

## Influence of Activated Carbon in the Photodegradation of Methylene Blue

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### Abstract

Photodegradation of methylene blue (MB) on TiO<sub>2</sub> in presence of activated carbons (AC) was studied. Apparent first order rate constant for the degradation of MB was higher in presence of any AC indicating that the binary materials TiO<sub>2</sub>-AC showed a clear enhancement in the photocatalytic activity relative to TiO<sub>2</sub> and this enhancement was associated with the properties of AC.

### Introduction

An important quantity of the total world production of azo-dyes is released in textile effluents with concomitant environmental hazards [1]. Different technologies for the removal of dyes are adsorption, bio- and chemical degradation methods including advanced oxidation technologies as heterogeneous photocatalysis [1]. Photocatalysis and adsorption with activated carbon (AC) have received an increase attention for the degradation of different organic molecules [2-4] and azo-dyes [5-7]. Recently, it was observed that surface functionalization of activated carbon (AC) play an important role on TiO<sub>2</sub> photoactivity on phenol and 4-chlorophenol degradations [5-7]. Furthermore, in system TiO<sub>2</sub>-AC was showed a slight modification in the band-gap energies of TiO<sub>2</sub> by adding AC, favoring the absorption of light in the visible region [8]. On the other hand, the photodegradation of the azo-dye methylene blue has been studied in presence of carbon/TiO<sub>2</sub> composite material, which exhibited a strong photoactivity in the visible range presumably due to a direct optical charge transfer transition involving both the TiO<sub>2</sub> and carbon phase [9]. Moreover, hybrid materials prepared by carbothermal synthesis were combined with TiO<sub>2</sub> to photodegradation of methylene blue finding also a high photoactivity in the light visible range [10].

Having this in mind, the objective of this work is to study the photodegradation of methylene blue (MB) as a model azo-dye on TiO<sub>2</sub> in presence of activated carbon (AC) prepared by different methods.

### Experimental

Reference photocatalyst was the commercial TiO<sub>2</sub> P25 (Degussa). Four activated carbons were prepared from sawdust of Apamate wood (*Tabebuia Pentaphyla*) by different methods. Physical activation under CO<sub>2</sub> flow at 800°C and by pyrolysis under N<sub>2</sub> flow at 1000°C and these AC were denoted AC<sub>CO2-800</sub> and AC<sub>N2-1000</sub>, respectively. Then, AC were prepared by chemical activation after impregnation with 5% (w/w) of ZnCl<sub>2</sub> or with 5% (w/w) H<sub>3</sub>PO<sub>4</sub> following activation under N<sub>2</sub> flow at 450°C and denoted AC<sub>ZnCl2-5%</sub> and AC<sub>H3PO4-5%</sub>, respectively. AC and binary materials TiO<sub>2</sub>-AC were characterized by N<sub>2</sub> adsorption, X-ray diffraction (XRD), surface pH (pH<sub>PZC</sub>) and Infrared (FTIR). The experimental set-up consists in an open to air batch photoreactor of 200 mL made of Pyrex. Irradiation was provided by an Hg lamp (photo flux, 82.9 W·m<sup>-2</sup> UV, 362.6 W·m<sup>-2</sup> visible light). Photocatalytic tests were performed at 25°C with 62.5 mg TiO<sub>2</sub> and 6.2 mg AC under stirring in 125 mL of MB, 25 ppm (78.2 μmol·L<sup>-1</sup>) initial concentration. Samples were maintained in the dark by 60 min to complete adsorption at equilibrium.

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After centrifugation MB aliquots were analyzed by UV-spectrophotometer at 664 nm. Results were compared against those obtained with TiO<sub>2</sub> P25 alone.

## Results and Discussion

Texture and surface pH of the solids was studied. As H-type AC as L-type AC presented high surface areas BET ( $S_{BET}$ ) and a size of pores in the microporous range. For the case of mixed system TiO<sub>2</sub>-AC,  $S_{BET}$  decreases one order magnitude with respect to activated carbon. This fact can be attributed to a strong interaction between both solids in agreement with previous works [2-4]. H-Type AC presented basic  $pH_{PZC}$  which suggest the presence of basic oxygenated functional groups on the surface of carbon. This inference is verified from the FTIR analysis. In agreement with previous works [2, 11], Fig 1 shows

that functional groups are mainly basic such as cyclic ethers ( $-C-O-C-$ ) and quinones ( $C=O$ ) for the case of ac activated carbon prepared by physical activation such as AC<sub>CO<sub>2</sub>-800</sub> while for the case of AC prepared by chemical activation such as AC<sub>H<sub>3</sub>PO<sub>4</sub>-5%</sub> besides cyclic ethers group it can be observed from Fig. 1 that the main functional surface group in this AC was carboxylic acid ( $C=O$ ) in agreement with previous works [4, 11]. Finally, it should be remarked the fundamental stretching peak corresponding to phosphates in AC<sub>H<sub>3</sub>PO<sub>4</sub></sub> [4]. These trends were the same for the case of AC<sub>N<sub>2</sub>-1000</sub> [2] and AC<sub>ZnCl<sub>2</sub>-5%</sub> [4]. Fig 1 also shows that in presence of AC the TiO<sub>2</sub>-AC binary materials presented a broadening in the bulk framework corresponding to the Ti-O-Ti. We have associated this fact to the coordination of some functional carbon groups to the metallic centre in TiO<sub>2</sub> [2-4].

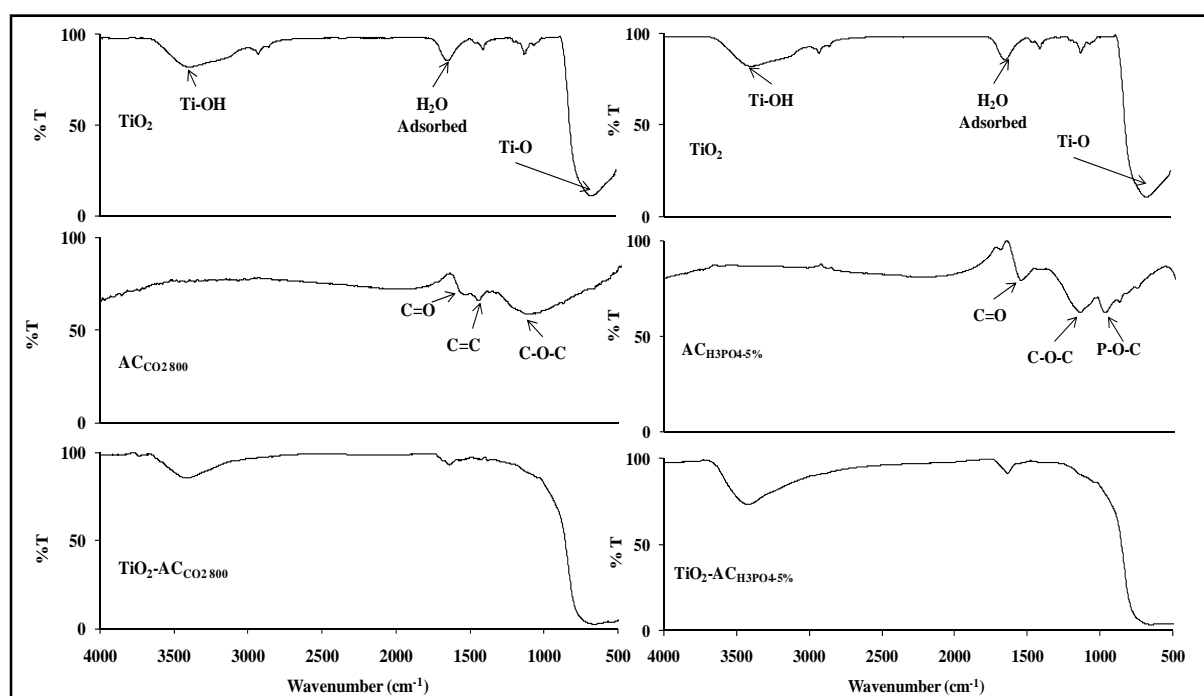


Fig. 1. FTIR spectra of some selected solids.

From the studies of the kinetics of adsorption in the dark of MB on TiO<sub>2</sub>, AC and TiO<sub>2</sub>-AC, we have found in all the samples that most of adsorption occurred within 30min but to ensure a proper equilibrium of adsorption, a period of 60 min was selected before the photodegradation experiments. Table 1 contains a summary of these values. 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<sub>2</sub> particles and AC, according to reported in previous works [2-4]. Kinetics of photocatalytic disappearance of MB in presence of TiO<sub>2</sub>-AC was performed. An example is showed in Fig. 2. Assuming a first-order reaction rate, linear transformations from the kinetic data of these figures permitted estimate as the apparent rate constant of first-order ( $k_{app}$ ) as photocatalytic

activity relative to  $\text{TiO}_2$  P25 alone ( $\varphi_{\text{rel}}$ ) defined as  $k_{\text{app-i}}/k_{\text{app-TiO}_2}$  (see Table 1). It can be seen that  $k_{\text{app}}$  obtained on all binary materials  $\text{TiO}_2$ -AC were clearly higher than that obtained on  $\text{TiO}_2$  alone. This enhancement in the photoactivity of  $\text{TiO}_2$  cannot be subscribed to the textural properties because adsorption in the dark was practically similar in all the cases. Therefore, the present results suggest that surface chemistry of AC plays the most important role. For example, AC can play the role of electron carriers that could inhibit the recombination of photoelectrons to improve the photoactivity of  $\text{TiO}_2$  which has been reported previously [2, 12]. Table 1 shows that  $\text{TiO}_2$ - $\text{AC}_{\text{H}_3\text{PO}_4-5\%}$ , presented a higher  $k_{\text{app}}$  with respect to  $\text{TiO}_2$ - $\text{AC}_{\text{N}_2 1000}$ .  $\text{AC}_{\text{H}_3\text{PO}_4-5\%}$  is the activated carbon

more acidic and lower surface area of the AC studied; however, some authors have reported that  $\text{TiO}_2$ -doped with P, leads to the formation of bond Ti-O-P [13], which could generate a widening in the energy separation of bands, favoring the absorption of light in the UV range and improving the photocatalytic activity under this type of light [14]. Finally, it is important to remark that the present AC showed a small but clear photoactivity in absence of  $\text{TiO}_2$  (Table 1), indicating the presence of a synergy effect between both solids because  $k_{\text{app}}$  are higher than the sum of the particular  $k_{\text{app}}$  of the solids separately. Our present enforces are aimed to understand the role of the  $\text{pH}_{\text{PZC}}$  and optoelectronic properties of different activated carbons.

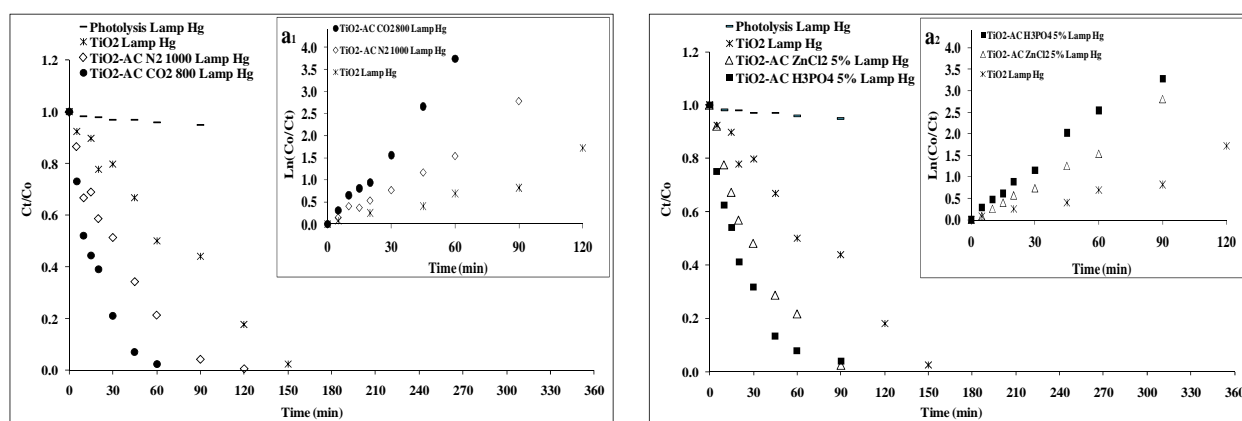


Fig. 2. Kinetic of disappearance of MB in presence of  $\text{TiO}_2$ -AC and lineal regression of kinetic data (inset figure).

**Table 1**

Summary of textural properties, surface pH ( $\text{pH}_{\text{PZC}}$ ) and kinetics parameters obtained in the photodegradation of Methylene Blue

Sample	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	Pore size ( $\text{\AA}$ )	$\text{pH}_{\text{PZC}}$	Ads <sup>a</sup> (%)	$k_{\text{app}} \times 10^{-3}$ ( $\text{min}^{-1}$ )	$I_{\text{F}}^{\text{b}}$	$\varphi_{\text{rel}}^{\text{c}}$
$\text{TiO}_2$ P25	45.17±0.16	577.86	6.5	25	12.10	1.0	1.0
$\text{AC}_{\text{CO}_2-800}$	942.86±1.41	6.29	8.5	33	4.04	---	0.3
$\text{TiO}_2 - \text{AC}_{\text{CO}_2-800}$	86.46±0.48	974.01	6.7	31	59.12	3.7	4.9
$\text{AC}_{\text{N}_2-1000}$	644.27±0.62	5.90	8.9	23	3.33	---	0.3
$\text{TiO}_2 - \text{AC}_{\text{N}_2 1000}$	60.40±0.39	1051.78	6.7	28	34.48	2.3	2.9
$\text{AC}_{\text{ZnCl}_2-5\%}$	689.39±0.61	5.89	6.0	27	1.10	---	0.1
$\text{TiO}_2 - \text{AC}_{\text{ZnCl}_2-5\%}$	92.51±0.50	979.03	6.4	26	28.85	2.2	2.4
$\text{AC}_{\text{H}_3\text{PO}_4-5\%}$	246.66±0.44	5.94	4.0	14	0.71	---	0.1
$\text{TiO}_2 - \text{H}_3\text{PO}_4-5\%$	63.38±0.39	1034.43	6.3	23	39.41	3.1	3.3

<sup>a</sup> After 60 min of adsorption in the dark. <sup>b</sup> Synergy defined as  $I_{\text{F}} = k_{\text{app-i}}/(k_{\text{app-TiO}_2} + k_{\text{app-AC}})$ .

<sup>c</sup> Relative photoactivity defined as  $\varphi_{\text{rel}} = (k_{\text{app-i}}/k_{\text{app-TiO}_2})$

## Conclusions

TiO<sub>2</sub>-AC showed an increase in photoactivity with respect to titania alone. This beneficial effect has been attributed a photosensitization of some specific functional groups of AC's surface such as cyclic ethers and carboxylate anions in AC<sub>CO<sub>2</sub>-800</sub> and AC<sub>H<sub>3</sub>PO<sub>4</sub>-5%</sub>, respectively, which can coordinates to the metallic Ti<sup>4+</sup> improving the photocatalytic activity of TiO<sub>2</sub>. The present AC showed a small but clear photoactivity in absence of TiO<sub>2</sub> which open the possibility in the future of free-TiO<sub>2</sub> photocatalytic reactions.

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