water permeability of the elaborated membranes.

Table 5  
 Characteristics of optimized kaolinite membrane and some ceramic membranes reported in literature

Material	Sintering temperature (°C)	Water permeability $L_p$ ( $L h^{-1} m^{-2} bar^{-1}$ )	Mechanical resistance (MPa)	Porosity (%)
Present work	1,100	2,129	20.2	40
Kaolin + phosphor + acid + starch (10 wt.%) [23]	1,100	31.39	11	36
Quartz + calcite (15 wt.%) [24]	1,375	16,000	17	42
Alumina corn starch (8 wt.%) [25]	1,400	–	15.47	46
Ball clay + corn starch (15 wt.%) [26]	1,200	0	27	24
Clay + corn starch (10 wt.%) [27]	950	620	14	35.8
Pozzolan + starch (10 wt.%) [40]	950	1,200	16	34

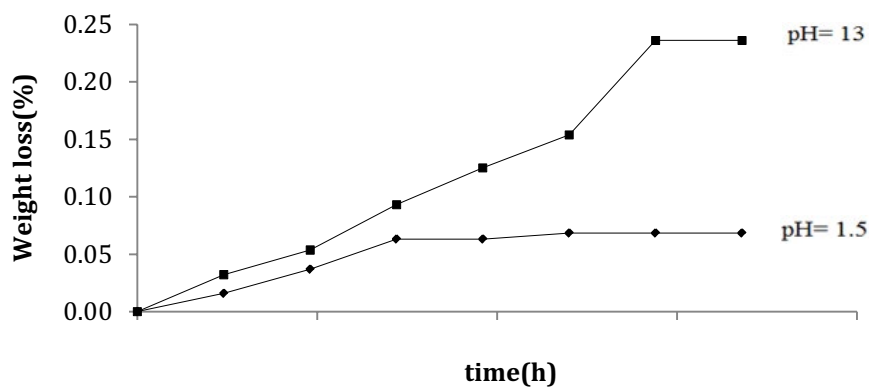


Fig. 10. Weight loss of optimized kaolinite membrane in acid and alkaline solutions at room temperature.

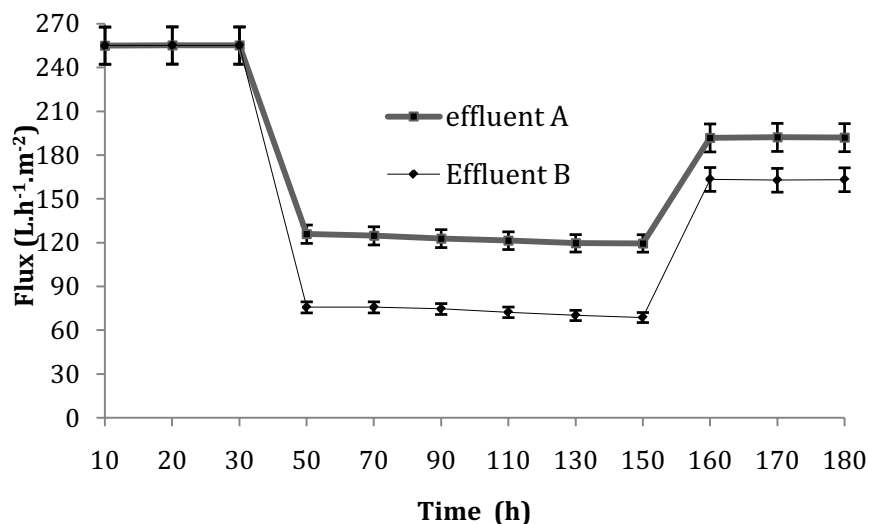


Fig. 11. Variation of (A) permeate fluxes of feeds and (B) as a function of time at 0.12 bar.

permeate flux decreased from 255 to 125  $L h^{-1} m^{-2}$  during the first minutes and then the flux is relatively stable at 119  $L h^{-1} m^{-2}$ . For feed (B), the permeate flux decreased from 255 to 75  $L h^{-1} m^{-2}$  in the first 20 min, then, weak flux decrease is observed after 120 min of filtration (final flux is 68  $L h^{-1} m^{-2}$ ). The observed flux decrease for both feed is attributed to the fouling phenomenon that is resulted from

deposition and accumulation of suspended particles on the membrane surface and/or inside of pores. These phenomena are accentuated when dead-end mode is applied [32]. In the present conditions, different fouling intensities are observed for both feeds. Thus, final permeate flux of feed (A) is almost two times higher than feed (B). This can be explained by the different in physicochemical properties of two feeds.



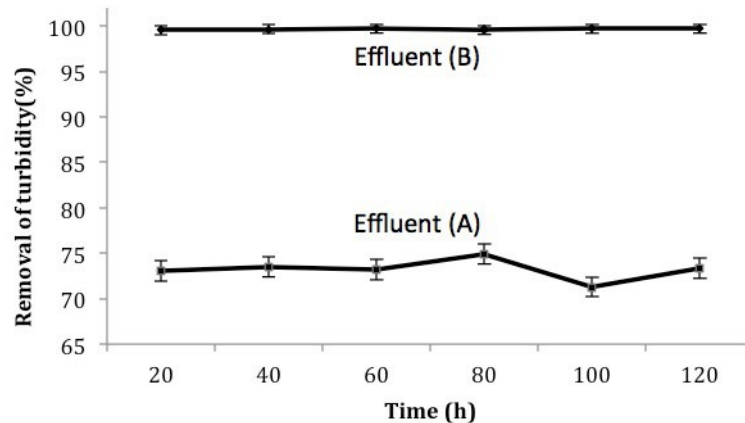


Fig. 12. Variation of (A) turbidity of feeds and (B) as a function of time at 0.12 bar.

However, after membrane cleaning, water flux is increased and found to be  $192 \text{ L h}^{-1} \text{ m}^{-2}$  for feed (A) and  $163 \text{ L h}^{-1} \text{ m}^{-2}$  for feed (B). FRR was calculated for both feeds and it is found that FRR is equal to 75.3% and 63.9%, respectively for feed (A) and (B). A higher FRR refers to good antifouling property. Therefore, it can be concluded that membrane is less fouled by filtration of feed (A) in comparison with filtration of feed (B). This is due to the fact that many complications during filtration such as blockage, plugging of pores, and because of the cake layer formation on the membrane surface [40].

Fig. 12 shows the evolution of turbidity for both feeds during filtration time. Turbidity rejection is 73.2% and 99.6%, respectively for feed (A) and (B). The membrane can eliminate almost all the suspended particles presented in feed (B) and significantly reduce the turbidity of raw seawater from  $6.3 \pm 0.1$  to  $1.6 \pm 0.1$  NTU. Generally, turbidity of seawater is related to colloidal particles and marine organisms. High turbidity is likely responsible for fouling of reverse osmosis membranes in the seawater desalination process [4].

COD rejection was found to be 49.6% for raw seawater (feed (A)), it decreased from  $5.9$  to  $2.93 \text{ mg L}^{-1}$ . COD is related to organic and inorganic substances, reducing these substances from seawater might reduce fouling of reverse osmosis membranes. In addition, the conductivity and pH of both feeds are remained constant during the filtration.

#### 4. Conclusion

This work describes the preparation of flat ceramic microfiltration membrane made from Moroccan natural kaolinite and starch. Starch was used as porosity agent in the optimization of membrane properties in terms of porosity, permeability, and mechanical strength. Different percentages of starch (0–15 wt.%) were used to optimize the membrane features. This work shows that there is a direct link between the amount of added starch and some physical properties of kaolinite membrane. The addition of starch increased the permeability and the porosity of the membrane; however, it decreased the mechanical strength. On the other hand, this work showed that when the amount

of starch is exceeded 10 wt.% its influence pore size diameter that is become obvious. The membrane with 10 wt.% of starch was considered as optimized membrane. It has an average pore size of  $2.3 \mu\text{m}$ , a porosity of 40%, a permeability of  $2,129 \text{ L h}^{-1} \text{ m}^{-2} \text{ bar}^{-1}$  as well as good mechanical strength and chemical stability. The optimized membrane was tested in filtration and showed potential results in turbidity and COD rejections of raw seawater. It was reduced the turbidity by 73.2% and the COD by 49.6%. In addition, the microfiltration membrane could remove practically all turbidity (99.6%) of agro-food model.

Finally, it was demonstrated that natural kaolinite could be used for preparation microfiltration ceramic membrane by dry route. Besides, the filtration tests proved that this membrane could found industrial applications due to its low cost materials and its filtration performance.

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