Photocatalytic Activity of TiO_2 on Activated Carbon Under Visible Light in the Photodegradation of Phenol

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Abstract: The photodegradation of phenol under visible light by using TiO_2 and activated carbon prepared by physical activation was performed. Activated carbon was prepared from *Tabebuia Pentaphyla* wood by physical activation under CO_2 flow at 800ºC. UV-Vis lamp with a high proportion of visible light was used. Kinetic results of phenol photodegradation indicated a beneficial effect between TiO_2 and AC. An increase of apparent first-order rate constant (k_{app}) by a factor of 1.74 in presence of TiO_2-AC was obtained in comparison than TiO_2 alone. This cooperative effect between both solids was ascribed to the high surface area and basic surface pH of this type of AC.

Keywords: Heterogeneous photocatalysis, Activated carbon, Phenol, TiO_2.

1. INTRODUCTION

Heterogeneous photocatalysis represent an efficient method of treatment of water and air [1,2]. This technique requires the presence of a semiconductor and up to now TiO_2 has been found as the best photocatalyst. Several attempts have been performed to increase its photocatalytic efficiency and one way to increase this photoactivity consists in adding an inert co-adsorbent as activated carbon (AC). This co-adsorbent has shown a remarkable increase in TiO_2 photoactivity [3-9] in the photodegradation of phenol, halo-phenols and acid herbicides. In these works, a synergistic effect between both solids in the photomineralization of these organic molecules has been reported. The physico-chemical properties of AC represent an aspect important in the photocatalytic reaction. For example, surface area of AC has an important role because it is involved in the creation of a common contact interface between both solids [3,4]. In addition, surface pH defined by the point zero charge of carbon (pH_{PZC}) seems to be the more important role because it remarkably affects photoactivity [5,6,9]. Recently, it has shown that surface functionalization of AC play an important function on TiO_2 photoactivity on phenol and 4-chlorophenol degradations [5,6]. For example, the use of specific L-type activated carbons (prepared by chemical activation) generate a synergy effect which could be attributed not only to a proper surface area but also to the presence of low surface concentration of acidic oxygenated groups in solution are dissociated to produce surface anions able to drive out electron density from aromatic system to TiO_2 [6,8]. For the case of TiO_2 in the presence of H-type activated carbons (prepared by physical activation), a beneficial effect on TiO_2 photoactivity has been attributed to the presence of an intimated contact interface spontaneously created between both solids that promotes a very well dispersed layer of TiO_2 nanoparticles [5]. Furthermore, authors have proposed that this type of activated carbons play the role of electron carrier that could inhibit the recombination of photoelectrons to improve the photoactivity of TiO_2 [5,8]. In order to verify this, the main objective of this work is to study the photodegradation of phenol by using TiO_2 and a specific H-type AC.

2. EXPERIMENTAL METHODS

Photocatalyst was TiO_2 P25 (Degussa). Activated carbon (AC) was prepared from sawdust of Tabebuia Pentaphyla wood by physical activation [5] under CO_2 flow at 800ºC and sample was denoted as $AC_{CO2\text{-}800}$. Samples were characterized by BET surface area (S_{BET}), Infrared (IR), surface pH (pH_{PZC}), and X-ray diffraction (XRD). Photocatalytic tests were performed at 25ºC with 200mg TiO_2 and 40mg AC under stirring in 200mL of 40ppm initial concentration of phenol. Samples were maintained in the dark for 60min to complete adsorption at equilibrium prior UV-irradiation and then the suspension was irradiated. After centrifugation aliquots were analyzed by UV-spectrophotometer Perkin Elmer, Lambda. UV-Vis lamp of Metal Halide was used for the photocatalytic tests. From $522.7W.m^{-2}$ of total radiation of this lamp, $70.2W.m^{-2}$ corresponds to UV radiation and about $452.5W.m^{-2}$ to the visible radiation. The total radiation flux was about $1.44x10^{17}photons.cm^{-2}.s^{-1}$.

3. RESULTS AND DISCUSSION

3.1. Characterization of Solids

Results of texture and surface pH of the solids are compiled in Table **1**. $AC_{CO2\text{-}800}$ presented a high surface area and a basic pH_{PZC} which suggest the presence of basic oxygenated functional groups on the surface of carbon. For the case of TiO_2-$AC_{CO2\text{-}800}$, the surface area BET clearly decreases one order magnitude with respect to $AC_{CO2\text{-}800}$. This fact can be attributed to a strong interaction between both the solids in agreement with previous works [3-7]. This inference can be verified by means of FTIR analysis is shown in Fig. (**1**), which shows the FTIR spectra of TiO_2

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with a peak located at about 3200–3600cm^{-1} which is associated at stretching vibration of the OH groups. In addition, it observed a broad peak identified to bulk Titania framework in the region from 400 to 800 cm^{-1} [10]. It is also important to remark that the TiO_2-AC system shows a broadening in this bulk titania framework region in presence of $AC_{CO2\text{-}800}$ and this behavior was also observed in a previous work [7]. In concordance, the corresponding signal to stretching vibration of peaks attributed to cyclic ethers and quinone in the activated carbon, located at 1100–1400cm^{-1} and 1610-1580cm^{-1}, respectively [11], clearly decreased. These changes in FTIR have been associated with a strong surface interaction between both solids consequence of ether groups coordination from carbon to the metallic centre in TiO_2 [5, 7]. XRD pattern of Fig. (**2**) shows no changes in the corresponding X-ray diffraction patterns for the case of TiO_2-AC in comparison than that obtained for TiO_2 alone. The only change detected in the XRD pattern of mixed system was a remarkable decrease in the main peaks of Anatase phase attributed to a dilution effect by means of the presence of AC. In other words in spite of surface oxygenated functional groups on AC are able to coordinate to Ti^{+4} in the semiconductor, this interaction was unable to change the crystalline phase that compose the P25 TiO_2.

Table 1. BET Surface Areas (S_{BET}) and Surface pH (pH_{PZC}) of the Solids Studied

System	S_{BET} ($m^2.g^{-1}$)	pH_{PZC}
TiO_2	45.2 ± 0.2	6.5
$AC_{CO2\text{-}800}$	943 ± 1	8.5
TiO_2-$AC_{CO2\text{-}800}$	86.5 ± 0.5	6.7

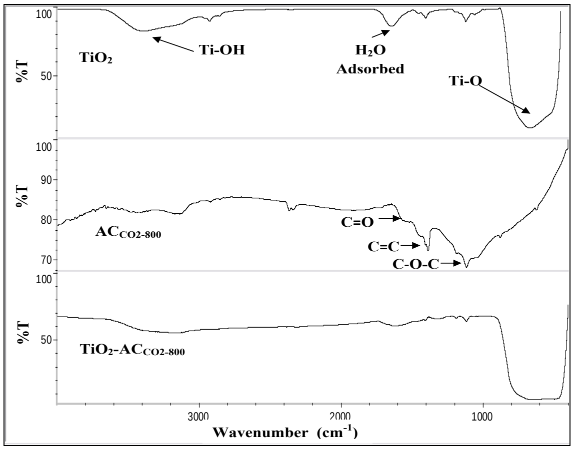

Fig. (1). FTIR spectra of the solids.

3.2. Kinetics of Phenol Adsorption in the Dark and Photodegradation

Fig. (**3**) shows the kinetics of adsorption in the dark of phenol followed by 120min under stirring. In all cases, adsorption occurred within 30min but to ensure the equilibrium of adsorption, a period of 60 min of adsorption in the dark was selected for the photodegradation experiments. The results in Fig. (**3**) indicated that there are no additive effects in the adsorption capacities of both solids after they are mixed. This difference was ascribed to a strong interaction between TiO_2 particles and AC, which creates an intimate interface between both solids according to reported in previous works [3-9]. Kinetics of photocatalytic disappearance of phenol is presented in Fig. (**4A**). It can be observed that the direct photolysis without solids can be neglected, because it only shows about 5% conversion. A second point to be considered corresponds to the fact that in the presence of TiO_2-AC system, the photodegradation of phenol was obtained in shorter reaction time than that required on TiO_2 alone. Assuming a first-order reaction rate, Fig. (**4B**) shows the linear transformation from the kinetic data of Fig. (**4B**). These regressions were employed to estimate the apparent rate constant of first-order (k_{app}). These values are shown in the Table **2**. It can be seen that k_{app} obtained on TiO_2-AC is clearly higher than that obtained on TiO_2 alone. Therefore, it can be considered, by means of the interaction factor (I_F) estimated from the comparison between the apparent rate constant of first-order ($k_{app\text{-}TiO2\text{-}AC}$)/($k_{app\text{-}TiO2}$) the presence of a synergetic effects between both solids. The results indicated that the combination of TiO_2-AC creates a kinetic synergy effect in phenol disappearance with an increase of in the rate constant by a factor of 1.75. This enhancement in the photoactivity of TiO_2 under visible light can be due to the textural properties and the surface chemistry of an H-type AC with a high surface area and basic pH_{PZC} in concordance with the presence of basic functional groups, as cyclic ethers and quinones detected in the FTIR spectra shown in Fig. (**1**). This AC can play the role of an electron carrier that could inhibit the recombination of photoelectrons to improve the photoactivity of TiO_2 which has been reported previously [5,8].

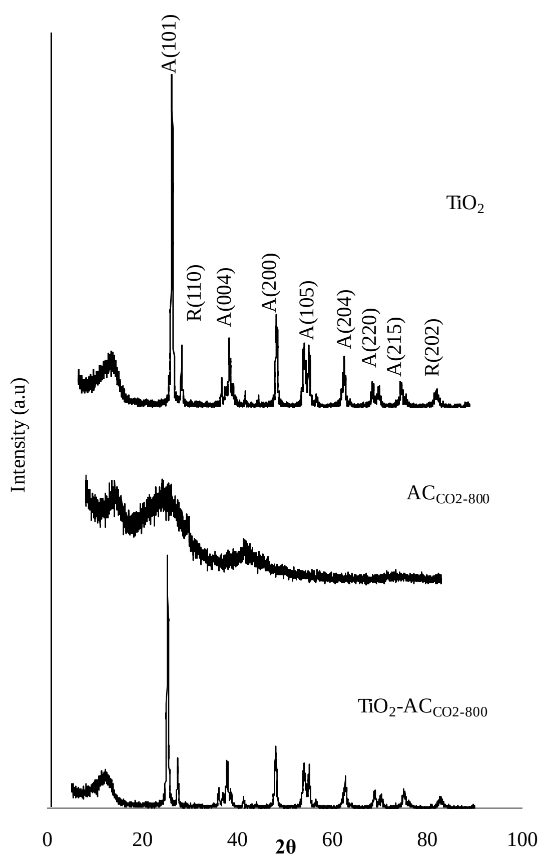

Fig. (2). XRD of TiO_2, $AC_{CO2\ 800}$ and TiO_2- $AC_{CO2\ 800}$.

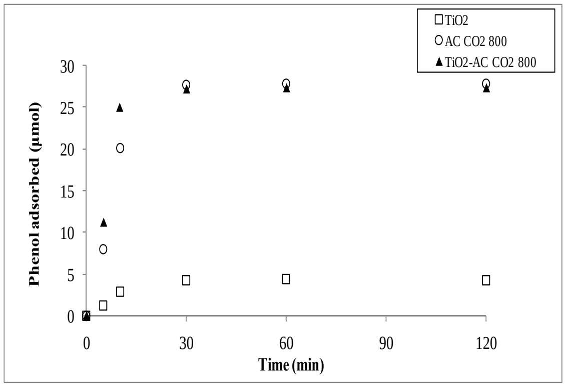

Fig. (3). Kinetics of phenol adsorption in the dark.

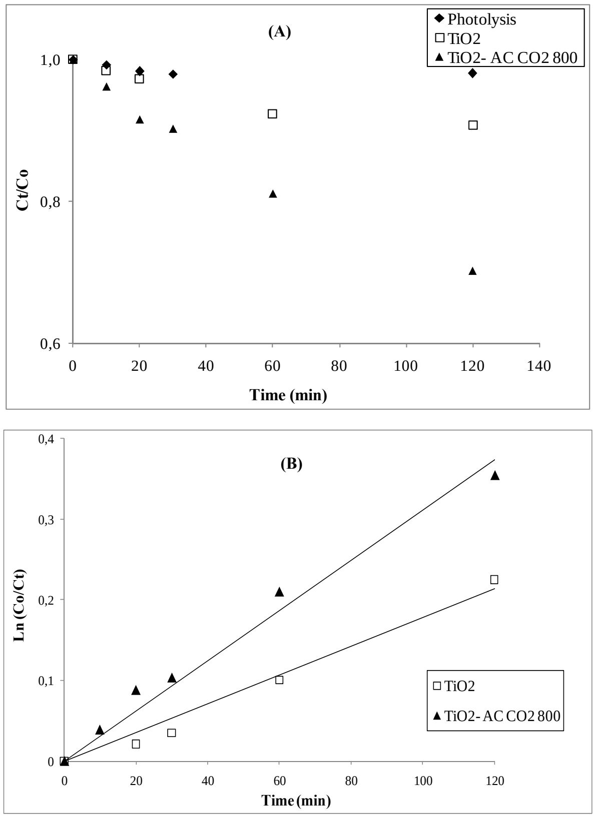

Fig. (4). (**A**) Kinetics of disappearance of Phenol. (**B**) Linear regression from kinetic data of Fig. (**4A**).

4. CONCLUSION

Results suggest that under visible light the combination TiO_2-AC creates a kinetic synergy effect in phenol disappearance with an increase in the rate constant by a factor of 1.75. This beneficial effect has been attributed to the specific properties of the AC that can induce the formation of a contact interface between both solids, where the AC could act as electron carrier and can drive out electrons from the TiO_2 surface and avoid the recombination of photoelectrons.

Table 2. Apparent First-Order Rate Constants (k_{app}) and Interaction Factor (I_F) Detected in the Photodegradation of Phenol

Photocatalysts	$k_{app}x10^{-3}$ (min^{-1})	R^2	I_F[a]
TiO_2	1.78	0.9794	1.00
TiO_2-AC_{800}	3.11	0.9776	1.75

[a] Interaction factor = ($k_{app-TiO2-AC}$)/($k_{app-TiO2}$).

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