Solar photocatalytic degradation of phenol using pyrolitic TiO_2 films deposited inside a tubing

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Abstract

Solar photocatalytic degradation of phenol was obtained using TiO_2 films deposited inside glass tubing. TiO_2 thin films inside tubing were obtained by spray-gel technique using a titanium isopropoxide solution conveniently diluted in ethanol. The gas carrier flux, air pressure and temperature were kept during deposition at 5 L/min, 200 kPa, and 200 °C, respectively. Experiments were performed using either the solar radiation or a 300 W lamp simulating the UVA solar radiation component. In order to concentrate the radiation a reflective surface was placed in the back part of the tube. The initial concentration of phenol solution was 20 ppm, and the phenol concentration during the experiment was followed using a standard colorimetric method when aminoantipirine reacts in the sample giving a colored complex. The volume of the phenol solution was limited with a solid aluminum rod placed axially to the glass tube. The obtained TiO_2 films were amorphous, but after an annealing at 450ºC for 1 h the films crystallize to anatase structure and present photocatalytic activity. The films morphology observed by scanning electron microscopy presented a uniform film and agglomerates of TiO_2, the size of the agglomerates increases as Ti isopropoxide/ethanol molar ratio of the starting solution decreases. The precursor concentration solution and film thickness of TiO_2 for phenol degradation was optimized.

1. Introduction

The degradation of organic pollutants in water by photocatalysis using TiO_2 has attracted extensive attention during recent 20 years and is an alternative to conventional water treatment technologies. This technology is very suitable for rural areas due to the low cost, easily in the implementation and the possibility of use the UV-A component of the solar radiation.

TiO_2 is a n-type wide gap semiconductor that can only be excited by high energy UV irradiation with a wavelength of no longer than 400 nm. Illumination of TiO_2 with photons of energies greater than the bandgap energy promotes electrons transitions from the valence band to the conduction band, leaving behind positive holes giving electron/hole pairs. The energy level of the lowest occupied state in the valence band potential is enough to promote the generation of hydroxyl radicals. The hydroxyl radical is a powerful oxidizing agent and attacks organic pollutants present at or near the surface of the photocatalyst, reaction are usually driving up to the complete mineralizing of the contaminant.

The use of TiO_2 nano-particles in suspension is efficient due to the large surface area of catalyst available to the reaction. But it has some drawbacks before its scaling up to industrial processes, as for example, the necessary additional filtration to remove the photocatalyst from the solution after the decontamination process, increasing cost and time of the cleaning process. It is also known that suspended particles agglomerates, then reducing its photocatalytic efficiency. Thus an alternative is immobilize the photocatalyst as a thin film onto a rigid substrate. Several alternatives have been implemented in this sense [1-5]. Direct impregnation of Degussa-P25 as a photocatalyst in the internal part of glass coils is mostly used [1,2]. Spray pyrolysis technique is a versatile and low cost technique that was also used to deposit specular catalyst inside glass tubing (internal diameter of 7 mm) [6]. In this work we perform TiO_2 thin films were obtained inside tubing by a spray-gel technique. The process basically consists in producing an aerosol from a gel, which is sprayed over a hot substrate, where the film will grow. Rough coatings were obtained inside glass tubing using a titanium isopropoxide solution conveniently diluted in ethanol. The influence

of an axial volume limitation device was analyzed, as well as the optimum film thickness necessary to drive photocatalytic reactions under a solar radiation was found.

2. Experimental

2.1 Film preparation. TiO_2 thin films were performed inside glass tubing which has an internal diameter of 47 mm, length of 300 mm and 5 mm thick. Before deposition the tubing was cleaned with n-hexane, sonicated for 1 h and dried at 70 ^oC. Treated tubes were placed in a home made spray pyrolysis system shown in Fig. 1. A medical nebulizer was used as an atomizer, which can move back and fort axially to the tube allowing a uniform film. Different amounts of titanium isopropoxide solution diluted in ethanol were used as spraying solution. The gas carrier flux, air pressure and temperature were kept during deposition at 5 L/min, 200 kPa, and 200 °C, respectively. Films were deposited using an ethanol to Ti isopropoxide molar ratio of 0.66, 0.19 and 0.026. The as deposited films were annealed in air at 450 ^oC for 1 h.

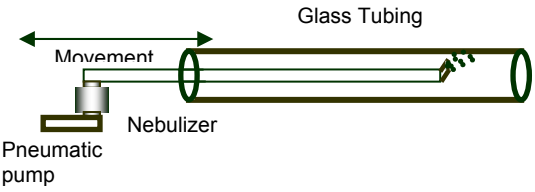


Figure 1. Spray pyrolysis deposition system for coating inside a glass tubing.

2.2 Film characterization. A rectangle sample of the film covered tubing was cut axially to characterized only one face of the film. X- ray diffraction experiments were performed using Phillips X-pert diffractometer operating with a CuK_α radiation (1.54 Å). The microstructure of the films was analyzed by a scanning electron microscope (SEM), a Phillips XL30 instrument provided with a energy dispersive x ray spectroscopy (EDS) micro-analyzer. The total optical transmittance was measured in the 200-800 nm wavelength range using a Perking Elmer Lambda 10 double beam spectrophotometer.

2.3 Photocatalytic activity measurements. Photocatalytic experiments were performed in TiO_2 coated tubing to photocatalytic degrade phenol. The coated glass tubing was filled up with phenol aqueous solution with a concentration of 20 ppm and closed both ends. In order to concentrate the radiation a reflective surface was placed in the back part of the tube. Experiments were performed under solar radiation or a 300 W lamp simulating the UVA solar radiation component as it is shown in Fig. 2.

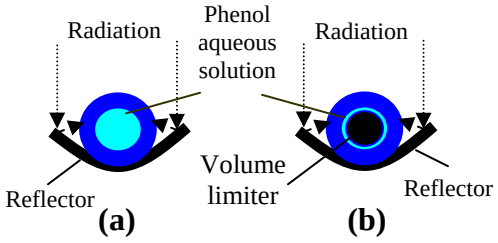


Figure 2. Irradiation scheme of the (a) TiO_2 coated glass tubing filled up with phenol aqueous solution with a concentration of 20 ppm, and (b) with volume limiter.

The global solar radiation and UV-A radiation was measured with a home made radiometer and a UDT radiometer with a 628UVA detector, respectively. Lamp intensity of 38 W/m^2 in the UV-A range was used, which is comparable of the UV-A radiation during a sunny day at Lima city. The volume of the phenol solution was limited with a solid aluminum rod placed axially to the glass tube (Fig. 2 b). Different volume of phenol aqueous solution was treated using a volume limiter with different diameter. The influence of TiO_2 film thickness in the photocatalytic degradation of phenol was study. The phenol concentration during the experiment was followed using a standard colorimetric method when aminoantipirine reacts in the sample giving a colored complex.

3. Results

3.1. X-ray diffraction. Fig. 3 shows the X-ray diffractograms for annealed films made from a solution with Ti isopropoxide/ethanol molar ratio of 0.026. The as deposited films are amorphous, however after an annealing at 450 ^oC for 1 h the films crystallize to anatasa TiO_2 phase with a grain size of 14 nm. The grain size was estimated from Scherrer´s formula [7]. Similar behavior was observed for films made from solutions with Ti isopropoxide/ethanol molar ratio of 0.19 and 0.66.

3.2 Scanning electron microscopy. Morphology of annealed TiO_2 films deposited from solutions with Ti isopropoxide/ethanol molar ratio of 0.026, 0.19 and 0.66 are shown in Fig. 4

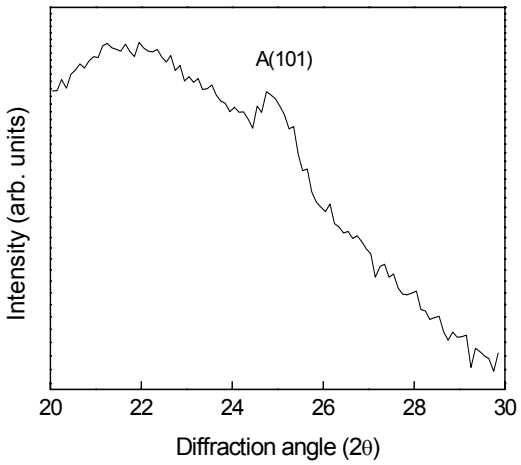


Figure 3. X-ray diffraction pattern for TiO_2 film deposited inside glass tubing after annealed at 450 ^oC.

The morphology of the films indicates a uniform thin layer onto which agglomerates are formed. The uniform thin layers for films made with Ti isopropoxide/ethanol molar ratio of 0.66 and 0.19 are crack-free, whereas the film made with a Ti isopropoxide/ethanol molar ratio of 0.026 has cracks. The size of the agglomerates increases as Ti isopropoxide/ethanol molar ratio of the starting solution decreases. Fig. 5 shows the results obtained by EDS of the compositions in regions I and II (Fig. 4b) of a film deposited using a solution of Ti isopropoxide/ethanol molar ratio of 0.19. The composition of the region I is titanium, oxygen, aluminum, sodium and silicon; where Al, Na and Si are associated to the glass substrate. The agglomerates (region II) has a higher concentration of titanium and oxygen, and lower concentration of silicon. Si correspond to the glass substrate. The uniform film layer and agglomerates are TiO_2. The film thickness was estimated from a cross section micrographs. The film thickness of the films was controlled depositing several layers. SEM micrographs of the cross-section of two representative annealed TiO_2 films obtained from solutions with Ti isopropoxide/ethanol molar ratio of 0.026 are shown in Fig. 6. It is noted that the film deposited with 4 and 10 layers has an approximately thickness of ~1.6 μm, and ~4.00 μm, respectively. The number of layer increases the film thickness. It is also observed that the films have very rough surface, characterized by agglomerates placed onto a continuous layer which is in agreement with the observed in Fig. 4.

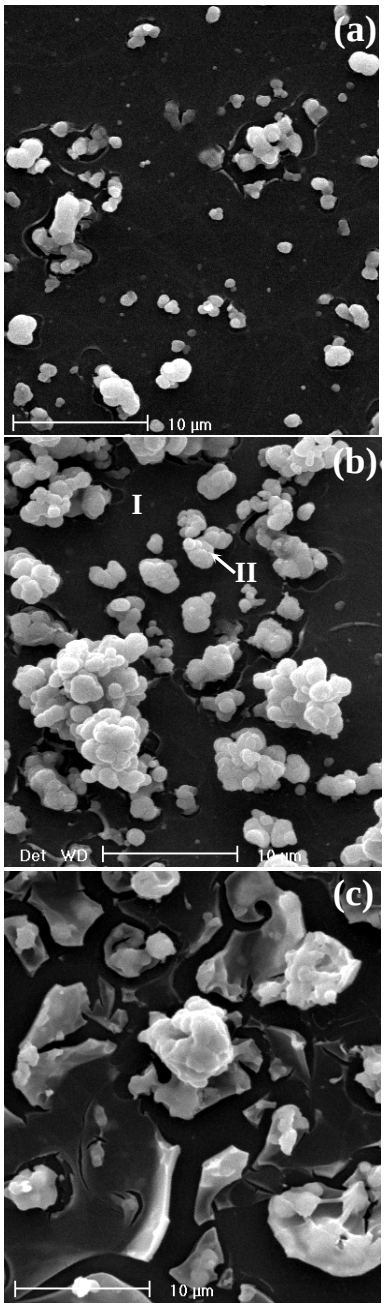
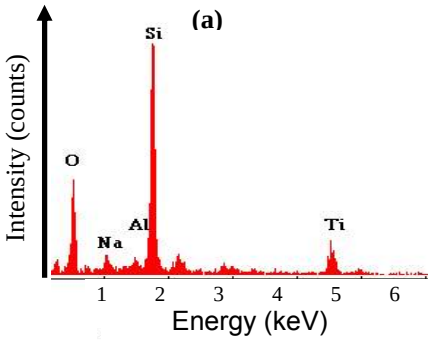


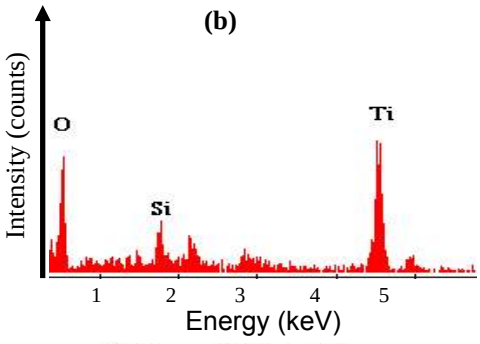
Figure 4. SEM Micrographs of annealed TiO_2 films obtained from solutions with Ti isopropoxide/ethanol molar ratio of (a) 0.66, (b) 0.19 and (c) 0.026.

3.3 Optical characterization. Figure 7 shows transmittance spectra for TiO_2 films deposited from solutions with Ti isopropoxide/ethanol molar ratio of 0.026 onto a plane glass substrate having four thickness. It is observed as a general trend that the transmittance decreases as the film thickness increases. It is well know that below 360 nm an strong absorption is expected due to the intrinsic absorption of the TiO_2 oxide, but in the visible range it is

due to light scattering due to its roughness, as it was observed by SEM micrographs (Fig. 4 and Fig. 6).



Element	Weight %	at %
O	37.20	53.42
Na	3.63	3.63
Al	2.12	1.80
Si	40.75	33.33
Ti	16.30	7.82
Total	100	100



Element	weight %	at %
O	46.41	70.82
Si	5.20	4.52
Ti	48.38	24.66
Total	100	100

Figure 5. EDS analysis of annealed TiO_2 films obtained from solutions with Ti isopropoxide/ethanol molar ratio of 0.19 in regions (a) I and (b) II, which corresponds to Fig. 4b.

Figure 8 shows the UV-A transmittance as a function of film thickness of TiO_2 coated tubing measured inside and outside the tube. Film thickness equal to cero signifies uncovered tubing. The measured UV-A trasmittance inside corresponds for a single wall covered tube and was fitted (full line in Fig. 8). The expected full coated tubing transmittance was calculated from the fitted curve considering two single wall covered tube and plotted in Fig. 8 (dotted line). Very well agreements between calculated and measured results were observed. In the irradiation scheme (Fig. 2) the light interact at least with four single wall covered tube. If we assume that the water, phenol or aluminum did not absorb in the UV-range, we can calculate the UV-A transmittance in function of the number of single wall covered tube (interface).

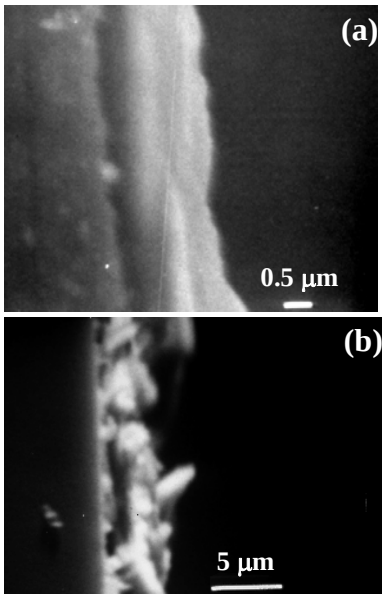


Figure 6. SEM micrographs of the cross-section of two typical Ti oxide films obtained from solutions with Ti isopropoxide/ethanol molar ratio of 0.026 with (a) 4 and (b) 10 layers.

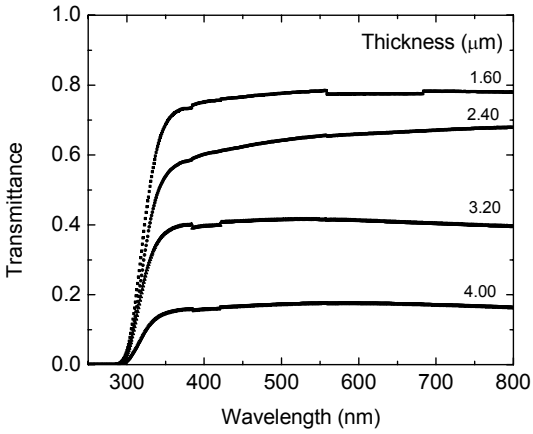


Figure 7. Spectral transmittance for TiO_2 films obtained from solutions with Ti isopropoxide/ethanol molar ratio of 0.026 and having the shown thickness.

3.4 Photocatalytic activity. TiO_2 coated tubing filled with phenol aqueous solution with a concentration of 20 ppm were irradiated for 4 h with lamp intensity of 38 W/m^2 in UV-A range. The volume of the phenol solution was varied using an aluminum rod placed axially inside the coated tubing (Fig. 2b). Aluminum rod of 1.2, 3.2 and 3.7 cm diameter was used as volume limiter. Table 1 shows the results of phenol photodegradation for different phenol volumes for TiO_2 films obtained from Ti

isopropoxide/ethanol molar ratio of 0.026. It can be seen that the phenol degradation depends of the relation of the available photocatalyst with the contaminant volume.

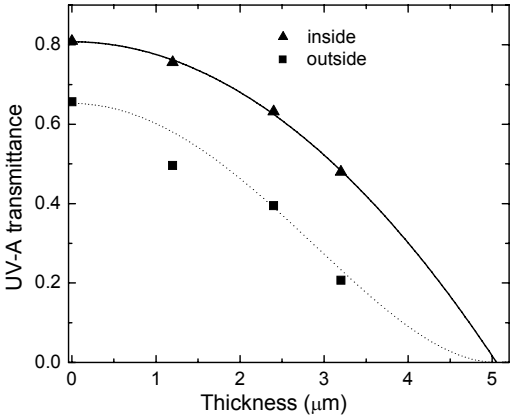


Figure 8. UV-A transmittance as a function of TiO_2 films thickness deposited with Ti isopropoxide/ethanol molar ratio of 0.026 measured inside (▲) and outside (■) the tubing. The full and dotted line is fitted and calculated, respectively.

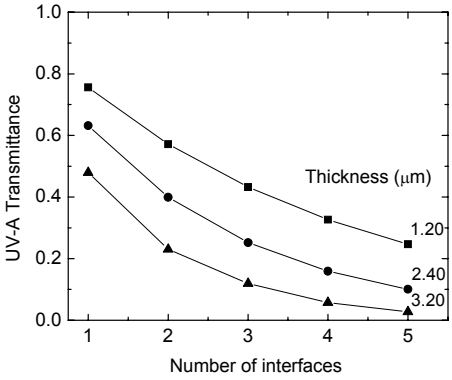


Figure 9. UV-A transmittance for TiO_2 films deposited with a Ti isopropoxide/ethanol molar ratio of 0.026 as a function of the number of interfaces that light pass through and having the shown thickness.

The influence of Ti isopropoxide/ethanol molar ratio in starting solution and the film thickness in the phenol photodegradation is shown in Fig. 10. The phenol volume treated is 400 and 200 mL in Fig 10a and 10b, respectively. The phenol photodegradation of 400 mL (Fig. 10a) increases with the film thickness. Slight difference has the TiO_2 films obtained with Ti isopropoxide/ethanol molar ratio of 0.66 and 0.19. When phenol volume treated is 200 mL (Fig. 10b), an increment in the phenol degradation is observed in all cases. TiO_2 films deposited with Ti isopropoxide/ethanol molar ratio of 0.66 and 0.19 has a similar behavior for 200 and 400 mL of phenol treated; only a larger difference for 1.2 μm film thickness is observed. The phenol degradation for TiO_2 films deposited with Ti isopropoxide/ethanol molar ratio of 0.026 has a maximum degradation when film thickness is between 1.2 to 2.4 μm, and diminished for thicker films.

Table 1. Phenol photodegradation after 4 h of irradiation for different phenol volume using TiO_2 coated tubing with Ti isopropoxide/ethanol molar ratio of 0.026. The initial concentration of phenol aqueous solution was 20 ppm.

Al rod diameter (cm)	Phenol degradation after 4 h (%)	volume (mL)
0	10	400
1.2	11.4	300
3.2	14.9	200
3.7	22.4	100

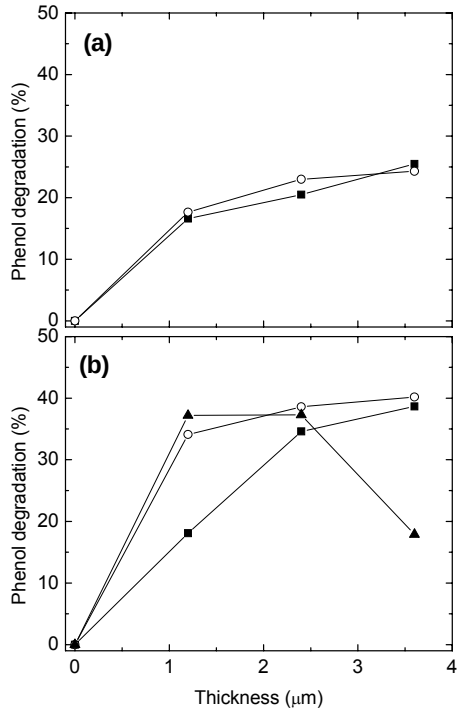


Figure 10. a) 400 and b) 200 mL phenol photodegradation as a function of film thickness for TiO_2 coated tubing obtained with Ti isopropoxide/ethanol molar ratio of (■) 0.66, (○) 0.19 and (▲) 0.026. The initial concentration of phenol aqueous solution was 20 ppm.

Phenol degradation with 2.4 μm thick TiO_2 coated tubing under solar radiation and a lamp intensity of 38 W/m^2 in the UV-A range was performed for 4 h. Fig. 11 shows the solar radiation of a typical summer day in Lima. After the irradiation time the phenol degradation in both experiments was similar.

A degradation of 31.6 and 34.4 % were obtained for the experiments performed under solar radiation and with UV-A lamp, respectively. The slight difference is attributed to the fact that the solar radiation is not constant during the experiment and the average was less than 34 W/m^2.

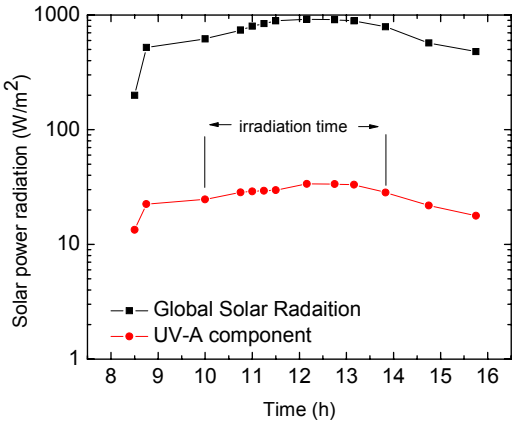


Figure 11. Global solar radiation and UV-A component during a typical sunny day in Lima. The irradiating time of the sample is shown.

4. Conclusions

Photocatalytic TiO_2 films were deposited inside glass tubing. As deposited films were amorphous, however after an annealing at 450 ^oC for 1h the film crystallize to anatasa TiO_2 phase with a grain size of 14 nm. The film morphology of TiO_2 films depends of the Ti isopropoxide/ethanol molar ratio of the starting solution. The optimum volume for phenol degradation is 200 mL. TiO_2 film obtained with Ti isopropoxide/ethanol molar ratio of 0.026 with a film thickness between 1.2 to 2.4 μm showed the maximum phenol photodegradation.

Acknowledgements

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