

Analysis of the Photocatalytic Potential of the C/TiO₂ Composite

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Keywords: Titanium oxide, Amorphous carbon, Phenol red, Photocatalysis.

Abstract. The control of environmental pollution has led to an intensive search for innovative and efficient technologies for wastewater treatment, especially those with toxic or non-biodegradable compounds. In this sense, this work involved the preparation of a hybrid composite of TiO₂ with amorphous carbon by partial pyrolysis method and the analysis of their photocatalytic potential using phenol red dye as a test molecule. The composite was characterized by X-ray diffraction (XRD), infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The evaluation of morphology and the structural characterization of the powder confirmed the formation of the hybrid composite of TiO₂ dispersed in a carbon matrix with turbostratic structure, organized in the shape of overlapping plates. The composite presented a discoloration rate of 67% after 4 hours of irradiation. The photocatalytic reaction follows a kinetics of first order type.

Introduction

Contamination of the environment, especially water, has been identified as one of the great problems of modern society. Currently, new standards and increasingly restrictive laws are emerging in order to minimize the environmental impact. In this sense, an increase of searches related to the wastewater treatment processes that ensure a low level of contaminants safely, quickly and with low cost have been performed [1,2]. The high efficiency and low cost of the photocatalytic degradation employing semiconductors has been recognized as an environmentally friendly technique for removal of recalcitrant contaminants in aqueous environments [2,3]. One of the most used semiconductors in photocatalysis is the TiO₂ due its low cost, good chemical stability and high photocatalytic efficiency [2]. However, the use of this semiconductor has still some limitations such as the high rate of recombination of charge carriers in function of its bandgap (3.2 eV), beyond its limited absorption for radiation up to 385 nm. In this sense, some methods have been adopted to extend the TiO₂ absorption range and decrease the rate of electron-hole recombination. Among these methods can be highlighted the sensitization, doping and the combination with others semiconductors or charge carriers such as polymers and carbon matrixes [1,2].

Carbon in several forms such as nanotubes, graphene, pyrocarbons, graphite, activated carbon, amorphous carbon has been considered as promising material for various applications as electronic and optical devices and as photocatalysts [4]. The combination of carbonaceous materials with semiconductors have been reported as promising materials in the photocatalytic degradation of compounds such as 2-propanol, 4-chlorophenol, methylene blue, rhodamine B, phenol red, etc. [4-9]. Furthermore, carbonaceous materials have a high surface area and play a role of photo-assistance to the semiconductor decreasing the electron-hole recombination rate and increasing process efficiency. In this sense, this work aimed the preparation and the structural characterization of a hybrid composite based on TiO₂ with amorphous carbon, as well as the evaluating of its photocatalytic activity using phenol red dye as test molecule.

Experimental

Synthesis

C/TiO₂ hybrid composite was prepared by partial pyrolysis method, similar to the process developed by the Pechini method. The method consists in formation a polymeric resin produced by the polyesterification of metal chelates with hydroxycarboxylic acids and a polyhydroxy alcohol such as ethylene glycol [10, 11]. The starting reagents for preparing the composite were TiO₂, citric acid (C₆H₈O₇·H₂O) and ethylene glycol (HOCH₂CH₂OH). Citric acid was solubilized in ethylene glycol (mass ratio of 40:60) with continuous magnetic stirring at 70°C, to promote polyesterification. After the polyesterification reaction, a polymeric gel was formed and the semiconductor was gradually added. The resulting material was maintained in a beaker and subjected to a primary calcination in a box-type furnace. The calcination was performed in a single step in static air atmosphere from room temperature to 300 °C at a heating rate of 1 °C / min. The material obtained was deagglomerated in agate mortar with a 325-mesh minimum, obtaining the hybrid composite termed C/TiO₂.

Characterization

Structural characterization of the TiO₂ and C/TiO₂ powders was carried out by X-ray diffraction using a Shimadzu diffractometer (XRD-6000 model) with Cu Ka radiation ($\lambda = 1.54060$) and a graphite monochromator in the range of $5^\circ \leq 2\theta \leq 80^\circ$ with a scan step of 0.02° and counting time fixed of 0.6s. Divergence, scattered and receiving radiation slits were 1° , 1° and 0.3 mm, respectively. The analysis of chemical bonds was performed by infrared spectroscopy. Samples were diluted in KBr in the ratio 1:100 and pressed into pellet form. The measurements were carried out in the region of $4000\text{--}400\text{ cm}^{-1}$ with resolution of 8 cm^{-1} and 100 scans, using an infrared spectrometer Shimadzu (IR Affinity model). The analysis of the microstructure of materials was performed by scanning electron microscopy (SEM) using a microscope Carls Zeiss EVO LS15 model, operating at 30 kV on samples coated with a thin gold film. The photocatalytic activity of the composite was evaluated as a function of the degradation reaction of the phenol red dye as test molecule. A low power (15 W) UV lamp (285 nm) was used as an irradiation source. The initial concentration of dye was of $3.53 \times 10^{-5}\text{ mol.L}^{-1}$ in basic medium (pH = 9). The mass of catalyst was of 300 mg. In order to well-establish the photocatalytic behavior of the hybrid composite the kinetic of phenol red disappearance in the presence of the TiO₂ was also followed. The concentration of phenol red in solution was determined by the changes in absorbance at 430 nm using a UV-Vis spectrophotometer. The disappearance of phenol red was investigated in terms of the conversion of X obtained by the following equation:

$$X = [(C_0 - C_t)/C_0] \cdot 100 \approx [(A_0 - A_t)/A_0] \cdot 100 \quad (1)$$

where C_0 is the initial concentration of phenol red dye, C_t is the concentration at the reaction time t and A_0 and A_t are the initial absorbance and the absorbance at reaction time t , respectively.

Results and Discussion

Structural Characterization

Fig. 1 shows the X-ray patterns of the TiO₂ and C/TiO₂ composite. The XRD pattern of the composite shows crystalline diffraction peaks that can be indexed as Bragg reflections of TiO₂ anatase with tetragonal symmetry and space group I41/amd (JCPDS 22-1272 card) [12]. The presence of the amorphous carbon matrix can be observed at around $2\theta \approx 20^\circ$ where a small halo of diffraction is observed, see inset of Fig. 1.

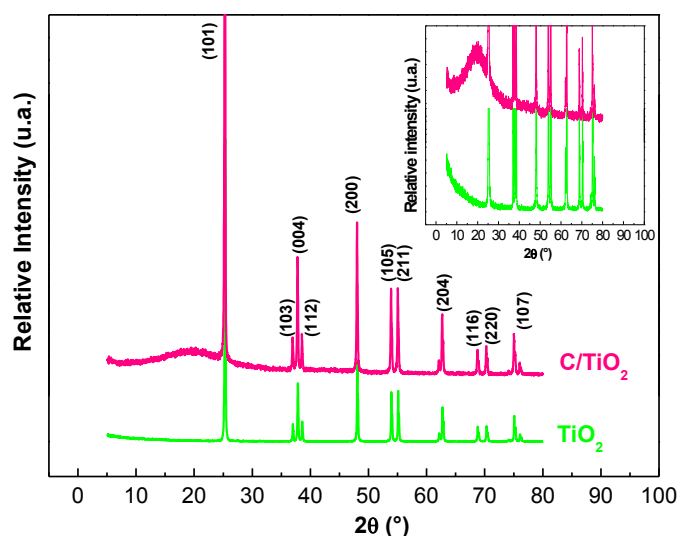


Fig. 1. XRD pattern of the TiO_2 and C/TiO_2 powders.

The profile obtained of the amorphous carbon matrix indicates that this matrix has a structure of the random type comprising two different carbon species [13]. The first type consists in a short-range graphite-like structure with micro crystallites. In terms of crystallinity, this structure is positioned between graphite carbon and amorphous carbon, so-called turbostratic or reticular random. The second species corresponds to the amorphous carbon, a kind of highly disordered carbon and non-aromatic type. While amorphous carbon contributes to the diffractogram profile, ranging the intensity of the background noise, the turbostratic specie is responsible for the appearance of halo associated with the interplanar spacing between the graphitic layers (L_a), corresponding to the plane (002) of the graphite structure [13,14]. This parameter has significant importance in carbonaceous materials arising from pyrolysis since it can be related to the size of microcrystal graphite-type, which in turn can be related to the porosity of these materials. This relation is established in the sense that the higher the parameter (L_a) higher the porosity of material, which is of great importance, for example, in the production of activated carbons [13,14].

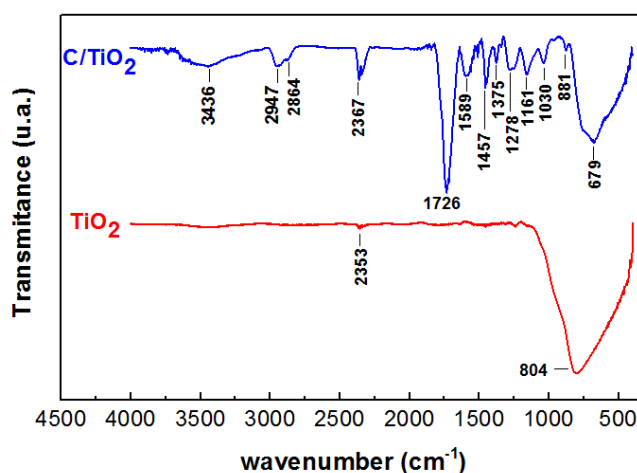


Fig. 2. FTIR transmittance spectrum of the TiO_2 and C/TiO_2 powders.

C/TiO_2 spectrum shows absorption band positioned at 3436 cm^{-1} associated with hydroxyl stretching vibration of adsorbed water or surface carboxylic groups. Bands in the region between $2947\text{--}2864\text{ cm}^{-1}$ can be associated with CH_2 or CH_3 . The band positioned at 1726 cm^{-1} corresponds to the stretching vibrations of the $\text{C}=\text{O}$ bonds. Deformation vibrational of the OH and C-H groups are observed between $1598\text{--}1409\text{ cm}^{-1}$ and the bands in the range between 1030 cm^{-1} and 1278 cm^{-1} can be assigned to the stretching vibration of C–O bonds [8, 9, 15, 16]. The stretching vibrations of Ti–O bonds were identified at 804 cm^{-1} and at 679 cm^{-1} , in the TiO_2 and C/TiO_2 spectra, respectively [15, 16].

Table 1. Assignment of the FT-IR absorption bands of TiO₂ and C/TiO₂ powders.

Assignments	Wavenumber (cm ⁻¹)	Reference
ν_{sim} (OH) water	3436	[8,9,15,16]
ν_{sim} (C-H)	2947-2864	[8,9,15,16]
ν_{sim} (CO ₂)	2367-2353	[8,9,15,16]
ν_{sim} (C=O) ester	1726	[8,9,15,16]
δ O-H, δ_{ass} C-H	1598-1409	[8,9,15,16]
ν (C-O) éster, δ_{sim} C-H	1278-1030	[8,9,15,16]
ν_{sim} (C-C)	881	[8,9,15,16]
Vibrations Ti-O	804-679	[15,16]

The morphology of the powders was investigated by scanning electron microscopy. For the analysis were used two types of detectors: secondary electrons (SE) and backscattered electrons (BSD). Fig. 3 shows the micrographs of the TiO₂ and C/TiO₂ powders.

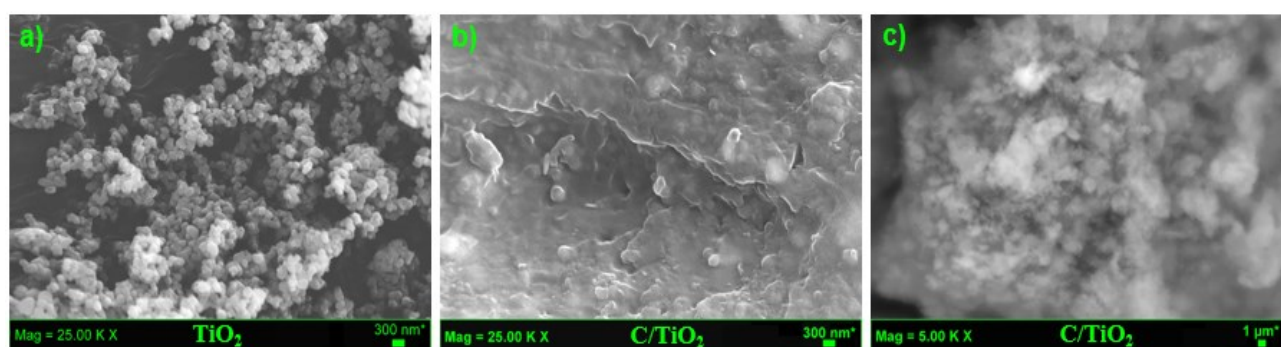


Fig. 3. SEM images: a) TiO₂ using secondary electrons, b) C/TiO₂ using secondary electrons e c) C/TiO₂ using backscattered electrons.

The micrograph of the TiO₂ powder shows agglomerated particles with different sizes and of spheroidal shape. The average particle size for the TiO₂ is at around 196.42 nm. The micrographs obtained for the composites showed the presence of clusters of different sizes and shapes, constituting a matrix with low carbon content organized in the form of overlapping plates. These results are in according to X-ray diffraction data. The average agglomerate sizes for the composite was at around 32.75 μ m.

Photocatalytic activity

The photocatalytic activity for the C/TiO₂ composite was investigated as a function of phenol red dye disappearance under ultraviolet radiation in basic medium (pH = 9). Fig. 4 shows the photodegradation curves of the dye.

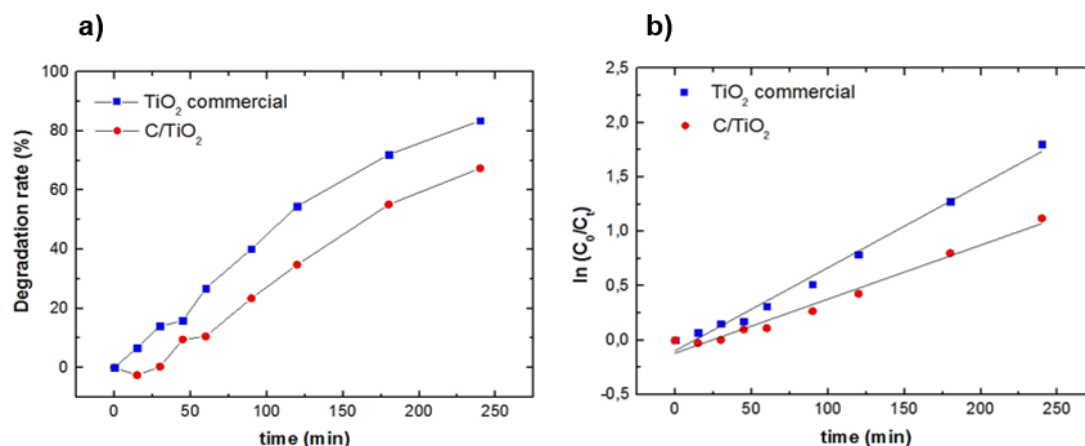


Fig. 4. a) Conversion of phenol red dye on UV-irradiated, b) linear regression $\ln(C_0/C_t)$ as a function of time for the TiO₂ and C/TiO₂ photocatalysts.

In according to Fig. 4 (a) the C/TiO₂ composite showed a lower photocatalytic activity than TiO₂. This fact can be related to a strong interaction between titania particles and amorphous carbon matrix, which creates an intimate interface non-accessible to phenol molecules from the solutions [17,18]. In this sense, as consequence of this common interface between both solids, created during along the homogenization of suspended mixture, some of total number sites of adsorption would be lost. Furthermore, in the experimental conditions used in this work (basic pH) the surface of the oxide is negatively charged. According to the zero point charge of TiO₂ (pH around 7) its surface is presumably positively charged in acidic and negatively in basic medium. When the organic dye as a contaminant contains negatively charged sulfonate groups in the structure, basic solution not favor adsorption of the dye into TiO₂ surface, decreasing degradation efficiency of photocatalytic process [19]. Thus, the pH medium can significantly influence in the photocatalytic process investigated, which can become more efficient in lower pH values.

Fig. 4(b) shows the linear regression $\ln(C_0/C_t)=f(t)$ of the kinetic data from Fig. 4(a). A summary of the kinetic parameters obtained in the phenol red photodegradation on UV-irradiated TiO₂ and C/TiO₂ composite is given in Table 2. The near to unit value of the correlation coefficient (R) showed in Table 2 indicates that phenol red photodegradations with 300 mg.L⁻¹ photocatalysts concentration follow a first order kinetics [8,9,19].

Table 2. Summary of kinetic parameters for the phenol red dye photodegradation.

Catalyst (300 mg.L ⁻¹)	Rate constant k/(min ⁻¹)	Correlation coefficient, R	t _{1/2} (min)
TiO ₂	0.00763	0.98824	90.84
C/TiO ₂	0.00496	0.97459	139.74

Conclusions

A new synthetic route was used to prepare Ti dispersed in an amorphous carbon matrix. After 240 min of irradiation, the degradation rate of the phenol red dye by the amorphous carbon matrix C/TiO₂ composites was at around 70% phenol red conversion being lower than TiO₂, which reached 80% phenol red conversion. From a practical point of view, C/TiO₂ is able to phenol conversion, however, the photocatalytic activity showed be strongly influenced by the pH medium. Degradation of the phenol red dye by the photocatalysts followed a first order kinetic.

Acknowledgments

The authors are grateful to the Brazilian research agencies: FAPESP, CNPq and UNESP/PROPe for financial support.

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