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Sol–gel preparation of titania multilayer membrane for photocatalytic applications

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Abstract

The main goal of the present study is to prepare a titania membrane with high permeability and photocatalytic activity for environmental applications. In this investigation a mesoporous titania multilayer membrane on alumina substrate is successfully fabricated via the sol–gel processing method. The prepared titania polymeric sol for the membrane top layer has an average particle size of 11.7 nm with a narrow distribution. The resulting TiO_2 multilayer membrane exhibits homogeneity with no cracks or pinholes, small pore size (4 nm), large specific surface area (83 m^2/g), and small crystallite size (10.3 nm).

The permeability and photocatalytic properties of the titania membrane were measured. The photoactivity of the titania membrane was examined to be 41.9% after 9 h UV irradiation based on methyl orange degradation. This measurement indicates high photocatalytic activity per unit mass of the catalyst. Through multilayer coating procedure, the photocatalytic activity of the membrane improved by 60% without sacrificing the membrane permeation. The prepared TiO_2 photocatalytic membrane has a great potential in developing high efficient water treatment and reuse systems due to its multifunctional capability such as decomposition of organic pollutants and physical separation of contaminants.

Keywords: A. Sol–gel processes; B. Porosity; E. Membranes; Titania

1. Introduction

Ceramic membranes are gaining an essential role in separation technology, especially in combination with catalytic properties. Ceramic membranes are generally prepared in monolayer and multilayer configurations. The advantages of a monolayer membrane are its low cost and simple preparation procedure. However, monolayer membranes cannot perform nanofiltration processes. As a result, to have a membrane with high performance parameters such as low cut-off values or high water fluxes, a multilayer configuration should be obtained [1]. Ceramic membranes are generally known for their high permeability, superior chemical stability, high mechanical and thermal resistance, long life and excellent anti-fouling properties [2–5].

Alumina, titania and zirconia are considered as the most common porous ceramic membrane materials. Among ceramic membranes, titania has received significant attention due to its high water flux, chemical stability and high photocatalytic activity in aqueous solutions [6–8]. One of the most important applications of the titania membranes is photocatalytic degradation of toxic components. Photocatalysis is an alternative economical and harmless technology for removal of organic impurities from air and water. During the photocatalysis process, illuminated semiconductor absorbs light and generates active species, which leads to complete oxidation of organic components [9].

Titania nanoparticles with high degree of crystallinity, high specific surface area and high porosity exhibit a pronounced photocatalytic activity in various chemical processes [10,11]. However the usage of titania nanoparticles create common industrial issues such as the need for separation or filtration steps, the problematic use in continuous flow systems, and the particle aggregation [12,13]. Although the titania nanoparticles have shown higher efficiency compared to that of the titania layer, the above issues have significantly limited their usage in

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industrial applications. Therefore, titania membranes are considerably utilized in industrial applications due to their suitable usage procedure.

The purpose of this investigation is to prepare a crack-free titania multilayer membrane on α-Al_2O_3 support with enhanced photocatalytic properties. The membrane configuration contains a support, an intermediate layer, and a top layer. This study examines the optimum processing conditions for the preparation of TiO_2 polymeric sol, top layer deposition, and drying and calcination of the layer to create a crack-free titania multilayer membrane. Further more this research examines the permeability and photocatalytic properties of the prepared multilayer membrane and compares them with those of a titania membrane with just one intermediate layer (a colloidal sol–gel derived layer).

2. Experimental methods

In our previous research, we have shown fabrication of a titania membrane with one titania layer on an alumina support via the colloidal sol–gel route [14]. The support preparation, the procedure for preparing colloidal sol, and the colloidal layer have been thoroughly discussed elsewhere [14]. In this investigation a titania multilayer membrane is fabricated via the polymeric sol–gel route. This multilayer membrane is fabricated by depositing the polymeric sol as a top layer on the intermediate layer (prepared in our previous work). Therefore, the cross-section of the final membrane consists of α-Al_2O_3 support, one colloidal sol–gel derived intermediate layer and a polymeric sol–gel derived top layer. This paper focuses on the polymeric sol preparation and top layer deposition techniques, as well as the final membrane characterization such as its permeation and photocatalytic activity.

2.1. Preparation of the membrane top layer by polymeric sol–gel process

TiO_2 polymeric sol was obtained via tetra isopropyl orthotitanate ($Ti(OC_3H_7)_4$) (Merck, 821895) as a titania precursor. A solution of water and nitric acid in isopropanol (Merck, 109634) was added dropwise to a solution of tetra isopropyl orthotitanate in isopropanol during high speed stirring. The molar ratio for tetra isopropyl orthotitanate/isopropanol/H_2O/HNO_3 of the final sol was 1/6/0.9/0.6 respectively. The stirring step was continued for 3 h to get a stabilized sol. For the preparation of a very fine polymeric top layer no high molecular weight organic additives could be added, compared to the colloidal route. During the sol preparation, the used water was less than the hydrolysis stoechiometric amount ($[H_2O]/[Ti] < 4$), and the hydrolysis and condensation reactions were precisely controlled. The final product was a transparent titania polymeric sol.

The sol was then aged for 72 h in order to increase the viscosity of the dipping solution and to prevent the penetration of the polymeric sol into the pores of the intermediate layer. A titania multilayer membrane was then formed by dip-coating the colloidal titania membrane in the titania polymeric sol.

The obtained titania multilayer membrane was dried at room temperature for 24 h. The drying process was continued in air for 1 h at 30 °C followed by 3 h at 40 °C. The membrane was subsequently calcined for 1 h at 450 °C with a heating rate of 10 °C/h.

2.2. Characterization

Particle size distribution of the polymeric sol was determined by the dynamic light scattering technique (Malvern UK, 3000HSA). This test shows the size distribution of the polymeric structures in the sol. TGA technique was used in order to determine the burn out temperature of the volatile materials and to examine the calcination conditions. The crystal structure and the phase transformation of the membrane top layer during the calcination process were identified using X-ray diffraction technique with a Cu Kα wavelength (XRD, Jeol8000 diffractometer). N_2-sorption measurements were performed (Micrometrics, Gemini 2375V4.02) to determine the BET[1] surface area and the pore size of the top layer. The microstructure of the top layer was examined for any defects or cracks using the scanning electron microscope (PhillipsXL30).

2.3. Photocatalytic activity of the titania multilayer membrane

The photocatalytic activity of the prepared titania multilayer membrane was evaluated from the photodegradation of methyl orange in an aqueous solution. For this measurement, the prepared titania membrane was placed on a petri-box containing 30 ml of $5\ \mathrm{mg\ l^{-1}}$ aqueous solution of methyl orange. The petri-box was placed in a home-fabricated box and it was irradiated by a UV source (125 W, emission spectrum range of 360–415 nm) which has the maximum intensity of about 370 nm (i.e. close to the anatase band gap). To measure methyl orange concentration, the UV–Visible spectrophotometer was used at the wavelength of 464 nm, which corresponds to the maximum adsorption of methyl orange. The change in the concentration of methyl orange was measured in the presence of the titania multilayer membrane as a function of time. The result of this measurement was compared to the amount of methyl orange decomposed in the presence of the titania membrane with just one colloidal (intermediate) layer.

2.4. Permeability of the membrane

The permeability of the prepared titania membrane was examined with a home-fabricated membrane chamber with a dead-end filtration type fitting the size and shape of the support [15]. This system has been established based on the standard of ASTM S316. The permeability of the membrane was determined by direct measurement of nitrogen permeate flow at 25 °C at trans-membrane pressure (TMP) from 0 to 3 bar.

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[1] Brunauer–Emmett–Teller equation.

Table 1
Experimental conditions for preparation of the stable titania polymeric sol.

Type of the sol	$[H_2O]/[Ti]$	$[H^+]/[Ti]$	pH	Temperature (°C)
Polymeric	0.9	0.6	3	25

$H^+ = HNO_3$.

Table 2
The effect of pH on the polymeric sol stability.

pH	$[H^+]/[Ti]$	Product stability
<3	0.8–1	A sol (stable for several days)
3	0.6–0.7	A sol (stable for several months)
>3	0.5	A stable gel

3. Results and discussion

3.1. Titania polymeric sol

Table 1 shows the experimental conditions for the polymeric sol synthesis. A suspension of small nanometer-sized particles was obtained by reacting the precursor with a little amount of water ($[H_2O]/[Ti] = 0.9$). It should be noted that the success of the sol–gel process to get a stable polymeric sol with required properties such as small particle size depends on the ability to control the hydrolysis and condensation reactions. To control these reactions, the hydrolysis ($[H_2O]/[Ti]$) and the inhibition ratios ($[H^+]/[Ti]$) should be controlled.

Table 2 shows the effect of pH and H^+ concentration on the polymeric sol stability. According to this table, the sol pH is an important factor in preparing a desired polymeric sol and consequently a proper multilayer membrane. This table clearly shows that with increasing the pH to the value of 3, the titania sol becomes more stable. This table also reveals that above the pH of 3 the sol converts to a gel.

Fig. 1 shows the effect of pH on the particle size distribution of the titania polymeric sol. Graph (a) in this figure shows that at pH level of 3 the titania sol consists of particles with a mean size of 11.7 nm and a minimum size of 5.8 nm. On the other hand, graph (b) of this figure shows that at pH level of 2 the mean particle size is 21.7 nm. Comparing graphs (a) and (b) in Fig. 1, it can be seen that the particle size distribution is more widespread and the mean particle size is larger in the sol of pH 2.

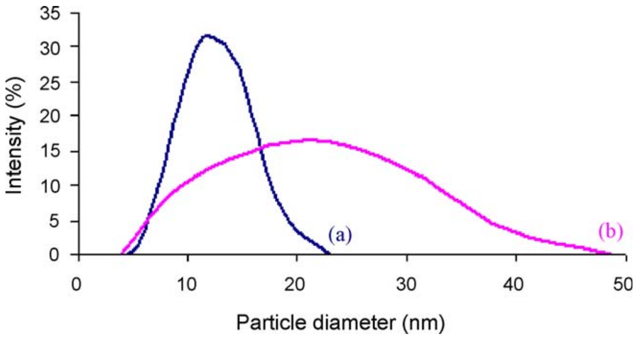

Fig. 1. The effect of pH on the particle size distribution for the titania polymeric sol, determined by the dynamic light scattering technique after sol aging of 72 h: (a) pH 3 and (b) pH 2.

The measurements executed in this study clearly reveal that at pH values lower than 3 (high H^+ concentration) hydrolysis occurs faster than condensation leading to the formation of longer chain polymers and a more stable sol. At pH levels below 3 the stability of the sol is limited to less than a week (Table 2). On the other hand, in pH ranges higher than 3 (low H^+ concentrations) the hydrolysis and condensation reactions are both catalyzed and occurred almost simultaneously. As a result the product will be a precipitate or a gel depending on the hydrolysis ratio (Table 2).

These investigations show that the optimum inhibition ratio for the polymeric sol is 0.6 and the sol optimum pH is equal to 3. Due to the optimum pH, the sol is stable and has much smaller nanometer-sized particles to produce a defect free top layer.

3.2. Titania multilayer membrane

3.2.1. Structural properties

TGA investigations for the top layer of the membrane indicate that all the organic materials, nitric acid, and water are fully removed below 400 °C. Therefore the titania multilayer membrane can be calcined at a low temperature and 400 °C is the minimum possible calcination temperature. A low calcination temperature has several advantages such as a reduced pore and crystallite size, and inhibition of the anatase to rutile phase transformation.

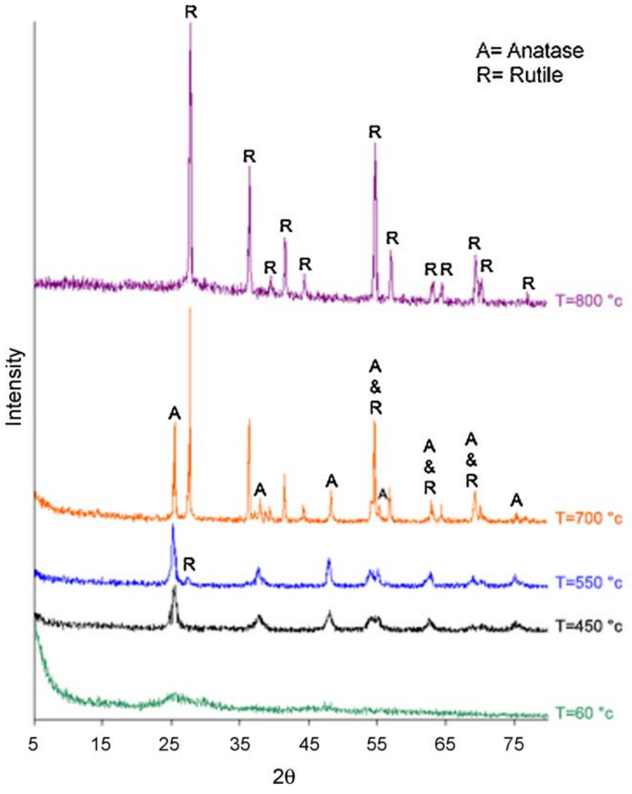

Fig. 2. XRD patterns of the top layer showing the phase transformation into anatase (A) and rutile (R) after the calcination process for 1 h at 60, 450, 550, 700, and 800 °C.

Fig. 2 shows the XRD patterns of the top layer as a function of calcination temperature. According to this graph, the anatase to rutile phase transformation in the polymeric titania occurs at 550 °C. By increasing the temperature above 550 °C, the amount of rutile phase increases and the system only consists of the rutile phase at 800 °C.

Several factors should be considered to select an optimum calcination temperature for the titania layer. First volatile materials should be completely burned out, and titania should remain crystalline with an optimum crystallite size. Moreover, titania should remain only in the anatase form after calcination.

According to Scherer's equation [16] at peak (1 0 1), the crystallite size of titania, calcined for 1 h at 450 °C was determined as 10.3 nm. The optimum crystallite size for anatase in order to get the highest possible photoactivity is in the range 8–10 nm [17]. This range provides the best photoactivity for the membrane which will be discussed later in Section 3.2.3 (the photocatalytic properties of the membrane).

Considering the above factors, the investigations performed in this study show that the optimum calcination temperature for the membrane top layer is 450 °C.

It should be noted that anatase to rutile phase transformation is detrimental to the membrane preparation process since it takes place by coalescence of small anatase particles into larger rutile grains. This coalescence is typically accompanied by considerable grain and pore growth [18]. At this temperature range, surface diffusion accompanied by neck-formation between the ceramic grains leads to a gradual decrease in the surface area and a slight increase in the pore size and pore volume [1]. The investigations in this study show as a result, lowering the calcination temperature is essential to have a minimal crystallite size in titania.

Fig. 3 and Table 3 show the results of N_2-sorption measurements. The specific surface area and the pore size were measured 83 m^2/g and 4.0 nm, respectively. The specific surface area measurement was based on the BET model and the pore size was characterized based on the Kelvin equation assuming the pores to be cylindrical [19–21].

The prepared membrane is mesoporous according to the hysteresis in Fig. 3 and its pore size in Table 3 [22]. According to the N_2-sorption results in Fig. 3 and our previous work [14], the prepared multilayer membrane is composed of one mesoporous top layer, a mesoporous intermediate layer, and a macroporous alumina support. Therefore, there is a pore gradient from support through the top layer that can improve the membrane efficiency and prevent early clogging of the membrane.

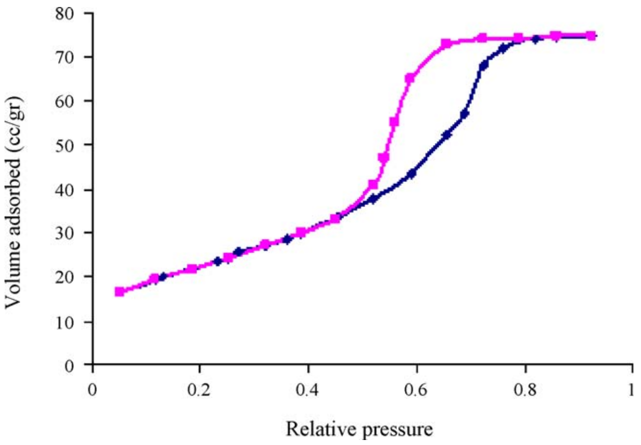

Fig. 3. N_2-sorption hysteresis of the mesoporous top layer, calcined at 450 °C for 1 h.

Table 3
BET surface area and pore size of the mesoporous top layer, calcined at 450 °C for 1 h.

Type of material	Specific surface area (m^2/g)	Pore size (nm)
Membrane top layer	83	4.0

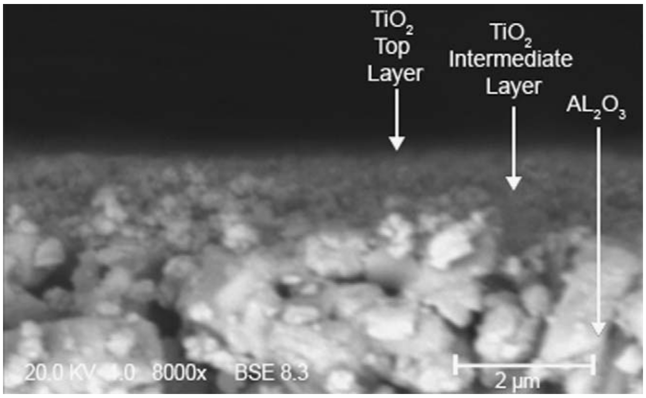

Fig. 4. SEM cross-section image of the titania multilayer membrane, calcined at 450 °C for 1 h.

3.2.2. Microstructure

Fig. 4 shows the prepared multilayer membrane consisting of a support and two titania layers; the colloidal intermediate layer and the polymeric top layer. The interface between the intermediate layer and the top layer is not observable since both layers are TiO_2 and the top layer is expected to be less than 100 nm [1].

Fig. 5 shows the cracks at the polymeric top layer in the multilayer membrane. This figure shows the importance of the heating rate during the drying and calcination steps. A controlled temperature profile can reduce the stresses originating from the removal of volatile materials and the layer shrinkage [23]. It can also reduce the stresses developing from unequal thermal expansion coefficient of the support and the titania layer [23]. Previous investigations have specifically shown that in titania membranes relaxation of the stresses that develop in the structure during drying and calcination steps cannot easily take place due to the spherically shaped titania particles [24]. As a result the heating rate should be slow enough to prevent cracking of the membrane.

Cracks in Fig. 5 can be attributed only to high levels of stress generated by rapid heating rate. Stresses which can be generated during the anatase to rutile phase transformation had no crack-producing effect on the prepared membrane. Although phase transformation stresses can cause severe cracking of the layer but according to Fig. 2, the phase

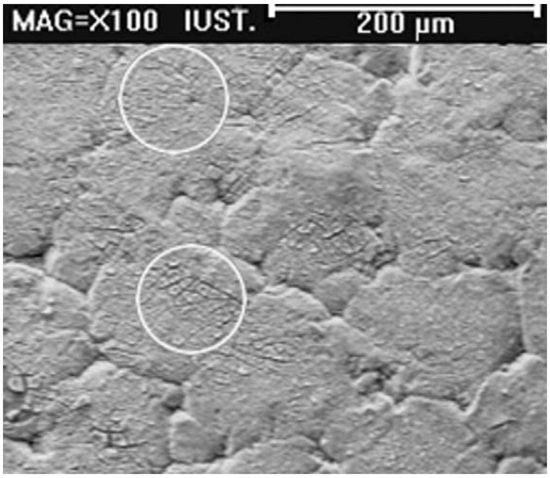

Fig. 5. SEM top image of the titania multilayer membrane showing cracks at the top layer. This sample was calcined at 450 °C for 1 h at a heating rate of 10 °C/min. Cracks are caused because of the rapid heating rate.

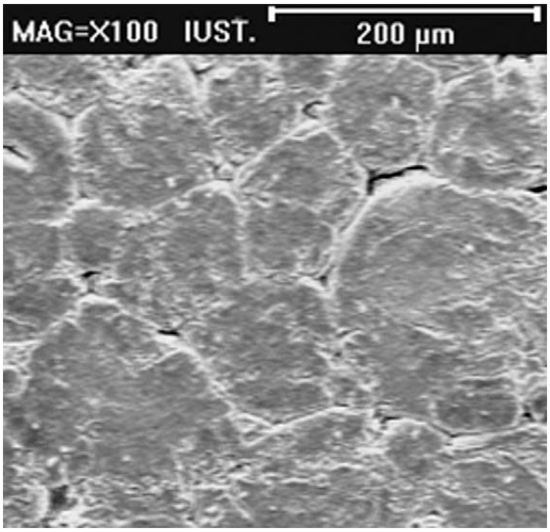

Fig. 6. SEM top image of the titania multilayer membrane, crack-free top layer, calcined at 450 °C for 1 h at a heating rate of 10 °C/h.

transformation temperature in the titania powder is 550 °C. As mentioned in Section 2 the used calcination temperature is 450 °C which is far lower than the phase transformation temperature. On the other hand, studies show the crystallization of titania in thin layer form occurs at higher temperatures than in the powder form [25,26]. Therefore, the amount of rutile phase in the prepared titania layer and the risk of cracking due to the phase transformation is negligible.

Fig. 6 shows a crack-free top layer membrane which was calcined at 450 °C for 1 h by heating rate of 10 °C/h. There is no crack at the top layer, therefore, the mentioned conditions are optimum. As a result, by controlling the calcination condition and the heating rate a defect-free titania multilayer membrane can be prepared.

3.2.3. Photocatalytic properties

Table 4 shows the photocatalytic properties of the prepared monolayer and multi-layer titania membranes. Our experiment shows that after 9 h UV irradiation, methyl orange is degraded to about 41.9% via the multilayer membrane.

As discussed in our previous research [14], a small sized support with a diameter of 15 mm has been chosen for this investigation. As a result the contact surface between the multilayer membrane and the solution is very small. Although the membrane maintains a relatively small surface contact with the solution, the photocatalytic test indicates that the degradation of methyl orange is significant. This significant degradation results from the fact that the TiO_2 photocatalyst, immobilized onto a thin membrane, maintains a high photocatalytic activity per unit mass of the catalyst. The high photocatalytic activity measured here also points to the precise processing conditions in this investigation.

In order to examine the effect of membrane on the degradation process, the methyl orange solution was also irradiated in the absence of the photocatalyst to examine its stability. In that case, results verify that the organic compound is not decomposed even after long UV irradiation time. Therefore the degradation of methyl orange is due to the presence of the titania membrane as a catalyst and UV irradiation by itself has no degradation effect in the absence of the titania membrane.

According to Table 4 the photoactivity of the two prepared membranes show that the specific surface area of the membrane strongly affects the photocatalytic activity of the membrane. The photoactivity of the multilayer membrane is approximately 60% higher than that of the monolayer membrane. The higher photoactivity in the multilayer membrane results from higher specific surface area of the polymeric top layer. A high specific surface area leads to a decrease in the volume electron–hole recombination and increases the number of active sites on the surface of the photocatalyst. An increase in the number of active sites on the surface of the photocatalyst clearly leads to a faster rate for electron–hole reactions with the surrounding substrate. It should be noted that photocatalytic efficiency does not increase monotonically with increasing surface area since surface recombination of charge carriers also plays an important role in photocatalytic reactions in ultrafine particles [27,28].

The measurement in this study shows the crystallite size of the prepared top layer is 10.3 nm. This value fits the optimum range for the crystallite size in order to have enhanced photocatalytic activity. Previous investigations have clearly shown smaller crystallite sizes cause blue shift in the light absorption spectrum and favors surface recombination of the photo-exited holes and electrons and larger crystallites exhibit lower surface area and thus a smaller number of active sites per unit mass of the catalyst [17].

Another factor which strongly affects the photoactivity of the membrane is the titania crystallographic phase. Among the titania polymorphs anatase has the highest photocatalytic activity [29,30]. According to Fig. 2 the prepared membrane is only in the anatase form which enhances the prepared membrane photoactivity.

Considering the above results, optimum processing conditions in this study have led to enhanced phase structure,

Table 4
Photocatalytic properties of the prepared titania membranes, comparison between a membrane with one intermediate layer and a multilayer membrane, calcined at 450 °C for 1 h.

Type of the titania membrane	Decomposition after 3 h UV radiation (%)	Decomposition after 6 h UV radiation (%)	Decomposition after 9 h UV radiation (%)
Membrane with one intermediate layer	15.8	20	27.1
Multilayer membrane	24.5	32.7	41.9

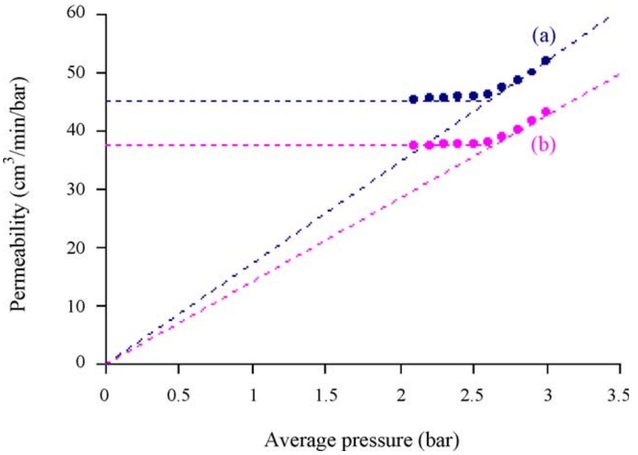

Fig. 7. Permeability of the membranes: (a) monolayer and (b) multilayer.

crystallite size, and specific surface area which result in high phtocatalytic activity of the membrane.

3.2.4. Permeability

Permeability of the membrane was measured to evaluate the integrity and the properties of the membrane, as shown in Fig. 7. Graph (a) in this figure clearly shows the permeability of the titania membrane with just one intermediate layer. Graph (b) of this figure reveals the permeability of the multilayer membrane. The figure shows that depositing the top layer on the intermediate one has a small effect on the permeability of the multilayer membrane and the membrane permeation is reduced by a small amount. The lower permeability of the multilayer membrane is explained by its smaller pore size. The membrane flow comes in at the pressure of 2.1 bar due to the membrane small pore size. The horizontal part in graph (b) of Fig. 7 reveals that the membrane permeability is essentially independent of the average pressure. Therefore, the experimental results demonstrate that the mechanism of transport in the membrane dominantly involves Knudsen diffusion. Knudsen diffusion plays an important role in a mesoporous membrane with a small pore size. In this region the membrane permeability is independent of the applied pressure [31].

4. Conclusion

A crack-free nanostructured titania multilayer membrane was successfully fabricated via the sol–gel process. The optimum processing conditions in the fabrication of multilayer membrane such as the calcination time and temperature have been successfully characterized and their effect on the crystallographic phase, specific surface area, crystallite size, microstructure and photocatalytic activity of the final membrane were examined. The prepared TiO_2 membrane has promising structural properties such as homogeneity, large surface area (83 m^2/g), and small pore size (4 nm).

The prepared mesoporous membrane has enhanced photocatalytic properties such as active anatase phase, small crystallite size (10.3 nm), and high material crystallinity. The photocatalytic properties of the titania multilayer membrane based on methyl orange degradation was measured to be 41.9% after 9 h UV irradiation. This prepared multilayer membrane shows 60% higher photocatalytic activity compared to that of the single colloidal layer. This is due to higher specific surface area of the top layer in the multilayer membrane. Therefore, using a multilayer membrane with tailor-made properties increases membrane photocatalytic activity without sacrificing its permeation, compared to a colloidal monolayer membrane. The prepared photocatalytic membrane has great implication for environmental application due to its simultaneous photocatalytic, disinfection, and separation functions.

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