

Photocatalytic Activity of ZnO-Biochar Hybrid Composites

J. Matos*, R. Montaña, E. Rivero, J. Velasco, G. Ledezma

Department of Photocatalysis and Alternative Energies. Venezuelan Institute for Scientific Research (IVIC), 20632, Caracas 1020-A, Venezuela

Abstract

Photodegradation of methylene blue (MB) was studied on ZnO in presence of home-made biochars prepared by different methods. MB photodegradation was performed under UV-visible irradiation to verify the scaling-up of ZnO-AC hybrid materials. It was verified that oxygenated surface groups on carbon were photochemically active in the photodegradation of MB and a synergy effect between both solids has been estimated from the first-order apparent rate-constants. This effect enhances the photoactivity of ZnO up to a factor about 2.5 and the difference in photoactivity in the binary materials was associated to the surface properties of AC.

Introduction

The study and develop of novel advanced oxidation processes (AOP's) for the remediation of polluted water [1] is an important challenge for science. Regarding to dyes and azo-dyes, an important quantity of the total world production of these molecules is released in textile effluents [2]. Different technologies for the removal of dyes are adsorption, bio- and chemical degradation methods including AOP's as heterogeneous photocatalysis. Since heterogeneous photocatalysis emerged as an efficient method for purifying water and air [3-5] several attends such as ion doping or metal depositions have been used to increase the photoefficiency of semiconductors [3, 6, 7] with TiO₂ and ZnO two of the most studied. Another way to possibly increase the photoactivity of semiconductors consists of adding an inert co-adsorbent [8-11] such as activated carbon (AC). Our groups have reported a synergy effect between AC and TiO₂ or ZnO in the photocatalytic degradation of model pollutants such as phenol [9], 4-chlorophenol [10-13] and 2-propanol [6]. This effect has been ascribed to a contact interface that promotes an efficient diffusion of pollutants from AC to photoactive semiconductor and also is able to introduce changes in the surface of the semiconductor by the photo-assistance of oxygenated functional groups on the AC surface [6, 10-12]. Photocatalysis by semiconductors and adsorption with activated

carbon (AC) have received an increase attention for the degradation of different dyes [14-16]. Thus, the objective of this work is to study the photodegradation of methylene blue (MB) as a model dye under UV-visible irradiation of ZnO in presence of different biochars characterized by different texture and surface functionalities.

Experimental

Methylene blue (MB) was analytical grade and purchased from Aldrich. A standard ZnO was provided by the American Chemical Association. Biochars denoted as activated carbons (AC) were prepared by different methods. In summary, the biochars were prepared by physical activation of the sawdust of a soft wood (*Tabebuia Pentaphyla*) under CO₂ flow at 800 °C or by pyrolysis under N₂ flow at 1000 °C by 1 h. These AC were denoted AC_{CO₂-800} and AC_{N₂-1000}, respectively. Chemical activation by impregnation with 5% (w/w) of ZnCl₂ and H₃PO₄ following activation under N₂ flow at 450 °C by 1 h and was also performed and the biochars were denoted AC_{H₃PO₄-5%} and AC_{ZnCl₂-5%}. The following photocatalysts ZnO/AC_{CO₂}, ZnO/AC_{N₂}, ZnO/AC_{ZnCl₂}, and ZnO/AC_{H₃PO₄} were obtained with the relative amount semiconductor: AC, expressed in mass, i.e. 10:1, by mixing about 62.5 mg ZnO with 6.3 mg AC in 125 mL of deionized H₂O and this slurry was vigorously stirred for 20 min at room temperature, filtered and dried by 2 h at 100 °C.

* Corresponding author. E-mail: jmatoslale@gmail.com

Textural characterization was performed by N_2 adsorption-desorption isotherms at 77 K in a Micromeritics ASAP-2020 instrument. BET method was used to obtain the surface area. Surface pH (pH_{PZC}) of bare biochars, ZnO and mixture of solids were obtained by the drift method [17] by comparing the pH measured after 48 h stirring (to achieve the equilibrium of charges) with that of initial buffer solutions.

The experimental set-up under UV-visible irradiation consists in an open to air batch photoreactor [18] of about 200 mL cylindrical flask made with Pyrex with a bottom optical window of 6 cm in diameter. Irradiation was provided using a 250W Hg lamp (LHg) UV. Irradiation was filtered by a circulating water cell (thickness ca. 2.0 cm) to remove IR beams and prevent any heating of the suspension. The photocatalytic tests were performed at 25 °C under stirring using 62.5 mg of ZnO and/or 6.3 mg AC in 125 mL of methylene blue (MB), [12.5 ppm (39.1 $\mu\text{mol/L}$) initial concentration]. The samples were maintained in the dark for 60 min in order to complete adsorption at equilibrium and then the suspension was irradiated. After centrifugation MB aliquots were analyzed using an UV-spectrophotometer Perkin Elmer, Lambda 35 at 664 nm and the MB concentrations were estimated using a standard calibration curve. Tests were done by triplicate and the reproducibility of results was better than 3%.

Results and Discussion

Characterization of AC

Table 1 shows a summary of the BET surface area (S_{BET}) and pH_{PZC} of AC, ZnO, and the hybrid ZnO/AC photocatalysts. Most of biochars showed high BET surface areas (S_{BET}). It can be seen from the SEM micrography in Fig. 1 that ZnO is a non-porous material with a mean size of ZnO particles in the micrometer range. This is in agreement with the very low surface area of ZnO, about 6 $\text{m}^2\cdot\text{g}^{-1}$. For the hybrid ZnO/AC materials, S_{BET} decreases one order magnitude with respect to the biochar. This fact can be attributed to a strong inter-

action between both solids [7]. It can be seen from Table 1 that biochars prepared at high temperature ($AC_{CO2-800}$ and $AC_{N2-1000}$) developed basic pH_{PZC} while biochars prepared by chemical activation at 450 °C ($AC_{ZnCl2-5\%}$ and $AC_{H3PO4-5\%}$) showed acid pH_{PZC} suggesting the presence of different oxygenated functional groups (basic and acids) on the surface of AC. This fact has been already verified by our group in previous works regarding the photoproduction of hydrogen [7] and 4-chlorophenol [10-13]. We have found that functional surface groups in $AC_{CO2-800}$ are mainly basic such as cyclic ethers ($-C-O-C-$) and quinones ($C=O$) [13, 19]. For the case of $AC_{H3PO4-5\%}$ [6] the main functional surface group was carboxylic acid ($-COOH$). It should be remarked the presence of phosphates in the FTIR spectra in the AC_{H3PO4} [11, 13, 20]. As expected, ZnO presented a basic surface pH and with the exception of the ZnO/ AC_{H3PO4} the ZnO/AC binary material are characterized by basic surface pH. This basic surface pH promotes an efficient dispersion of ZnO particles on the surface of AC as can be clearly seen in the SEM micrography from Fig. 1 where the mean size of ZnO particles are clearly smaller than that observed on the bare ZnO. This fact has been already reported by our group for the TiO_2/AC binary materials [10] and it was ascribed to a stabilization of the zeta potential of the semiconductor by contact with basic AC [21].

Table 1

Summary of BET surface area (S_{BET}) and surface pH (pH_{PZC})

Sample	S_{BET} ($\text{m}^2\cdot\text{g}^{-1}$)	pH_{PZC}
$AC_{CO2-800}$	943	8.5
$AC_{N2-1000}$	644	8.9
$AC_{ZnCl2-5\%}$	689	6.0
$AC_{H3PO4-5\%}$	247	4.0
ZnO	6	9.1
ZnO/ $AC_{CO2-800}$	92	9.0
ZnO/ $AC_{N2-1000}$	65	9.2
ZnO/ $AC_{ZnCl2-5\%}$	69	7.8
ZnO/ $AC_{H3PO4-5\%}$	28	6.6

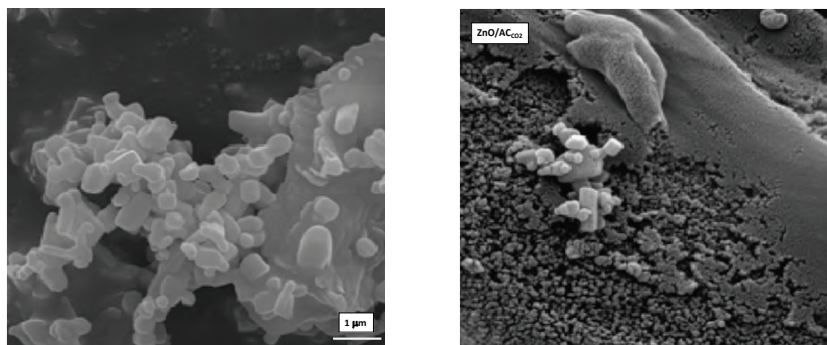


Fig. 1. SEM micrographs of ZnO (left) and ZnO- AC_{CO2} (right).

Adsorption in the Dark and Photodegradation of MB

Figure 2 shows the kinetics of adsorption in the dark of MB on AC, ZnO and ZnO/AC. It can be seen that most of adsorption occurred within 30 min but to ensure the equilibrium of adsorption a period of 60 min of adsorption in the dark was selected prior to the photodegradation experiments. MB adsorbed

values after 60 min are summarized in Table 2. It can be seen that there are no additive effects in the adsorption capacities of ZnO and AC after they are mixed. This can be easily verify from adsorption values in Table 2 obtained after achieve the equilibrium of adsorption. This is in agreement with a strong interaction between ZnO and AC previously reported by our group for ZnO/AC [6] and TiO₂/AC [9] binary photocatalysts.

Table 2

Adsorption in the dark (Ads_{dark}) of MB, first-order apparent rate-constants (k_{app}), square linear regression factor (R^2), photocatalytic activity relative to ZnO (ϕ_{photo})^b

Sample	Ads_{dark}^a (μmol)	$k_{\text{app}} \times 10^{-3}$ (min^{-1})	R^2	ϕ_{photo}^b
AC _{CO2-800}	2.203	1.20	0.9605	0.01
AC _{N2-1000}	2.208	4.50	0.9838	0.05
AC _{ZnCl2-5%}	0.327	0.80	0.9336	0.01
AC _{H3PO4-5%}	0.660	0.78	0.9831	0.01
ZnO	0.985	93.2	0.9177	1.0
ZnO/AC _{CO2-800}	2.342	152.3	0.8397	1.6
ZnO/AC _{N2-1000}	2.210	146.0	0.8102	1.6
ZnO/AC _{ZnCl2-5%}	1.221	229.4	0.9734	2.5
ZnO/AC _{H3PO4-5%}	0.769	27.8	0.9743	0.3

^aAfter 60 min adsorption in the dark. ^b $\phi_{\text{photo}} = (k_{\text{app-i}}/k_{\text{app-TiO}_2})$.

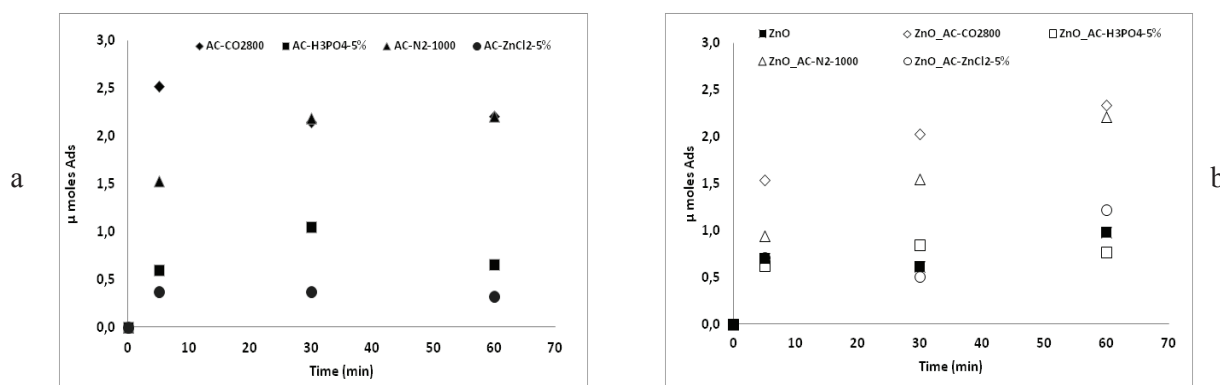


Fig. 2. Kinetics of MB adsorption in the dark: (a) – Biochars; (b) – ZnO/AC materials.

Figure 3 shows the kinetics of MB photodegradation under UV irradiation. Direct photolysis (not shown) was previously verified [16, 18] and it was negligible in the same experimental conditions. Therefore, it can be concluded that the MB disappearance showed in Fig. 3 is due to the photodegradation of the dye. It must be point out that the present biochars are lightly photoactive in agreement with previous results from Bandosz [22], Velasco [23], and our group [24]. It can be seen from Fig.

3 that time required for total disappearance of MB is clearly shorter in presence of biochars suggesting an important synergy effect between both solids. Assuming a first-order reaction mechanism [4], the linear regressions of the kinetic data from Fig. 3 was performed to estimate the first-order apparent rate-constants (k_{app}). Table 2 contains a summary of the kinetic results obtained for the MB photodegradation. The first-order apparent rate-constants permits to estimate the photoactivity relative to ZnO

defined by the expression: $\phi_{rel} = (k_{app-i}/k_{app-ZnO})$. It can be seen from k_{app} values in Table 2 that with the exception of ZnO/AC_{H3PO4-5%} the others ZnO-AC hybrid materials have higher photoactivity than that obtained on ZnO alone and this enhancement was up to about 2.5 times higher on ZnO/AC_{ZnCl2-5%}. It is interesting to point out that no correlation between the MB adsorbed in the dark and the photoactivity was detected indicating that besides the texture the surface functionalities of AC play an important role upon the photoactivity of ZnO. In previous works of 4-chlorophenol photodegradation [10-13] our group have showed that oxygenated functional groups in the biochar framework

play a double role in photocatalytic degradation of 4-chlorophenol. First, biochars play the role of electron carriers that could inhibit the recombination of photoelectrons to improve the photoactivity of the semiconductor. Second, under UV irradiation several functional groups on carbon's surface are able to excited electrons from π to π^* orbital and then being injected into the conduction band of the semiconductor [16]. This phenomenon has been described by our group as a photo-assisting process on TiO₂/AC photocatalysts [6, 7, 24] and therefore further analysis must be performed in order to verify this same behaviour on the present ZnO/AC hybrid photocatalysts.

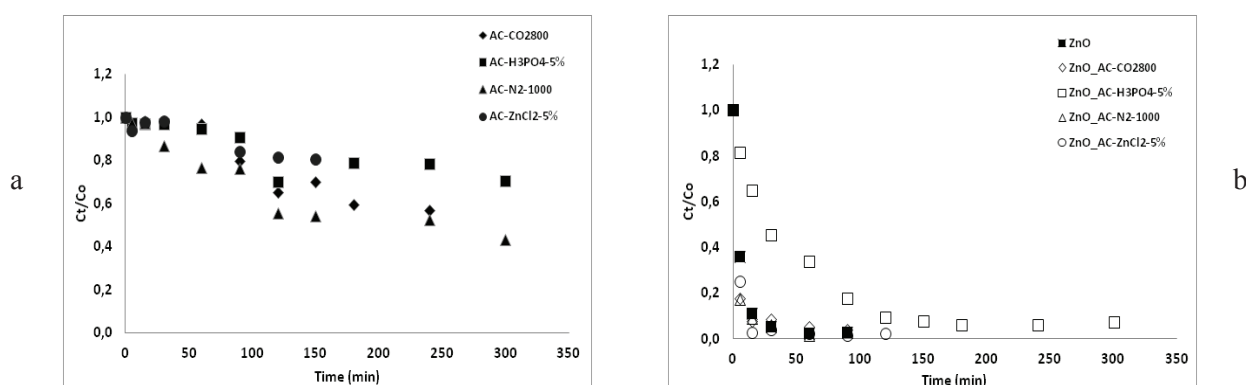


Fig. 3. Kinetics of MB photodegradation: (a) – Biochars; (b) – ZnO/AC materials.

Conclusions

MB photodegradation was studied under UV irradiation of binary ZnO/AC materials. A clear increase in the photocatalytic activity of ZnO was detected and it was verified that biochars were intrinsically photoactive and the enhancement in the photocatalytic activity of ZnO was estimated from the first-order apparent rate-constants in the MB photodegradation. The photocatalytic activity of ZnO enhances up to a factor about 2.5 and it was associated to the specific oxygenated functional groups on biochar surface besides the textural properties.

References

- [1]. R. Andreatti, V. Caprio, A. Insola, R. Marotta, *Catal. Today* 53 (1999) 51–55.
- [2]. A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard, J.M. Herrmann, *Appl. Catal. B: Environ.* 31 (2001) 145–157.
- [3]. J.M. Herrmann, J. Didier, P. Pichat, *Chem. Phys. Lett.* 108 (1984) 618–622.
- [4]. J.M. Herrmann, C. Guillard, P. Pichat, *Catal. Today* 17 (1993) 7–20.
- [5]. O. Legrini, E. Oliveros, *Chem. Reviews* 93 (1993) 671–698.
- [6]. J. Matos, E. García-López, L. Palmisano, A. García, G. Marci, *Appl. Catal. B: Environ.* 99 (2010) 170–180.
- [7]. J. Matos, T. Marino, R. Molinari, H. García, *Appl. Catal. A: Gen.* 417–418 (2012) 263–272.
- [8]. T. Torimoto, Y. Okawa, N. Takeda, H. Yoneyama, *J. Photochem. Photobiol. A: Chem.* 103 (1997) 153–157.
- [9]. J. Matos, J. Laine, J.M. Herrmann, *Appl. Catal. B: Environ.* 18 (1998) 281–291.
- [10]. T. Cordero, J.M. Chovelon, C. Duchamp, C. Ferronato, J. Matos, *Appl. Catal. B: Environ.* 73 (2007) 227–235.
- [11]. T. Cordero, J.M. Chovelon, C. Duchamp, C. Ferronato, J. Matos, *J. Photochem. Photobiol. A: Chem.* 191 (2007) 122–131.
- [12]. J. Matos, A. García, T. Cordero, J.M. Chovelon, C. Ferronato, *Catal. Lett.* 130 (2009) 568–574.
- [13]. J. Matos, A. García, P.S. Poon, *J. Mater. Science* 45 (2010) 4934–4944.
- [14]. W. Wang, C. Gomes, J.L. Faria, *Appl. Catal. B: Environ.* 70 (2007) 470–478.

- [15]. J.M. Peralta-Hernández, J. Manríquez, Y. Meas-Vong, F.J. Rodríguez, T.W. Chapman, M.I. Maldonado, L.A. Godínez, J. Hazar. *Mater.* 147 (2007) 588–593.
- [16]. J. Matos, A. García, L. Zhao, M.M. Titirici. *Appl. Catal. A: Gen.* 390 (2010) 175–182.
- [17]. M.V. Lopez-Ramon, F. Stoeckli, C. Moreno-Castilla, F. Carrasco-Marin. *Carbon* 37 (1999) 1215–1221.
- [18]. J. Matos, M. Rosales, A. García, C. Nieto-Delgado, J.R. Rangel-Mendez, *Green Chem.* 13 (2011) 3431–3439.
- [19]. A.P. Terzyk, *Colloids Surf. A: Physicochem. Eng. Aspects* 177 (2001) 23–45.
- [20]. J. Laine, A. Calafat, M. Labady. *Carbon* 27 (1989) 191–195.
- [21]. J. Matos, A. Corma. *Appl. Catal. A: Gen.* 404 (2011) 103–112.
- [22]. T.J. Bandoz, J. Matos, M. Seredych, M.S.Z. Islam, R. Alfano. *Appl. Catal. A: Gen.* 445–446 (2012) 159–165.
- [23]. L.F. Velasco, I.M. Fonseca, J.B. Parra, J.C. Lima, C.O. Ania. *Carbon* 50 (2012) 249–58.
- [24]. J. Matos, M. Hofman, R. Pietrzak. *Carbon* 54 (2013) 460–471.

Received 12 April 2014