

Photocatalytic degradation of phenol using TiO₂ nanocrystals supported on activated carbon

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Abstract

It has been deposited titanium oxide on activated carbon (AC) in two forms as powder and as a pellet. This oxide was obtained using sol-gel process based on titanium isopropoxide and isopropyl alcohol. Nanocrystalline TiO₂ anatase phase on activated carbon was obtained using an adequate thermal treatment of 325 °C by 5 h considering the thermal instability of the AC. The resulting material was characterized by spectroscopic X-ray fluorescence, scanning electron microscopy with energy dispersive X-ray microanalyses (EDX), and Brunauer–Emmett–Teller (BET) surface area measurements. Activity measurements performed under UV lamp and solar irradiations have shown good results for the photo degradation of phenol in aqueous solution. For solar applications, a polyethylene terephthalate bottle containing the photocatalysts was filled up with the contaminated water and placed for a few hours under the solar radiation of a couple of sunny days. The results indicate that 20 ppm of phenol can be removed by using this method.

1. Introduction

Photocatalytic degradation of organic compounds has been proposed as a viable alternative for the decontamination of either waste water or drinking water for human use [1-4]. Indiscriminate use of agrochemicals, inadequate industrial waste disposal and even the worldwide employed method of potabilization by using chlorine are the main causes for the pollution of water sources.

UV-irradiated titanium dioxide in intimate contact with an aqueous solution of the pollutant develops a redox environment capable of oxidizing them into nontoxic substances. Photocatalytic activity of TiO₂ strongly depends on its microstructural and physical properties. A way to increase TiO₂ photocatalytic activity is the preparation of a nanostructural TiO₂ to get a high surface area that is directly related with catalytic activity. However, small TiO₂ powder photocatalysts have to be removed from the degraded solution by centrifugation and filtration. The design of titanium oxide photocatalyst anchored or embedded onto support materials with large surface areas which could condense diluted polluted substances would be of great significance, not only to avoid the filtration of small photocatalyst particles, but also to obtain higher efficiency. Many alternatives have been proposed in the last few years, which

have tried a variety of supporting materials and coating methods in different arrangements for degradation of several organic compounds [5]. One possible way was the use of materials such as silica, alumina, zeolites or clays [6], but no improvement of photoefficiency was observed. Activated carbon (AC) is another type of coadsorbent that has been used in photodegradation of organic pollutants in aqueous phase [7-10] and according to our knowledge, using AC support has been reported up to now the more promising results, which is attributed to the synergistic effect between the AC and the TiO₂. In this paper, it was done a study of the photocatalytic effect of the activated carbon impregnated with TiO₂. Titanium oxide was synthesized by sol-gel method from titanium isopropoxide to get anatase phase. Catalyst was tested in the photocatalytic degradation of aqueous phenol solutions with either UV lamp or solar radiation.

2. Experimental

TiO₂/AC samples were prepared from alkoxide precursor in the following way: 5 g of activated carbon powder (Darco ® G-60, 100 mesh, Aldrich) was homogenized and settled in 30 mL titanium isopropoxide (97%, Aldrich) solution at 30% in isopropyl alcohol (99.5%, Riedel deHäen) during 12 h. After

that time, it was observed a polymerized gel, which was dried at 96°C for 5 h. This process was repeated 4 times trying to get more impregnation of TiO₂ on activated carbon. After the impregnation process has finished, the material is calcined under static air at 300, 325 and 350 °C for 5 h. The same process was used to support TiO₂ (anatase) on activated carbon pellets (~5 mm o.d. and ~10 mm long). Elementary analysis was done using X-ray Fluorescence spectroscopy. A Cd-109 source was used to activate the Ag K_α radiation of 22.101 KeV utilized to impinge to the sample, from which the energy of the x-ray emitted is detected by a Si-Li detector. X-ray diffraction (XRD) patterns were obtained using a Philips X-Pert diffractometer with a Ni filter and a Cu K_α radiation source. Scanning electron microscopic analysis were performed with a Phillips XL30 TMP SEM microscope containing an EDAX DX4i probe for the energy dispersive X-ray microanalyses (EDX). Brunauer–Emmett–Teller (BET) surface area measurements were carried out by N₂ adsorption at 77 K in a manual volumetric adsorption/desorption equipment.

An aqueous solution of phenol was used as a model contaminant for study the photocatalytic performance of the prepared materials. For the catalytic study it was prepared two reaction systems (Fig. 1). The photoreactor system shown in Fig. 1a was used for in door experiments using a high pressure 300 W Osram Ultra-Vitalux lamp. An air flow was supply to increased oxidative photo degradation. The UV-A radiation of the lamp (310 - 400 nm of wavelength) was measured with an UDT radiometer 628UVA. 0.1 g of TiO₂/AC powder in 200 mL of 40 ppm phenol aqueous solution was placed in 500 mL photoreactor and irradiated with 37.5 W/m² of UV-A range light for 1h. The irradiation started after one hour of adsorption in the dark. 5 mL samples were collected each 10 min and filtered before analysis. The phenol concentration was measured with the photocolourimetric method of 4-amino-antipirine [11] analyzed with a 21 D Spectronic spectrophotometer. For outdoor experiments closed plastic polyethylene terephthalate (PET) bottles were placed horizontally and exposed to sun in a clear day (Fig. 1b). No stirring or aeration was implemented. The solar global radiation was measured with a home-made radiometer calibrated with a Haenni Solar 130 radiometer and the UV-A component with an UDT radiometer 628UVA. To perform out door experiments, 200 mL of 20 ppm of

phenolic water was used. Contaminated water samples were placed in 500 mL plastic PET bottles with 0.1 g of TiO₂/AC powder or 1.01 g of TiO₂/AC pellets under the sun irradiation in a clear day for 1 and 4 h. 5 mL sample each 20 min and 1 h were collected during 1, and 4 h of irradiation time, respectively.

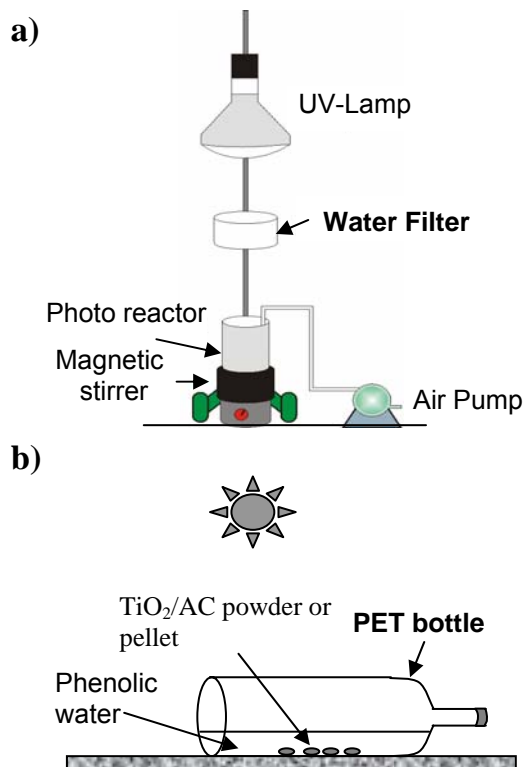


Figure 1. (a) Photocatalytic reactor system for degradation with UV lamp and (b) the out door experimental set up under solar irradiation.

3. Results and discussion

3.1 Synthesis and characterization
Qualitative analysis by X-ray fluorescence of Fig. 2 showed that impurities like iron, strontium and zirconium were presented in samples. It is observed that when it is used the AC powder as substrate the ratio of the intensity peaks of Ti respect to the other elements is higher (Fig. 2a) than when AC pellets are using as substrate (Fig. 2b). It reveals that Ti is in larger amounts in the powdered activated carbon than in the pellet. However it should be notice that powder from the pellets was used for this analysis. Impurities are in very low quantities so they are not significant for the composition of materials.

In Fig. 3 the diffraction patterns for powder samples of TiO₂/AC prepared as explained

above is presented. It shows an evolution of anatase phase with increasing the calcination temperature performed during 5 h. It can be seen that for 300°C there is a small anatase peak, which increase in intensity at 325°C and 350°C. An increase in temperature produces thermal destruction of the AC pellet. In that sense and considering the thermal instability of the AC the selected treatment for powder samples was 325°C for 5 hours. The main grain size D , for the obtained TiO_2 was ~ 12 nm estimated from XRD data by applying the Scherrer's formula [12], i.e:

$$D = \frac{K\lambda_x}{\beta \cos \theta} \quad (1)$$

Where K is a dimension less constant equal to 0.9, λ_x is the X-ray wavelength, and β is the full width at the half maximum of the diffraction peak. Similar results are expected in the pellet samples.

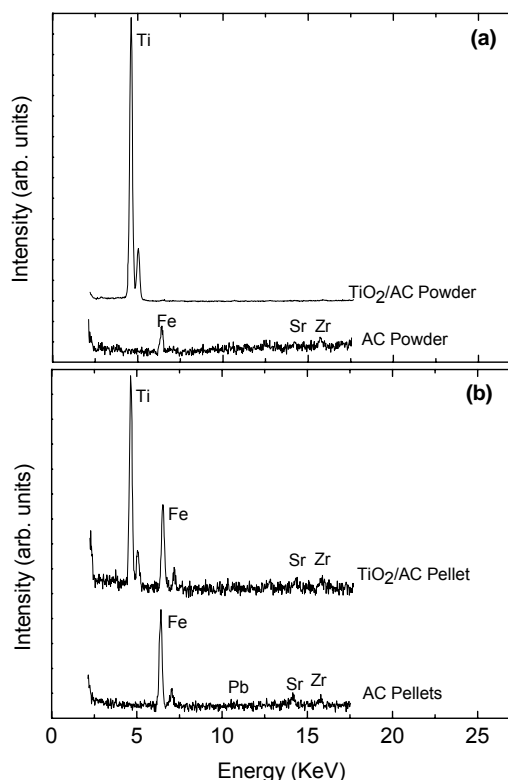


Figure 2. Elemental analysis by X-ray fluorescence spectroscopy: (a) activated carbon and TiO_2/AC powders, and (b) activated carbon and TiO_2/AC pellet powders.

Specific surface areas $S_{\text{B.E.T}}$, were calculated for TiO_2/AC samples calcined at 325°C for 5 hours. Differences between TiO_2/AC pellet and TiO_2/AC powder carbon are shown in Table 1. As expected, the AC pellets present less superficial area than AC powder samples. However, for the case of the

TiO_2/AC samples, the TiO_2/AC powder samples present less area than the unsupported AC powder, but the TiO_2/AC pellets samples, presents slightly a larger surface than unsupported AC pellet. This could indicate that TiO_2 has dispersed in higher grade on the AC powder than on the AC pellet sample. This fact is clearly observed under SEM analysis.

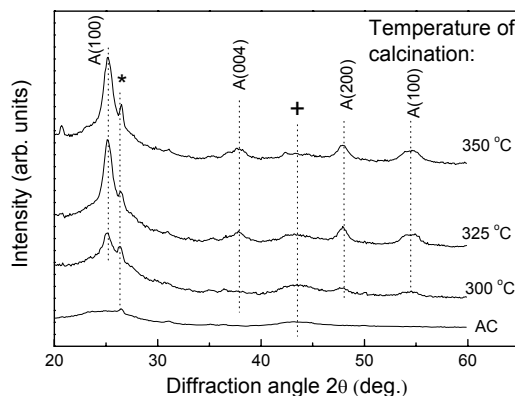


Figure 3. Diffraction patterns of TiO_2/AC powder after different thermal treatment. Diffraction peaks from quartz (*) and graphite (+) are also indicated.

Table 1. Specific surface area of samples obtained by B.E.T method.

	S_{BET} AC Powder (m^2/g)	S_{BET} AC pellet (m^2/g)
AC	1007 ± 15	688 ± 44
TiO_2/AC	704 ± 10	780 ± 54

Figure 4 presents in part (a) only the AC powder and in part (b) the TiO_2/AC powder. It is observed clearly from Fig. 4 the agglomerates of TiO_2 placed on top of the AC powder. The pellet sample of TiO_2/AC was also analyzed by SEM. Figure 5 shows a cross sectional picture of a typical TiO_2/AC pellet, in which there are a enormous density of porous and cavities, explaining then the large surface area obtained by BET (Table 1). EDX analysis performed on the pellet in three different regions: I, II, and III (Fig. 5) are presented in Fig. 6 and in Table 2. It is observed that the larger amount of Ti and O is placed on the lateral places, but when the EDX probe is going deep into the pellet, the percentage of Ti and O decrease remarkably, for example in the case of Ti ~ 76 wt% at the wall (region I), fall to ~ 7 wt% in the region II, and only 2 wt % near the center (region III), but for powder samples Ti quantities was more than 50 wt%. The catalyst is not uniformly distributed on the AC pellet substrate; this fact can be seen in the SEM micrograph (Fig. 7). In Fig. 7a is presented a

SEM picture of the lateral wall of the TiO₂/AC pellet and in Fig. 7b is shown the transversal one.

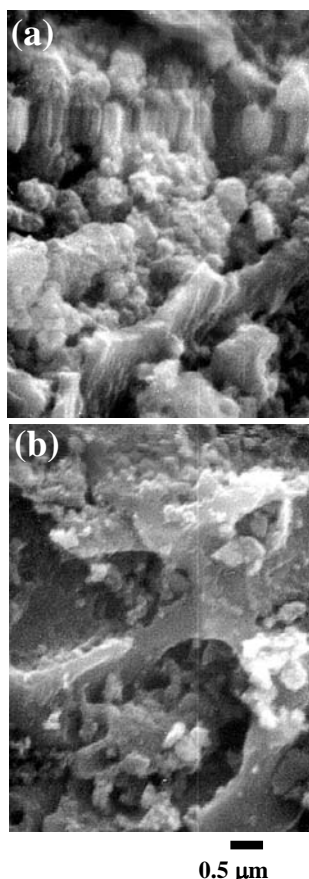


Figure 4. SEM micrographs of (a) AC and (b) TiO₂/AC powders.

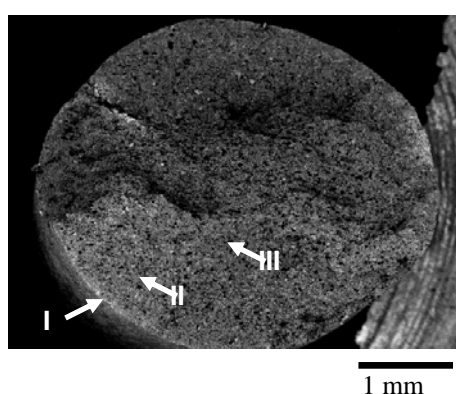


Figure 5. Cross sectional SEM of a TiO₂/AC pellet in which three different regions are pointed out.

3.2 Photocatalytic degradation of phenol

3.2.1 Experiments performed under UV-irradiation. Experiments were performed in the reactor explained above and presented in Fig 1a. Fig. 8 has shown the relative concentration of phenol, C/Co, for different times during the UV-irradiation. The initial phenol concentration, Co, was 40 ppm. It can

be observed that for the adsorption of phenol in the dark on TiO₂/AC powder has reached a constant value C/Co of 0.7 after 1 h, however if it is used only the AC powder, the adsorption increase and it is observed that after 10 min of adsorption, a minimum in the concentration is reached. This fact is in agreement with the surface area obtained by S_{B.E.T.}, which is higher for the AC powder than for the TiO₂/AC powder. However, when UV-A light illuminates the reactor, a photocatalytic degradation of phenol is observed. Illumination starts after 60 min of adsorption in the dark, during which it reach a constant value. After the sample is placed under UV-A illumination, then consistently is observed a decrement of the relative concentration of phenol.

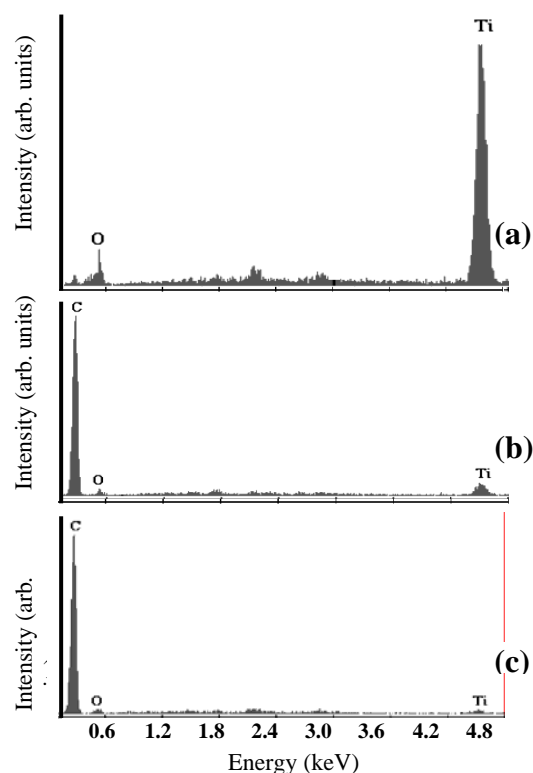


Figure 6. EDX diagrams of a TiO₂/AC pellet obtained in the three different regions pointed out in Fig 5: (a) region I, (b) region II, and (c) region III.

Table 2. EDX elemental composition of a TiO₂/AC pellet in three different regions indicated in Fig. 5.

Region	C Wt%	O Wt%	Ti Wt%
I	-	23.71	76.29
II	86.26	6.90	6.84
III	92.57	5.42	2.02

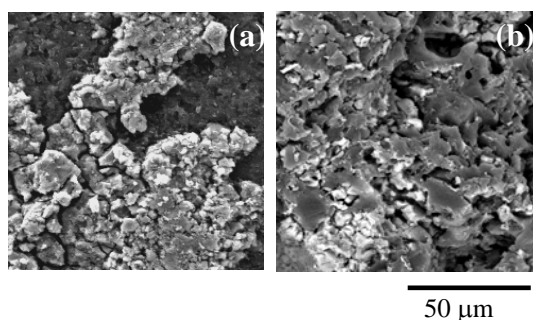


Figure 7. Cross sectional SEM of a TiO_2/AC pellet: (a) lateral view (probe was placed on to region I, Fig. 5), (b) cross sectional view (probe was placed on region II, Fig. 5).

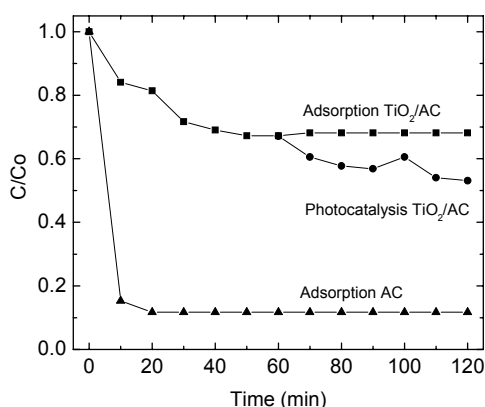


Figure 8. Relative concentration of phenol (C/C_0) vs. time obtained in a typical photocatalytic experiment performed with TiO_2/AC powder (●), and the adsorption in the dark of AC (▲) and TiO_2/AC (■) powders.

3.2.2 Experiments performed under solar irradiation. Figure 9, 10 and 11 shows typical experiments of photocatalytic degradation of phenol under solar radiation of TiO_2/AC samples. It was performed in the PET bottles explained in the experimental section for TiO_2/AC powder (Fig. 9) and with TiO_2/AC pellets (Figs. 10 and 11). The global solar radiation and its UV-A component are shown in part (a) of each figure, and the relative concentration of phenol during its photocatalytic degradation under solar radiation is presented in part (b) of each of these figures. In Fig. 9 it can be observed that with 200 mL of 20 ppm phenol solution, the TiO_2/AC powder in the dark adsorbs rapidly the phenol. In this case adsorption seems to continue up to 80 min in which evidence of photocatalytic degradation is observed. It is also observed that there is no evidence of phenol photolysis under solar irradiation. In Fig. 10 is presented solar photocatalytic experiments using 200 mL of 20 ppm phenolic solution with TiO_2/AC

pellets. It is observed that in the dark there is adsorption of phenol, in this case the adsorption (Table 3 and Fig 10) is not as fast as it was for the case of TiO_2/AC powder (Fig. 8). The adsorption of phenol on AC pellet is slightly higher than that on TiO_2/AC pellet. This fact seems to indicate that the variation of the surface area in the AC pellet present a nil change in comparison with the TiO_2/AC pellet, in accordance with the $S_{B.E.T.}$ measurements.

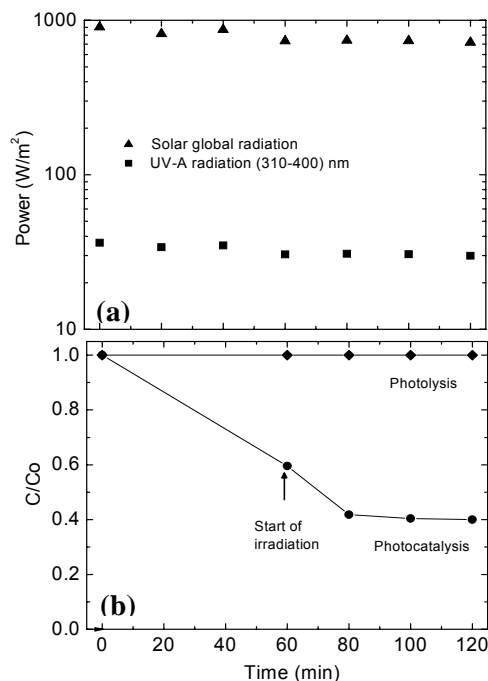


Figure 9. (a) The solar radiation power in the global range and UV-A component and (b) the relative concentration of phenol (C/C_0) vs. time in a typical solar photocatalytic experiment performed with TiO_2/AC powder placed in PET bottles filled up with phenolic water.

In Fig. 10 is also observed that after four hours of radiation, there is no evidence of photolytic degradation of phenol, a small decrement of the concentration due to adsorption phenomena is observed, but in this case is much slower than for TiO_2/AC powder samples. By photocatalysis, around 50% of the phenol was degraded. Experiments performed in two consecutive days (Fig. 11) shown that a complete degradation can be obtained in a continuous irradiation during different days. It is also observed that in between the irradiation times, the adsorption of phenol continue but in an low quantity as can be seen in Fig. 11. It is also notice that comparable degradation were obtained for experiments repeated under the same condition with the same photocatalyst and no evidence of

photocatalyst drain or inactivation was observed. It necessary to point out that AC powder can perturbs the transmission of light to the surface of titania, however, this inhibition is largely compensates by a strong beneficial effect in phenol adsorption followed by a transfer of phenol to TiO₂ [7]. The driving force for this transfer is probably the difference in phenol concentration between AC and TiO₂ that causes surface diffusion of phenol to titania.

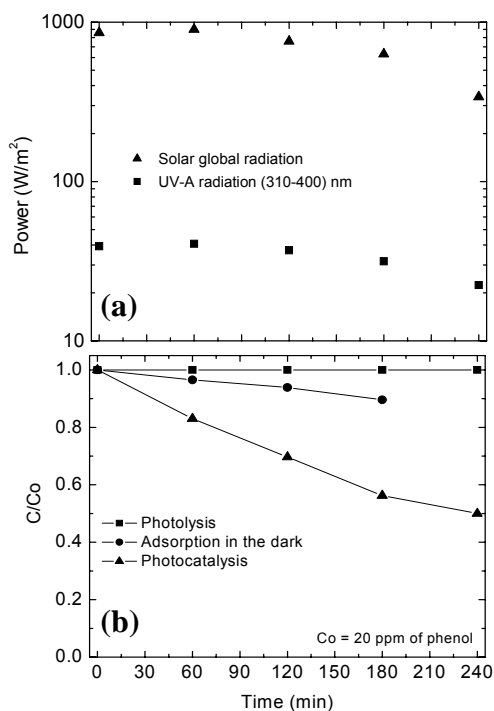


Figure 10. (a) The solar radiation power in the global range and UV-A component and (b) the relative concentration of phenol (C/C_0) vs, time in a typical solar photocatalytic experiment performed with TiO₂/AC pellets placed in PET bottles filled up with phenolic water.

Table 3. Relative concentration of phenol, C/C_0 , at different times due to adsorption in the dark of 1.0 g AC pellet and 1.0 g TiO₂/AC pellet. Initial concentration of phenol, C_0 , was 20 ppm.

Time (min)	0	60	120	180
AC (C/C_0)	1	0.95	0.91	0.86
TiO ₂ /AC (C/C_0)	1	0.97	0.94	0.90

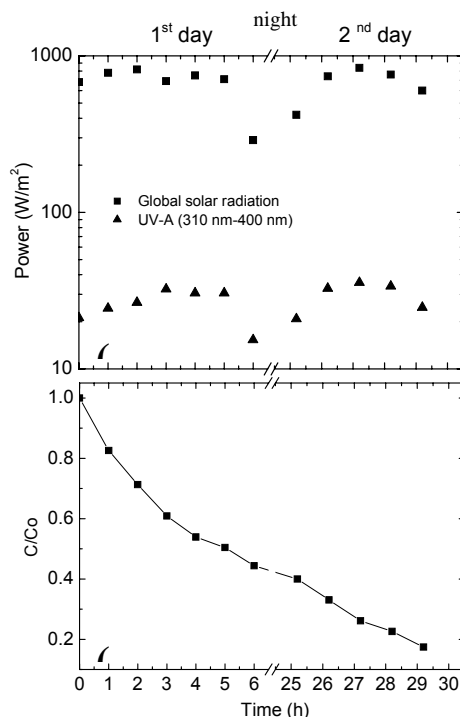


Figure 11. (a) The solar radiation power in the global range and UV-A component and (b) the relative concentration of phenol (C/C_0) vs, time during two consecutive days in a typical solar photocatalytic experiment performed with TiO₂/AC pellets placed in PET bottles filled up with phenolic water.

4. Conclusions

Photocatalytic materials based on TiO₂/AC have been fabricated. Both, the TiO₂/AC pellet and TiO₂/AC powder present good photocatalytic performance. From the practical point of view, the solar irradiation of TiO₂/AC pellets placed inside a PET bottle (a common waste) containing contaminated water is in our opinion an alternative viable for its application. Even in places in which not many sunny hours per day are available, because the treatment is additive in irradiation time without be much influenced due to its permanence in the dark, during which a small adsorption of the contaminant is observed. Such a system would be particularly important for the detoxification and decontamination of polluted water in rural areas of developing countries.

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