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Synthesis of Nano Porous Silica-titania Membrane with Photocatalytic Properties

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Abstract

In this study, the photocatalytic properties of nanoporous silica-titania membrane was investigated. For this purpose, nano-porous silica-titania membrane was prepared by sol-gel process using tetraethyl orthotitanate and tetraethyl orthosilicate with the intermediate layer of colloidal titania on α-alumina support. The as-prepared membrane was characterized by FTIR, XRD, FESEM and BET techniques. The specific surface area of microporouse silica -30% titania powder was 507 m^2/gr. In addition, the photocatalytic activity of the as-prepared membrane was studied for methyl orange photo-degradation under UV light (λ_{max} =256 nm). The results showed that the removal efficiency of silica- titania membrane was 91.4%after 6 hours.

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1. Introduction

Nowadays removing hazardous organic pollutants from wastewater is necessary [1]. Photocatalytic process is known as a good technology for the treatment of purification [2,3]. Heterogeneous photocatalysis, have also been widely used for the degradation of water contaminants in environment due to a complete decomposition of organic pollutants without employing chemical substrates [4,5].

On the other hand, ceramic membranes show a very important activity for water purification [6]. Membrane separation techniques can transfers pollutants from a phase to another and shows a simple separation role [7].Among various materials used for photocatalytic applications, TiO_2 is the most attractive because of its advantages such as high stability, non-toxicity, inexpensive cost [8]. However, titania membranes have some disadvantages like low surface area and instability of titania phase at high temperatures [9]. It is found that anatase is the most photoactive form of titania, however, it is metastable in terms of thermodynamic. For enhancing photocatalytic activity of titania, it is necessary to increase temperature stability of anatase phase as well as the surface area [10,11].

Thus, many efforts have been dedicated to incorporate another inorganic oxide like silica into the titania framework to improve surface area and inhibit crystal growth and phase transformation [12-15]. Silica addition cause a considerable impact on the surface properties and increasing photocatalytic activity of titania [16]. Researchers reported that composite of titania and silica showed more photocatalyst for dye photo- degradation than pure titania [17-19].

In the present work, the nano porous silica-titania membranes are prepared by the polymeric sol-gel method on the alumina support and were characterized by several methods. Then the photocatalytic capabilities of the prepared membranes were studied by removal efficiency of methyl orange in aqueous media.

2. Experimental part

2.1. *Materials*

ð• ž ª-alumina powder were purchased from Baikalox France. Tetraethyl orthotitanate (TEOT) ($C_4H_{20}O_4Ti$), Nitric acide (HNO_3) and isoporopanol (ISP) (C_3H_8O) were provided from Merck. Also, ISP, TEOT, Nitric acid and tetraethyl orthosilicate (TEOS) and acetyl acetone (AcAc) were used for the preparation of polymeric sol of titania–silica. Methyl orange ($C_{14}H_{14}N_3NaO_3S$) (Figure 1) with molar mass of 327.34 g/mol was used as the model pollutant for investigation
of photocatalytic activity of the synthesized membrane. All the chemicals used in this work were of analytical grade and used as received without further purification. Deionized water (DI) was used throughout the experiment.

2.2. *Synthesis of membrane*

2.2.1. Alumina Substrate.

To create the membrane substrate, ð• › ¼-Al_2O_3 powder was shaped into a disk with 4.7 mm in diameter and 2 mm in thickness using a uniaxial press under the pressure of 110 MPa. The sintering process was carried out at 1400 ° C during 2 hours.

2.2.2. Membrane Interlayer.

To create the membrane interlayer, the deposition of the colloidal titania sol on the alumina substrate was carried out.
The titania colloidal sol was obtained by
hydrolysis of TEOT through the addition of an H_2O and IS. Then, Titanium hydroxide was removed from the solution by rotary system. The solution
was peptized with nitric acid by adjusted pH to 1 and was refluxed at about 60 ° C for 20 h, which resulted in a semiopaque

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titania dispersion. Afterwards, the sol was poured in beaker and held for 20 min in an ultrasonic bath to break the gglomerated particles. Finally, a clear blue stable sol was obtained. Moreover, a solution of PVA was added to the obtained sol as binder.

2.2.3. Membrane Top Layer.

The top layer of membrane was made of silica-titania, which due to the difference in hydrolysis rate of titania and silica, first each of these two cells was prepared separately and then added to each other. To prepare silica sol, 5 ml of TEOS dissolved in 30 ml of in ISP by stirring for 1 h. Then 0.1 ml nitric acid is added dropwise to solution and stirring was continued for 3 h to get a stabilized sol. The obtained product was a transparent silica polymeric sol. Titania sol was prepared hydrolysis of TEOT by using nitric acid as catalyst and acetyl acetone for controlling the hydrolysis rate. After preparation of silica and titania sol, titania sol was added dropwise to silica sol. The obtained composite sol after stirring for 2 h were deposited on the colloidal titania-coated alumina substrate by dip-coating method with a constant rate of 6 mm/min and immersion time of 30 s. The supported polymeric titania gel layers were dried at room temperature for 24 h. Finally, heat treatment was done at different temperatures for 1 h with a heating rate of 1◦ C/min. The schematic for preparation of titania– silica composite membrane is shown in figure 1.

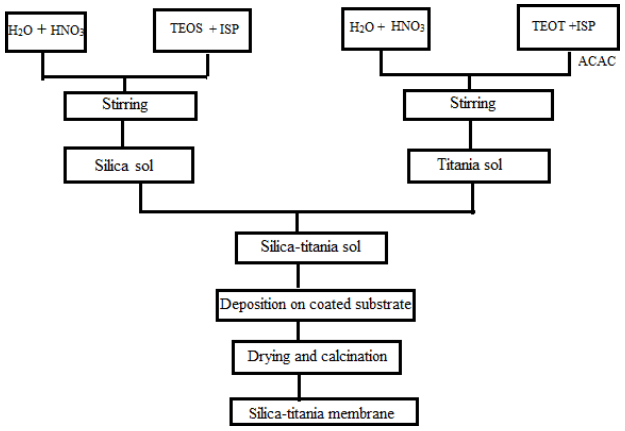

Figure 1: Preparation of the silica–titania composite membrane

***2.3.** Characterization*

Fourier transform infrared spectroscopy (FTIR, PerkinElmer Spectrum model Nicolet 670) was performed to study the structural and specific molecule-groups information. X-ray diffraction (XRD) with Cu Kα (Philips PW 1800) was used to identify phase composition and the crystallinity of samples. The structure and morphology of the membranes were characterized by using field emission scanning electron microscope (FE-SEM), Mira III FEG, TESCAN).

Furthermore, the photocatalytic activity of the products was calculated by the photodegradation of Methyl Orange (MO) aqueous solution [18]. Initial concentration of MO was set at 20 mg/l and membranes in this solution were subjected to UV-Vis spectrometer (λ_{max}=256nm, 60 W). The MO removal efficiency was obtained by the following Eq. (1):

$$\%Removal\ efficiency = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (1)$$

C_0 (mg/L) is the primary absorbance capacity of the dye solution, and C_t (mg/L) is the absorbance capacity of the dye solution at a specific reaction time. R is the removal efficiency [20].

3. Results and discussion

3.1. FT-IR analysis

Fourier transform infrared (FTIR) spectroscopy is a powerful and developed method for determining the structure and measurement of chemical species based on radiation absorption. In the FTIR spectroscopy pattern of silica-titania membrane (figure 2), the absorption at wavelengths 672, 653 and 700 cm^{-1} indicates the presence of Ti-O-Ti bonds [21].Also the absorbed bands at 790 and 1070 cm^{-1} are related to the symmetric and asymmetric tensile vibrations of Si-O-Si, respectively [22]. The adsorption peak at 1600 and 3400 cm^{-1} indicates the presence of hydroxyl groups and water adsorbed by the compound in the environment.

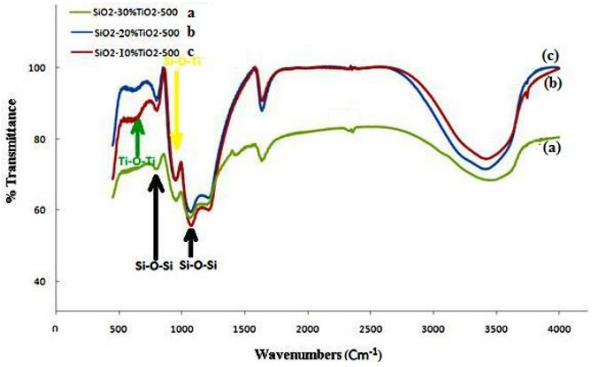

Figure 2 : FT-IR spectroscopy of 10,20 and 30% TiO_2-SiO_2

3.2. Phase analysis

X-ray diffraction analysis was used to identify the phases in the silica-titania membrane. Figure 3 shows XRD patterns of 30% titania- silica gel calcined at different temperatures.

As can be seen in figure 3, 30% titania- silica gel is amorphous up to 800 ° C and no crystalline phase is observed, which indicates that the two phases of silica and titania are not separated. This compound is suitable for membrane application, due to the need for amorphous structure to have a very small porosity size.

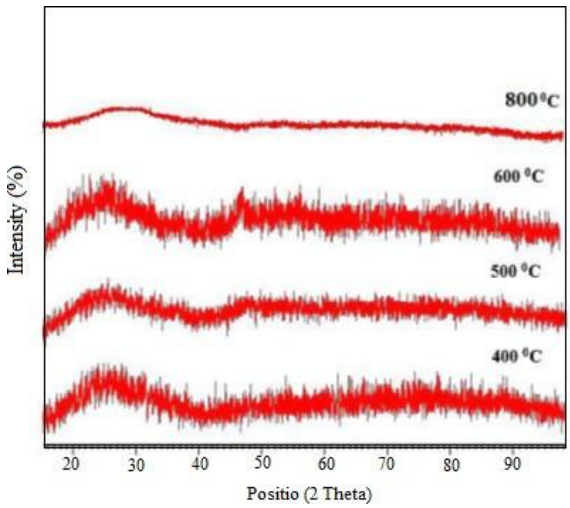

Figure 3: XRD analysis of calcined silica-30%titania at different temperatures

According to FESEM image (figure 4) of the surface analysis a smooth surface with no defect and 169 nm thickness was made on the intermediate layer (469 nm).

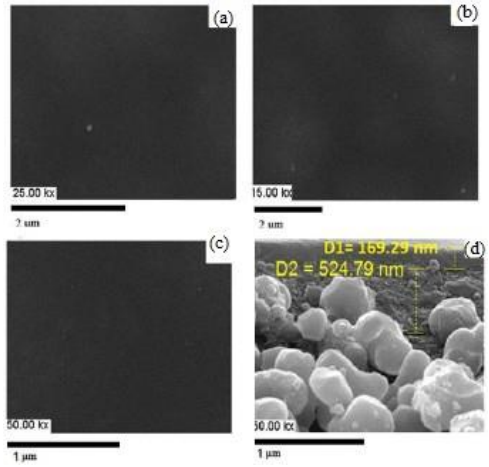

Figure 4:FESEM of Synthesized ammonia substrate in1400 C

Also, AFM micrographs were used to study the surface topography in two dimensions and three dimensions and to determine the porosity and roughness of the membrane surface roughness with a 30% of titania in silica-titania membrane.The results of this study are shown in the form of two-dimensional and three-dimensional images in the figure 5, which indicates the formation of a coating with a uniform surface without cracks.

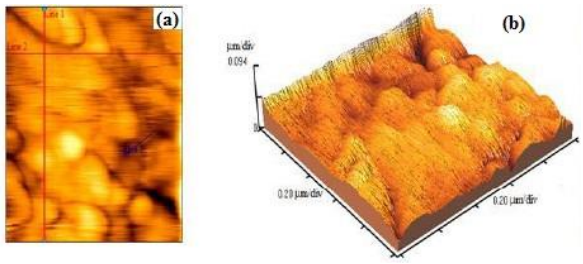

Figure 5: AFM micrographs (a) 2D and (b) 3D of the surface morphology of silica-30%titania

The specific surface area is one of the most important characteristics of the photocatalyst powder. The N_2 adsorption–desorption isotherms of silica-30% titania are shown in Figure 6. This isotherm corresponds to the adsorption isotherm of the first type, which is characterized by micro- porous materials with a porosity of less than 2 nm [23]. The specific surface area of the powder and the porosity area in this sample are 506.995 m^2/g and 218.56 m^2/g, respectively

The results of BET and BJH measurements for nanostructures are shown in figure 7. BJH analysis showed average pore volumes 18-45 A.

In mesoporous samples, because of the existence larger pores, number of molecules interacting with each other are higher, and so they display better catalytic properties. Hysteresis loops occur at low relative pressures (around 0.5) suggesting a narrow pore size distribution.

The pore size distribution confirms this assertion. Well- dispersed to solution tends to create small pore size and homogeneous product.

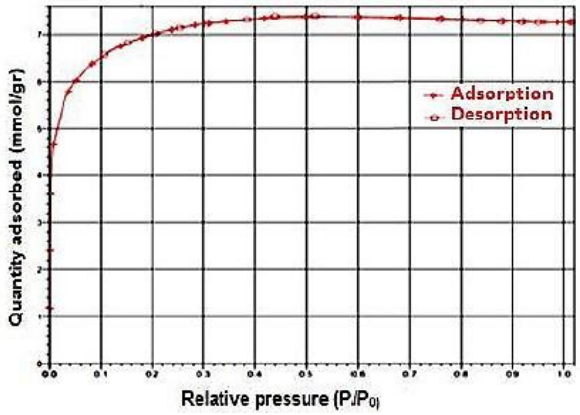

Figure 6: The results of N_2 adsorption and desorption isotherms of silica-30% titania

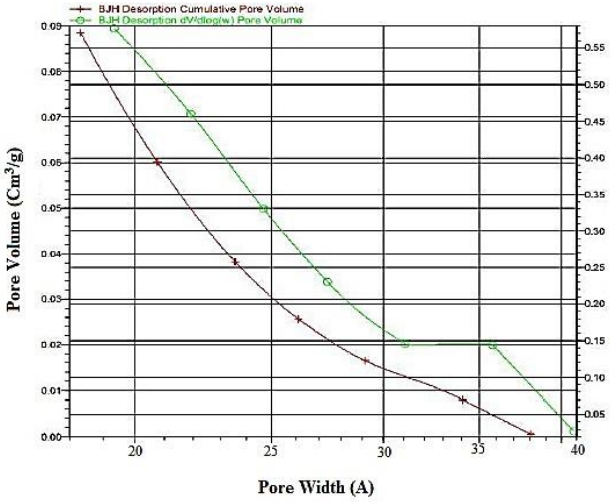

Figure 7: BJH pore diameter distribution of the silica-30% titania

3.3. *Photocatalytic properties*

The chemical structure of methyl orange as water pollutant is shown in figure 8.

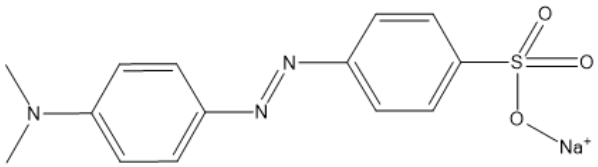

Figure 8: Chemical structure of methyl orange

The photocatalytic activity of silica-titania membrane was investigated by decomposition of MO contaminant. The photocatalytic activity of silica coatings with 10, 20 and 30% titanium was investigated. The results of this study are shown in figure 9 in terms of decomposition time. Also, the percentage of decomposition in terms of time is shown in figure 10. According to the decomposition percentage diagram, 40.67, 46.96 and 48.04% decomposition was performed in the first 30 minutes in 10, 20 and 30% titania compounds, respectively. The photocatalytic activity increased with increasing titania percentage. The decomposition rate after 360 minutes of UV irradiation, reached 88.82, 2.86 and 14.91%, respectively. To show the effect of the catalyst on the decomposition reaction, the decomposition changes without the presence of the catalyst were also examined.

According to the reported diagrams, the presence of catalyst has significantly increased the rate of decomposition. For example, the rate of decomposition by ST30% after 90 minutes is about 68%, which is three times the decomposition in the non-catalyst state with a value of 1.17%.

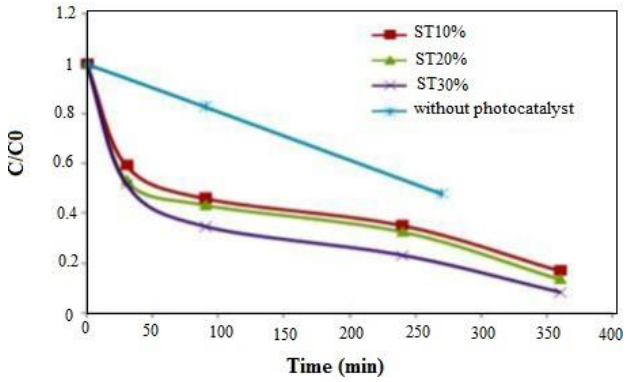

Figure 9: The photocatalytic activity of silica-10, 20 and 30% titania and without photocataluyst

Due to the absence of crystalline phase in silica-titania phase analysis, high percentage of contaminant decomposition and in other words good photocatalytic activity can be attributed to more adsorption of contaminants on the coating surface due to

the high specific surface area and thinning of the final coating. Because the thinness of the final coating has led to the

participation of the middle layer in the process of contaminant degradation. In addition, the high specific surface area has led to the absorption of more contaminants at the photocatalyst surface and therefore more decomposition.

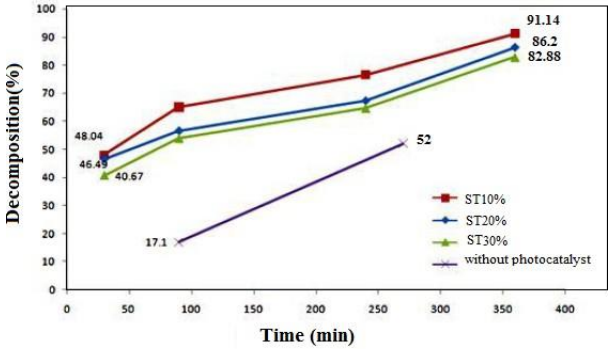

Figure 10: The decomposition curve of methyl orange in the presence of silica-10, 20 and 30% titania and without photocataluyst

4. Conclusion

In this work, nano structure silica-titania membrane was prepared by sol-gel route using TEOT and TEOS as precursors. The as- prepared sols were coated by immersion method on ð • ž ª -alumina disc and were heated to 200 ° C. Then, the coatings of each layer were calcined at 500 ° C. Several techniques such as FT-IR, XRD, FE-SEM were used for characterization of the membrane. The results showed that the presence of Si-O-Si, Ti- O-Si and Ti-O-Ti in FT-IR spectroscopy confirmed the Completion of hydrolysis reactions and solubility of Ti^{4+} ions in Si-O-Si network. The XRD analysis confirmed the amorphous phase in 30% silica-titania to 800 °C. Silica-30% titania coating with a specific powder surface of 506.995 m^2 / g and a porosity area of 218.56 m^2 / g as a microporous was introduced as a suitable coating for photocatalytic membranes with very good photocatalytic activity. The photocatalytic activity of silica-10, 20,30% titania membrane displayed that of the MO degradation by silica-30% titania after 6 hours of UV irradiation was 91.14%.

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