

Hybrid TiO₂-C composites for the photodegradation of methylene blue under visible light

Compositos híbridos TiO₂-C para la fotodegradación de azul de metileno bajo luz visible

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Abstract

Photodegradation of methylene blue (MB) on TiO₂ in presence of activated carbons (AC) was studied. Two different lamps were employed and results were compared against those obtained on a commercial TiO₂. Apparent first order rate constant for the degradation of MB was higher in presence of any AC in comparison of TiO₂ alone but much higher under visible light irradiation. It can be concluded that TiO₂ enhances its photoactivity by a factor up to 8.7 in the degradation of MB in presence of AC and this increase was associated with the surface properties of AC.

Resumen

En este trabajo se muestra la fotodegradación de azul de metileno (MB) sobre TiO₂ en presencia de carbón activados (AC). Se emplearon dos tipos diferentes de lámparas y los resultados se compararon contra los obtenidos sobre TiO₂ comercial. La constante aparente de velocidad de primer orden para la degradación de MB fue mayor en presencia de AC en comparación a la obtenida sobre el TiO₂ solo y mucho mayor bajo irradiación con luz visible. Se puede concluir que el TiO₂ aumenta su fotoactividad en un factor de hasta 8.7 veces mayor en la degradación de MB en presencia de AC. Este aumento fue asociado con las propiedades superficiales de cada AC.

1. Introduction

An important quantity of the total world production of azo-dyes is released in textile effluents [1]. Different technologies for the removal of dyes are adsorption, bio- and chemical degradation methods including advanced oxidation technologies as heterogeneous photocatalysis. Since heterogeneous photocatalysis with TiO₂ emerged as an efficient method for purifying water and air [2,3] several attempts such as ion doping or metal depositions have been used [4] to increase its photoefficiency. Another way to possibly increase the photoefficiency of TiO₂ consists of adding an inert co-adsorbent such as activated carbon (AC) [5,6]. A synergy effect between both solids has been observed in the photocatalytic degradation of model pollutants [7,8]. This has been ascribed to a contact interface that promotes an appropriated diffusion of pollutants from AC to photoactive titania and introduce changes in the semiconductor properties [5-8]. Photocatalysis and adsorption with activated carbon (AC) have received an increase attention for the degradation of different dyes [9-11] and halo phenol molecules [7] where recently, we have showed that surface functionalization of AC play an important role on TiO₂ photoactivity on 4-chlorophenol degradations [7]. The objective of this work is to study the photodegradation of methylene blue (MB) as a model dye on UV- and visible light irradiated TiO₂ in presence of activated carbons with different texture and surface functionalities.

2. Experimental

Methylene blue (MB) was analytical grade and purchased from Aldrich. For comparative purpose, photocatalyst was TiO₂ P25 (Degussa). H-type AC were prepared by physical activation of a soft wood under CO₂ flow at 800°C (AC_{CO2-800}) or by pyrolysis under N₂ flow at 1000°C (AC_{N2-1000}) while L-type AC were prepared by impregnation with 5% (w/w) of ZnCl₂ (AC_{ZnCl2-5%}) and H₃PO₄ (AC_{H3PO4-5%}) following activation under N₂ flow at 450°C. Samples were characterized by adsorption-desorption N₂ isotherms, infrared spectroscopy (FTIR) and surface pH (pH_{PZC}). The experimental set-up [11] consists in an open to air batch photoreactor of 200mL made of Pyrex. Irradiation was provided with two different lamps [11] with different UV proportions. One a Hg lamp (82.9 W.m⁻² UV and 362.6 W.m⁻² visible light) and metal halide (MH) lamp (70.2 W.m⁻² UV and 452.5 W.m⁻² visible). Photocatalytic tests were performed at 25°C with 62.5mg TiO₂ and 6.2mg AC under stirring in 125mL of MB, 25ppm (78.2μmol.L⁻¹) initial concentration or in 125mL of phenol, 50ppm (0.5x10⁻³mol.L⁻¹) initial concentration. Samples were maintained in the dark by 60min to complete adsorption at equilibrium before irradiation. After centrifugation of MB aliquots at some selected reaction times, samples were analyzed by UV spectrophotometer at 664 nm.

3. Results and discussion

Table 1 shows textural properties and pH_{PZC} of photocatalysts. AC developed high surface areas BET (S_{BET}) and the main pore width in the microporous range. For the hybrid TiO₂-AC, S_{BET} decreases one order magnitude with respect to AC. This is attributed to a strong interaction between both solids [12]. Table 1 shows H-type AC have basic pH_{PZC} while L-type AC have acid pH_{PZC} suggesting the presence of basic and acid oxygenated functional groups on the surface of H- and L-type AC, respectively as can be verified from FTIR spectra in Fig 1. It can be seen that functional surface groups principally are basic as cyclic ethers (-C-O-C-) and quinones (C=O) [7,13]. For the case L-type AC, these showed acid pH_{PZC} and by FTIR can be observed that the main functional surface group was carboxylic acid (C=O).

Table 1. BET surface area (S_{BET}), mean pore diameter (D) and surface pH (pH_{PZC}).

Tabla 1. Área superficial BET (S_{BET}), diámetro promedio de poro (D) y pH superficial (pH_{PZC}).

Sample	S _{BET} (m ² .g ⁻¹)	D (Å)	pH _{PZC}
TiO ₂ P25	45.2 ± 0.2	577.86	6.5
AC _{CO2-800}	943 ± 3	6.29	8.5
TiO ₂ -AC _{CO2-800}	86.5 ± 0.5	974.01	6.7
AC _{N2-1000}	644 ± 1	5.90	8.9
TiO ₂ -AC _{N2 1000}	60.4 ± 0.4	1051.78	6.7
AC _{ZnCl2-5%}	689 ± 2	5.89	6.0
TiO ₂ -AC _{ZnCl2-5%}	92.5 ± 0.5	979.03	6.4
AC _{H3PO4-5%}	247 ± 1	5.94	4.0
TiO ₂ -H ₃ PO ₄ -5%	63.4 ± 0.4	1034.43	6.3

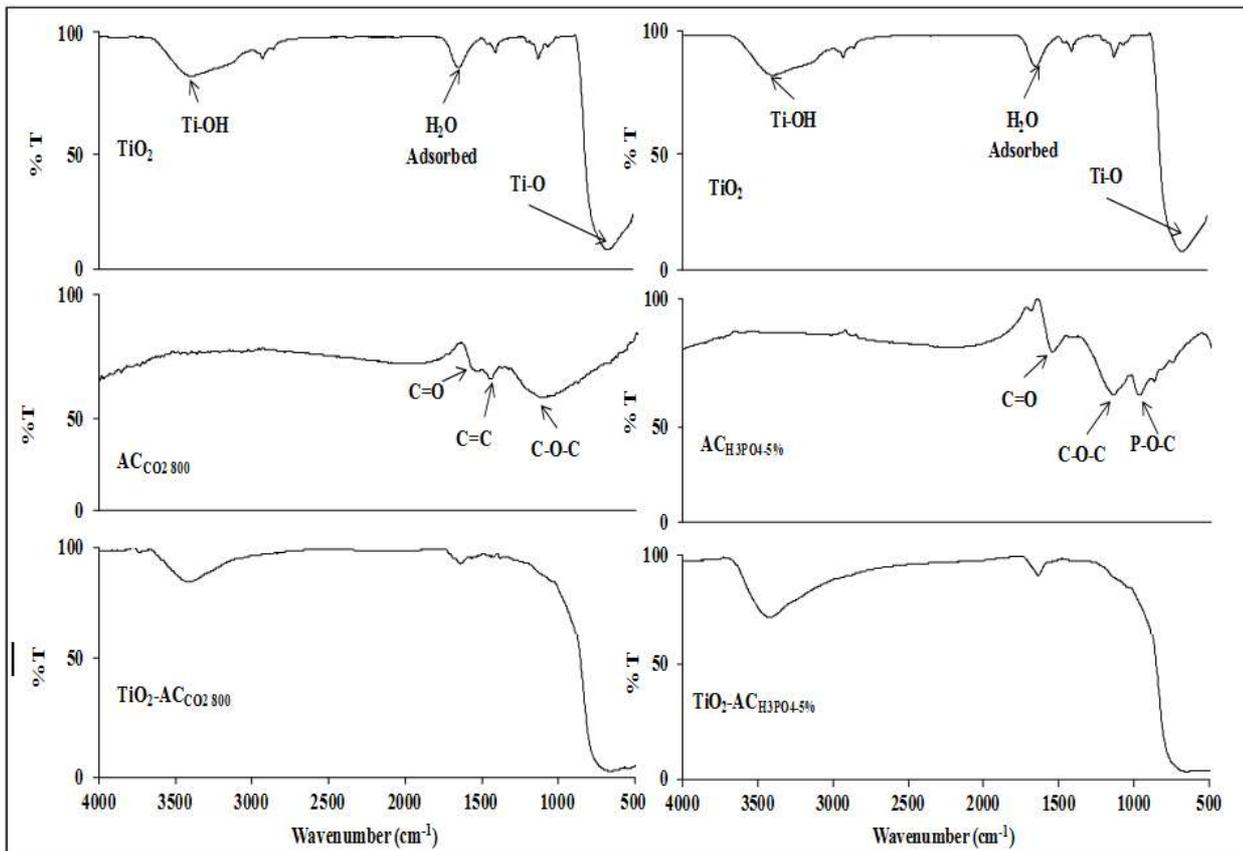


Figure 1. FTIR spectra of TiO_2 , ACCO2-800, ACH3PO4-5%, TiO_2 -ACCO2-800, and TiO_2 -ACH3PO4-5%
Figura 1. Espectro FTIR de TiO_2 , ACCO2-800, ACH3PO4-5%, TiO_2 -ACCO2-800, y TiO_2 -ACH3PO4-5%

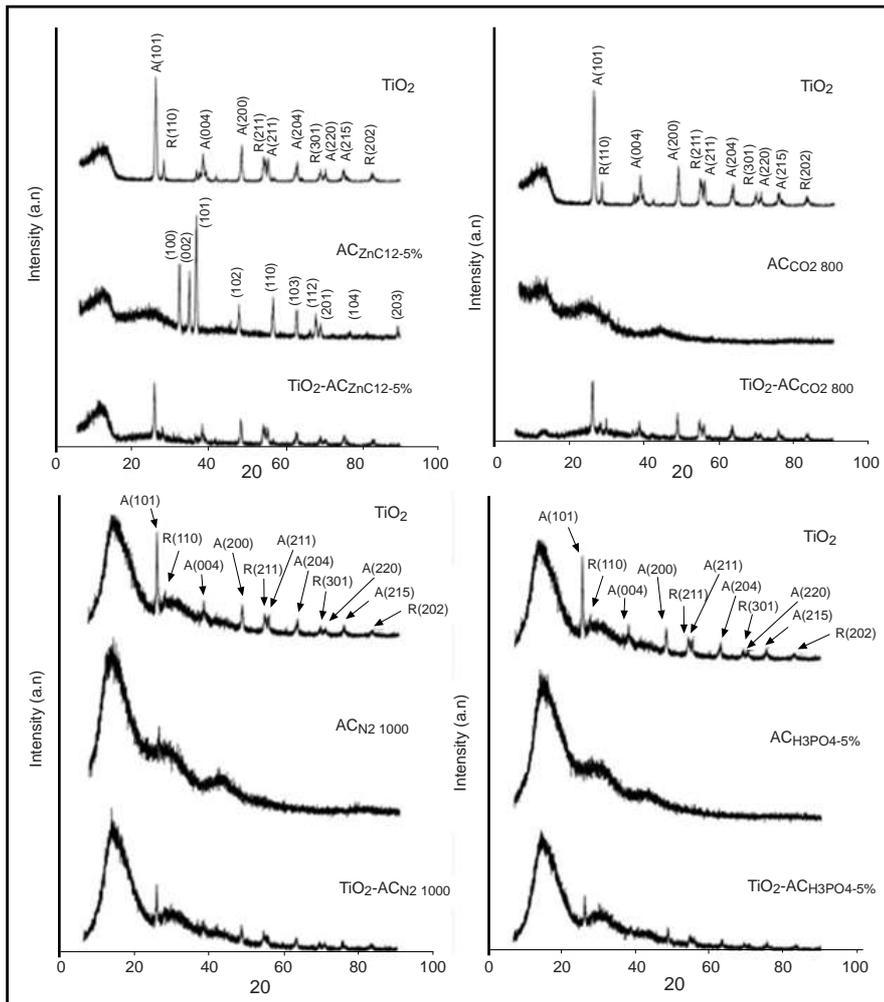


Figure 2. XRD patterns of TiO_2 , AC and binary materials TiO_2 -AC
Figura 2. Patrones de XRD de TiO_2 , AC y los híbridos TiO_2 -AC.

Furthermore, cyclic ethers were also detected (-C-O-C-). Finally, it should be remarked the presence of phosphates in $\text{AC}_{\text{H}_3\text{PO}_4}$ [7,8]. Fig. 1 shows that TiO_2 presented a broader peak in the region of bulk Titania in presence of AC. Also, the corresponding peaks in the AC clearly decreased in the binary materials probably by the coordination from carbon to the metallic centre in TiO_2 [7]. A similar behavior in the FTIR spectra for the other AC and the binary materials was found [7]. Fig. 2 shows the XRD patterns of TiO_2 , AC and the binary materials TiO_2 -AC. It can be seen that no changes in the corresponding XRD 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 the binary materials was a remarkable decrease in the main peaks attributed to a dilution effect by means of AC.

Fig. 3 shows the kinetics of adsorption in the dark of MB on AC and TiO_2 -AC. Adsorption occurred within 30min but to ensure the equilibrium of adsorption, 60 min of adsorption in the dark was selected prior to the photodegradation experiments. The results indicated that there are no additive effects in the adsorption capacities of both solids after they are mixed. It can be ascribed to a strong interaction between TiO_2 particles and AC [7]. Kinetics of photocatalytic disappearance of MB in presence of TiO_2 -AC under each lamp was performed. Fig. 4 shows an example of the kinetic of MB photodegradation under UV irradiated TiO_2 , TiO_2 - $\text{AC}_{\text{CO}_2-800}$, and TiO_2 - $\text{AC}_{\text{N}_2-1000}$ samples. Assuming a first-order reaction rate [7], linear transformations (figure inset Fig. 4) from the kinetic data were performed to estimate the apparent first-order rate constant (k_{app}).

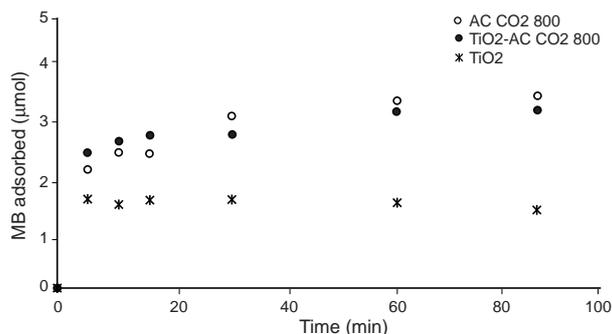


Figure 3. MB adsorbed in the dark on selected solids. **Figura 3.** MB adsorbido en la oscuridad sobre sólidos seleccionados.

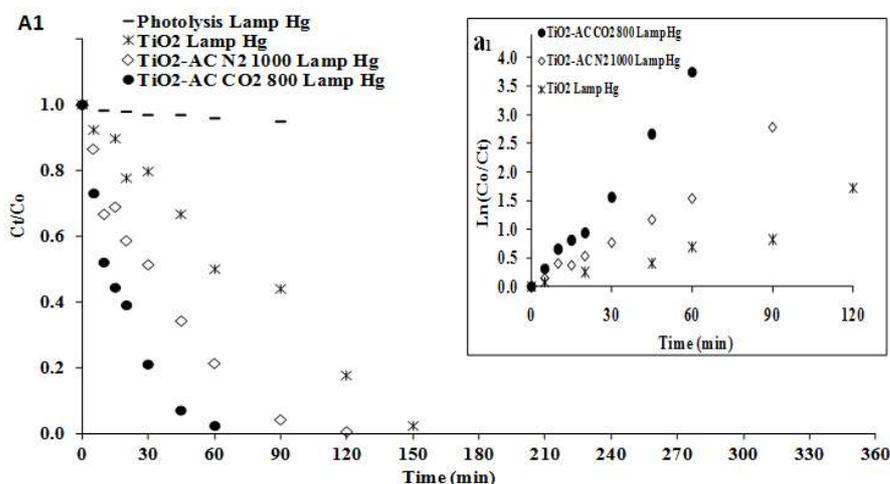


Figure 4. Kinetic of disappearance of MB on TiO_2 -AC under Hg Lamp (A1) and linear regression of kinetic data (a1). **Figura 4.** Cinética de desaparición de MB sobre TiO_2 -AC bajo la lampra de Hg (A1) y regresión lineal de los datos cinéticos (a1).

Table 2. Summary of kinetics parameters obtained in the photodegradation of MB.

Tabla 2. Resumen de parámetros cinéticos obtenidos en la fotodegradación de MB.

Sample	Ads ^a (%)	$k_{\text{app-UV}} \times 10^{-3}$ (min ⁻¹)	$I_{\text{F-UV}}^b$	$\phi_{\text{rel-UV}}^c$	$k_{\text{app-Vis}} \times 10^{-3}$ (min ⁻¹)	$I_{\text{F-Vis}}^b$	$\phi_{\text{rel-Vis}}^c$
TiO_2 P25	25	12.10	1.0	1.0	4.60	1.0	1.0
$\text{AC}_{\text{CO}_2-800}$	33	4.04	---	0.3	2.59	---	0.6
TiO_2 - $\text{AC}_{\text{CO}_2-800}$	31	59.12	3.7	4.9	39.89	5.5	8.7
$\text{AC}_{\text{N}_2-1000}$	23	3.33	---	0.3	2.24	---	0.5
TiO_2 - $\text{AC}_{\text{N}_2-1000}$	28	34.48	2.2	2.8	27.80	4.1	6.0
$\text{AC}_{\text{ZnCl}_2-5\%}$	27	1.10	---	0.1	2.54	---	0.6
TiO_2 - $\text{AC}_{\text{ZnCl}_2-5\%}$	26	28.85	2.2	2.4	14.63	2.0	3.2
$\text{AC}_{\text{H}_3\text{PO}_4-5\%}$	14	0.71	---	0.1	1.01	---	0.2
TiO_2 - $\text{H}_3\text{PO}_4-5\%$	23	39.41	3.1	3.3	13.39	2.4	2.9

^aAfter 60min of adsorption in the dark. ^b Synergy defined as $I_{\text{F}} = k_{\text{app-i}} / (k_{\text{app-TiO}_2} + k_{\text{app-AC}})$. ^c Relative photoactivity defined as $\phi_{\text{rel}} = (k_{\text{app-i}} / k_{\text{app-TiO}_2})$.

Table 2 contains a summary of the kinetic results of MB photodegradation. The apparent first-order rate constant permits to compare the photoactivity relative to TiO_2 defined as $\phi_{\text{rel}} = (k_{\text{app-i}} / k_{\text{app-TiO}_2})$ and the synergistic effect between TiO_2 and AC materials defined by: $I_{\text{F}} = [k_{\text{app-i}} / (k_{\text{app-TiO}_2} + k_{\text{app-AC}})]$. It can be seen from k_{app} values in Table 2 that binary materials TiO_2 -AC have higher photoactivity than that obtained on TiO_2 alone and this enhancement in the photoactivity was clearly higher with the MH lamp which has higher proportion of visible light with respect to the Hg lamp with an enhancement in the photoactivity up to 8.7 and 6.0 times higher than TiO_2 on TiO_2 - $\text{AC}_{\text{CO}_2-800}$ and TiO_2 - $\text{AC}_{\text{N}_2-1000}$. Both $\text{AC}_{\text{CO}_2-800}$ and $\text{AC}_{\text{N}_2-1000}$ can be classified as H-type [5] AC because its surface oxygenated functional groups are basic in nature as suggest FTIR spectra (Fig. 1) and basic pH_{PZC} in Table 1. In addition, it should be pointed out that the photocatalytic activity of AC is lower than that of TiO_2 alone, however, a clear synergistic effect between both solids was estimated (Table 2) being much higher under visible light irradiation. On the other hand, Table 2 shows that photoactivity of the binary materials TiO_2 - $\text{AC}_{\text{ZnCl}_2-5\%}$ and TiO_2 - $\text{AC}_{\text{H}_3\text{PO}_4-5\%}$ were only about 3 times higher than that on TiO_2 alone in any of cases of lamps studied. This fact has been attributed to a more acidic surface pH and to a lower surface area of these L-type AC (Table 2) [6,8].

In previous works [5,7] we have showed that oxygenated functional groups in the surface of AC play a double role in photocatalytic reactions. First, these AC can play the role of electron carriers that

could inhibit the recombination of photoelectrons to improve the photoactivity of TiO_2 and secondly, under visible light irradiation several functional groups on carbon's surface are able to excited electrons from π to π^* orbital to then be injected into the conduction band of TiO_2 [11]. This phenomena has been described by our group as a photo-assisting process [12,14]. In addition, our group has been previously reported for the case of the 4-chlorophenol photodegradation [5,7] that AC_{CO_2} has a stronger interaction than AC_{N_2} with Ti atoms in TiO_2 . We have shown that this interaction occurs by means of a common contact interface [7,15] spontaneously created during reaction between both solids by the coordination the oxygenated functional groups on AC_{CO_2} , mainly cyclic ethers and carboxylate anions (Fig. 1). This interaction is lower between TiO_2 with AC_{N_2} than with AC_{CO_2} because AC_{N_2} has lower oxygen composition, about 7% against 12wt%.

4. Conclusions

Hybrid TiO_2 -C materials showed a clear increase in the photocatalytic activity of MB photodegradation with respect to TiO_2 alone under the two lamps studied. This beneficial effect has been attributed to the properties of H-type AC (high surface area and basic pH_{PZC}). In general, a model dye-molecule such as methylene blue can be photodegraded in shorter reaction times by using hybrid TiO_2 -C composites than on irradiated neat TiO_2 .

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6. References

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