

Influence of Surface Properties of Activated Carbon on Photocatalytic Activity of TiO₂ in 4-chlorophenol Degradation

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Abstract: This work shows the influence of specific surface area (BET) and surface pH of different activated carbons on the photocatalytic activity of UV-irradiated TiO₂ in the 4-chlorophenol (4CP) photodegradation. Carbons were prepared from sawdust of *Tabebuia Pentaphyla* wood by physical activation with CO₂ and by pyrolysis under N₂ flow at temperatures from 450 up to 1000°C during 1h. Chemical activation was also performed by the impregnation of precursor with ZnCl₂, H₃PO₄ and KOH at different concentrations, followed by activation under N₂ flow at 450°C by 1h. Comparison of apparent first-order rate constants between TiO₂ against TiO₂-AC indicate that TiO₂ photoactivity is enhanced or inhibited as a function of AC properties and correlations with surface area and pH_{PZC} were found suggesting that surface pH of carbons is the most important parameter that influences TiO₂ activity in the 4CP photodegradation.

Keywords: TiO₂, Photoactivity, Activated carbon, 4-Chlorophenol.

1. INTRODUCTION

TiO₂ is the best photocatalyst for treatment of waste waters; however, two of the most important operational limitations are that most of commercial Titania has low surface area and its photoactivity is limited to UV irradiation. Several studies have been performed to solve the first limitation employing co-supports [1,2]. Particularly, activated carbons (AC) have shown to increase remarkably TiO₂ photoactivity in photodegradations of pollutants in waste waters [3-14]. This cooperative effect has been attributed not only to its high surface areas but also to the low-strength of adsorption that permits the diffusion of pollutants from support to active phase [2,3]. Concerning to the second limitation, the influence of carbon deposits or carbon-doped Titania has been performed [9-11] and different points of view have been established. A recent study suggest that there are no significant changes in band energy of Titania [12] as a consequence of interaction with carbon supports; however, another recent study about the preparation and characterization of an activated carbon-supported N-doped catalyst [15] has shown that a new band-gap level was formed by doped N and this TiO_{2-x}N_y-AC catalyst have been highly active in both visible and UV range. Most of works suggest that enhanced photocatalytic activity on TiO₂-AC catalysts is not due to a change in band energy of semiconductor and the influence of AC on TiO₂ should be associated, primary with the interaction between bulk AC and Ti-O bonds proposed by other authors

and us [7-9,12-14]. In short, though several studies show a beneficial influence of AC on TiO₂ few works correlate AC properties with TiO₂ photoactivity [4,13,14]. In that sense the present work show the influence of some surface properties of AC as specific surface area (BET) and surface pH on the photocatalytic activity of binary material TiO₂-AC in the 4-chlorophenol degradation.

2. EXPERIMENTAL

Experimental conditions have been reported by us [13,14] but they can be summarized as follows. High purity 4-chlorophenol (4CP) was purchased from Aldrich. Photocatalyst was TiO₂ P25 from Degussa. Activated carbons (AC) were prepared from sawdust of *Tabebuia Pentaphyla* wood by two different methods. Physical activation (H-type or close AC) by gasification with CO₂ and by pyrolysis under N₂ flow at temperatures from 450 up to 1000°C during 1h [13]. Chemical activation (L-type or open AC) was performed by the impregnation of precursor with ZnCl₂, H₃PO₄ and KOH at different concentrations, followed by activation under N₂ flow at 450°C by 1h [14]. Samples were denoted as AC_{CO2-i}, AC_{N2-i}, AC_{ZnCl2-i%}, AC_{H3PO4-i%} and AC_{KOH-i%}, being i the temperature of activation and/or the weight concentration (w/w) respectively. Photocatalytic test was performed at room temperature (20°C). 50mg TiO₂ and 10mg AC were added under stirring in 25mL of 0.78x10⁻³mol/L (about 100ppm) 4CP as initial concentration and maintained in the dark during 80min to reach complete adsorption at equilibrium. This apparent high amount of photocatalyst (TiO₂ + AC, 2.4g total solid powder/L) was chosen because an earlier study [3] it showed the best photocatalytic behaviour for phenol degradation. A batch photoreactor was employed

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Table 1. Summary of BET Surface Areas (S_{BET}) and surface pH (pH_{PZC}) of AC

System	S_{BET} (m^2/g)	$\text{pH}_{\text{PZC}}^{\text{a}}$
TiO₂	50 ± 2	6.5
AC_{CO2-900}	548 ± 21	9.1
AC_{CO2-800}	770 ± 16	8.5
AC_{CO2-700}	570 ± 14	8.0
AC_{CO2-600}	426 ± 13	7.2
AC_{CO2-450}	352 ± 5	6.3
AC_{N2-1000}	518 ± 17	8.9
AC_{N2-900}	590 ± 17	8.5
AC_{N2-800}	519 ± 15	8.0
AC_{N2-700}	388 ± 13	7.9
AC_{N2-600}	360 ± 12	7.1
AC_{N2-450}	31 ± 5	6.1
AC_{ZnCl2-65%}	2001 ± 10	4.5
AC_{ZnCl2-35%}	2485 ± 12	4.8
AC_{ZnCl2-5%}	561 ± 3	6.0
AC_{ZnCl2-1%}	30 ± 1	6.4
AC_{H3PO4-65%}	1569 ± 8	3.1
AC_{H3PO4-35%}	1987 ± 10	3.5
AC_{H3PO4-5%}	414 ± 2	4.0
AC_{H3PO4-1%}	188 ± 1	4.7
AC_{KOH-65%}	309 ± 2	6.1
AC_{KOH-50%}	476 ± 3	6.5
AC_{KOH-5%}	17 ± 2	7.5
AC_{KOH-1%}	5 ± 1	7.7

^a pH_{PZC} with less than 5% of standard deviation

[13]. It consists of a cylindrical flask (Pyrex, c.a. 60mL) with a bottom optical window of c.a. 3cm diameter and open to air. Irradiation was provided by a high-pressure mercury lamp (Phillips HPK, 125W) and it was filtered by a circulating-water cell (thickness, 2.5cm) and with a 340nm cut-off filter (Corning 0.52). Photons flux emitted by light source was determined by Actinometry using Uranyl Oxalate as actinometer and software Photon version 1.6 and a value close to $2.9 \times 10^{15} \text{photons} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ was obtained. Millipore disks (0.45 μm) were used to remove particulate matter from each aliquot (0.3mL) before analysis by HPLC. A Varian 9010 HPLC with a Spectra Systems UV 2000 absorbance detector adjusted at 280nm was used to determine 4CP concentrations as a function of UV-irradiation time. The column was Hypersil BDS C18, 5 μm , (125mm x 4mm, 5 μm). The mobile phase consisted of 45% methanol and 55% water (v/v), whose pH was adjusted to 3 using acetic acid. The flow-rate was 0.8mL.min⁻¹ and the injection volume was 200 μL . Textural characterization of TiO₂ and AC was performed by N₂ adsorption at 77K to obtain specific surface area BET (S_{BET}) in a Micromeritics ASAP-2010 apparatus. Surface pH (pH_{PZC}) of AC and Titania were obtained by drift method [16].

3. RESULTS AND DISCUSSION

3.1. S_{BET} and pH_{PZC} of Activated Carbons

Characterization of activated carbons has been reported [13,14] but Table 1 contains a summary of specific surface area (S_{BET}) and surface pH (pH_{PZC}) of activated carbons. As expected, the higher activation or carbonization temperatures, the higher the pH_{PZC} which indicate the presence of more basic functional groups on the surface of H-type AC. Concerning to BET surface areas, it can be seen from Table 1 that a maximum of 770m².g⁻¹ around 800°C (AC_{CO2-800}) and of 590m².g⁻¹ at 900°C (AC_{N2-900}) were reached for treatments under CO₂ and N₂ flows, respectively. However, it is important also to note that when wood is heated at higher temperatures a decrease in S_{BET} is observed. This has been attributed to an incipient graphitization of H-type AC [13]. Table 1 also shows specific surface area and pH_{PZC} of L-type AC. As expected, the higher the concentration of chemical compounds employed prior to the activation of AC, the lower pH_{PZC} of AC. This is a general trend for all types of L-type AC studied. AC prepared with H₃PO₄ showed lower pH_{PZC} values than those AC prepared with ZnCl₂. It can be noted from Table 1 that AC prepared with 1%w/w H₃PO₄ is clearly lower than that obtained for the same con-

centration of ZnCl_2 (4.7 against 6.4). This is the consequence of H_3PO_4 is a strong Brønsted acid while ZnCl_2 is a Lewis acid and therefore H_3PO_4 should introduce more acidic groups in AC surface. Also, it must be noted that AC prepared with KOH showed an apparent unexpected behaviour. Though KOH is a strong Lewis base, Table 1 shows that the higher KOH concentration the lower pH_{PZC} of AC. However, this lowering is only from 7.7 down to 6.1 for the increase of KOH concentration from 1 to 65% w/w. This result has been attributed to a high structural disorder in AC prepared with KOH [14]. Regarding S_{BET} , it can be seen from Table 1 that specific surface area shows a maxima of 2485, 1987, and $476\text{m}^2\cdot\text{g}^{-1}$ for ZnCl_2 (35% w/w), H_3PO_4 (35% w/w) and KOH (50% w/w), respectively. It is important to note that employing higher concentrations of chemical impregnators a clear decrease in S_{BET} was observed in all different types of AC prepared. This decrease in S_{BET} could be due to a high concentration of steam produced during the thermal decomposition of the impregnated compounds [14].

3.2. Adsorption of 4-Chlorophenol in the Dark

In preliminary studies [13,14] we have been reported 4-chlorophenol adsorption in the dark at 20°C on Titania (50 mg), H- and L-type AC (10 mg), and suspended mixtures TiO_2/AC with the same respective masses. Kinetics of adsorption in the dark was followed by 80min under stirring for different initial concentrations between 0.78×10^{-3} and $7.80 \times 10^{-3}\text{mol}\cdot\text{L}^{-1}$. In all cases, most of adsorption occurred within 20min but to ensure a proper equilibrium of adsorption a longer period (80min) of adsorption in the dark was considered prior to all photodegradation experiments [13,14]. From 4CP adsorbed in the dark, adsorption isotherms $n_{\text{ads}} = f(C_{\text{eq}})$ were estimated [13,14] considering n_{ads} as the number of mols of 4CP adsorbed ($n_{\text{ads}} = n_0 - n_{\text{eq}}$) and C_{eq} the 4CP concentration after equilibrium in the dark. Therefore, assuming the conventional Langmuir isotherm model with a surface coverage θ varying as

$$\theta = (n_{\text{ads}}/n_{\text{T}}) = [K_{\text{ads}} \cdot C_{\text{eq}} / (1 + K_{\text{ads}} \cdot C_{\text{eq}})] \quad (1)$$

the thermodynamic parameters of adsorption as total number of adsorption sites (n_{T}) and the adsorption constants (K_{ads}) were obtained from the linear transform $(1/n_{\text{ads}}) = f(1/C_{\text{eq}})$, with correlation coefficients in most of cases close or higher than 0.99. Values of n_{T} and K_{ads} for TiO_2 , H- and L-type AC and TiO_2/AC are given in Table 2. Remarkable differences can be detected when K_{ads} and n_{T} obtained on TiO_2/AC are compared with values obtained on TiO_2 alone and AC alone. It can be observed that n_{T} of 4CP adsorption on different $\text{TiO}_2\text{-AC}$ are smaller than those obtained on each solid alone. For example, total number of adsorption sites decreased by 28% and the adsorption constant increased by 14% if compared $\text{TiO}_2\text{-AC}_{\text{CO}_2\text{-900}}$ against $\text{AC}_{\text{CO}_2\text{-900}}$. Such differences are more pronounced for the AC prepared under N_2 flow. If photocatalyst $\text{TiO}_2\text{-AC}_{\text{N}_2\text{-900}}$ is compared against TiO_2 and $\text{AC}_{\text{N}_2\text{-900}}$, 45% of total sites of adsorption were lost. For the case of L-type AC, comparing $\text{TiO}_2\text{-AC}_{\text{ZnCl}_2\text{-35\%}}$ with TiO_2 and $\text{AC}_{\text{ZnCl}_2\text{-35\%}}$, the total number of adsorption sites decreased by 22%. Also, if compared $\text{TiO}_2\text{-AC}_{\text{ZnCl}_2\text{-5\%}}$ against TiO_2 and $\text{AC}_{\text{ZnCl}_2\text{-5\%}}$, decrease is more pronounced being of about 31% for the decrease in n_{T} . These results clearly suggest that there are no additive effects in 4CP adsorption

Table 2. Adsorption Constant (K_{ads}) and Total Adsorption Sites (n_{T}) for TiO_2 and $\text{TiO}_2\text{-AC}$

System	K_{ads} (L/mol)	n_{T} (μmol)
TiO_2	384	9.13
$\text{AC}_{\text{CO}_2\text{-900}}$	2715	20.3
$\text{TiO}_2\text{-AC}_{\text{CO}_2\text{-900}}$	3098	21.2
$\text{AC}_{\text{CO}_2\text{-800}}$	1940	19.2
$\text{TiO}_2\text{-AC}_{\text{CO}_2\text{-800}}$	1967	19.0
$\text{AC}_{\text{CO}_2\text{-700}}$	356	8.08
$\text{TiO}_2\text{-AC}_{\text{CO}_2\text{-700}}$	379	8.02
$\text{AC}_{\text{CO}_2\text{-600}}$	323	5.07
$\text{TiO}_2\text{-AC}_{\text{CO}_2\text{-600}}$	345	6.61
$\text{AC}_{\text{N}_2\text{-1000}}$	901	13.2
$\text{TiO}_2\text{-AC}_{\text{N}_2\text{-1000}}$	1395	12.0
$\text{AC}_{\text{N}_2\text{-900}}$	788	11.6
$\text{TiO}_2\text{-AC}_{\text{N}_2\text{-900}}$	1244	11.4
$\text{AC}_{\text{N}_2\text{-800}}$	633	10.8
$\text{TiO}_2\text{-AC}_{\text{N}_2\text{-800}}$	1168	10.2
$\text{AC}_{\text{ZnCl}_2\text{-35\%}}$	1281	43.3
$\text{TiO}_2\text{-AC}_{\text{ZnCl}_2\text{-35\%}}$	1274	40.9
$\text{AC}_{\text{ZnCl}_2\text{-5\%}}$	1185	19.3
$\text{TiO}_2\text{-AC}_{\text{ZnCl}_2\text{-5\%}}$	1121	19.6
$\text{AC}_{\text{H}_3\text{PO}_4\text{-35\%}}$	1161	27.6
$\text{TiO}_2\text{-AC}_{\text{H}_3\text{PO}_4\text{-35\%}}$	1577	26.6
$\text{AC}_{\text{H}_3\text{PO}_4\text{-5\%}}$	521	12.4
$\text{TiO}_2\text{-AC}_{\text{H}_3\text{PO}_4\text{-5\%}}$	360	12.7
$\text{AC}_{\text{KOH}\text{-50\%}}$	664	19.6
$\text{TiO}_2\text{-AC}_{\text{KOH}\text{-50\%}}$	527	20.4
$\text{AC}_{\text{KOH}\text{-5\%}}$	229	12.8
$\text{TiO}_2\text{-AC}_{\text{KOH}\text{-5\%}}$	214	11.8

between both solids. This fact has been already reported by some of us [3,6,13,14] and has been attributed to an interaction between Titania particles and AC particles by a common contact interface between both solids. This interface is non-accessible to 4CP molecules from solution and concomitantly, some of total number sites of adsorption would be lost. Finally, from these studies of adsorption in the dark we selected $0.78 \times 10^{-3}\text{mol}\cdot\text{L}^{-1}$ (about 100ppm) as initial concen-

Table 3. Results of Adsorption at Equilibrium in the Dark of 4CP (4CP_{ads-dark}) and Apparent First-Order Constant Rate (k_{app})

System	4CP _{ads-dark} (%) ^a	Θ = (n _{ads} /n _T) ^a	k _{app} × 10 ⁻³ (min ⁻¹)	F ^c
TiO ₂	9.8	0.213	2.02	1.00
TiO ₂ -AC _{CO2-900}	55.8	0.519	5.85	2.90
TiO ₂ -AC _{CO2-800}	45.0	0.467	4.91	2.43
TiO ₂ -AC _{CO2-700}	13.8	0.339	3.78	1.87
TiO ₂ -AC _{CO2-600}	7.6	0.228	2.29	1.13
TiO ₂ -AC _{CO2-450}	5.8	- ^b	2.16	1.07
TiO ₂ -AC _{N2-1000}	23.8	0.392	4.31	2.13
TiO ₂ -AC _{N2-900}	22.5	0.389	3.37	1.67
TiO ₂ -AC _{N2-800}	21.9	0.375	1.54	0.76
TiO ₂ -AC _{N2-700}	6.8	- ^b	1.34	0.66
TiO ₂ -AC _{N2-600}	5.8	- ^b	1.07	0.53
TiO ₂ -AC _{N2-450}	4.9	- ^b	0.92	0.46
TiO ₂ -AC _{ZnCl2-65%}	48.4	- ^b	1.98	0.98
TiO ₂ -AC _{ZnCl2-35%}	61.2	0.17	2.29	1.13
TiO ₂ -AC _{ZnCl2-5%}	34.8	0.62	4.49	2.22
TiO ₂ -AC _{ZnCl2-1%}	6.5	- ^b	1.59	0.79
TiO ₂ -AC _{H3PO4-65%}	44.1	- ^b	1.25	0.62
TiO ₂ -AC _{H3PO4-35%}	51.5	0.09	2.09	1.03
TiO ₂ -AC _{H3PO4-5%}	11.6	0.86	3.36	1.66
TiO ₂ -AC _{H3PO4-1%}	10.9	- ^b	2.01	1.00
TiO ₂ -AC _{KOH-65%}	32.9	- ^b	2.61	1.29
TiO ₂ -AC _{KOH-50%}	27.4	0.26	2.90	1.44
TiO ₂ -AC _{KOH-5%}	13.0	0.22	0.82	0.41
TiO ₂ -AC _{KOH-1%}	5.7	- ^b	0.53	0.26

^aEstimated from an initial 4CP concentration of about 0.78 × 10⁻³ mol/L (100 ppm)

^bNot estimated in this study

^cSynergy or inhibition described by: $F = [k_{app(TiO_2-AC)}/k_{app(TiO_2)} + k_{app(AC-i)}]$

tration of 4CP for the study of 4CP photodegradation [13,14]. This value was selected because in most of cases the surface coverage obtained from this initial concentration was between 0.2 and 0.5 and therefore it permits to follow properly the kinetics of 4CP photodegradation.

3.3. Influence of Specific Surface Area and Surface pH on Photoactivity of TiO₂

The photocatalytic degradation of 4CP on the present systems have been already reported by us in preliminary studies [13,14]. In those studies was observed that kinetic trends of 4CP disappearance in most of mixed systems TiO₂-AC followed an apparent first-order rate. In agreement, linear transformation of kinetic results, $\ln(C_0/C_t) = f(t)$, were employed to estimate apparent rate constant of first-order (k_{app}) as the best kinetic parameter [3] to compare the photoactivity of different photocatalyst. However, as we

noted above, a period of adsorption in the dark of 80min for 4CP onto the different materials was performed previous to the UV-irradiation. It is important to be noted that direct photolysis was negligible compared to the photocatalytic degradation. Also, the disappearance of 4CP under UV-irradiated for different AC's was negligible [13,14], which confirms that the present AC are photoinactive in agreement with previous results [3-7]. A summary of kinetic results in terms of surface coverage (Θ) of 4CP after equilibrium of adsorption in the dark, the apparent first-order rate constant (k_{app}) and synergy or inhibition effect between both solids (F) is presented in Table 3 where F is obtained by comparison between apparent rate constants:

$$F = [k_{app(TiO_2-AC)}/k_{app(TiO_2)} + k_{app(AC-i)}] \quad (2)$$

As indicated above, AC alone is non photoactive and therefore Eq. 2 reduced to

$$F = [k_{app}(TiO_2-AC)/k_{app}(TiO_2)] \quad (3)$$

where $k_{app}(TiO_2 + AC)$ and $k_{app}(TiO_2)$ are the apparent first-order rate constants obtained on TiO_2/AC and TiO_2 , respectively. Table 3 contains a summary of results that clearly show some correlations between photocatalytic activities of Titania with specific surface area BET (S_{BET}) and surface pH (pH_{PZC}) of H-type AC shown in Table 1. For example, it can be seen that the higher the S_{BET} and the higher pH_{PZC} of most of AC_{CO_2} and AC_{N_2} the higher photoactivity of TiO_2/AC in comparison than that of TiO_2 alone. Since AC is non-photoactive and $k_{app}(TiO_2-AC) > k_{app}(TiO_2)$, it can be inferred that there is a synergistic effect between both solids in such cases where $F > 1$. This cooperative effect shows a maxima of about 2.9 for the case of the more basic activated carbon studied, $pH_{PZC} = 9.1$ for AC_{CO_2-900} (Table 1). This correlation between Titania's photoactivity and the pH_{PZC} is particularly true when pH_{PZC} of AC prepared under CO_2 flow is higher than that of TiO_2 alone ($pH_{PZC} = 6.5$). Concerning to the

influence of L-type AC, in Table 3 can be seen that contrary to TiO_2-AC_{H-type} most of TiO_2-AC_{L-type} have low photoactivity than that of Titania alone (inhibiting effect, $F < 1$) giving a minimum of 0.26 for $TiO_2-AC_{KOH1\%}$. However, there are some cases to be considered carefully. For example, though pH_{PZC} of some L-type are remarkably lower than that of the semiconductor (Table 1) some of these AC also induces a beneficial effect on the photoactivity of TiO_2 (see F factor > 1 in Table 3). Table 3 shows for TiO_2-AC_{L-type} a maximum of 2.22 of synergy for $TiO_2-AC_{ZnCl_2-5\%}$ photocatalyst. These cases will be discussed later. The influence of S_{BET} and pH_{PZC} of AC on photoactivity of TiO_2 are showed in Figs. (1 and 2), respectively. Several features can be noted from these figures. For example, Fig. (1) show that if S_{BET} of AC is higher than $400m^2.g^{-1}$, the photoactivity of semiconductor clearly increase from close to unit up to a maximum synergy (Table 3) of about 3 for TiO_2/AC_{H-type} and 2.1 for TiO_2-AC_{L-type} . It is important also to remark that highest val-

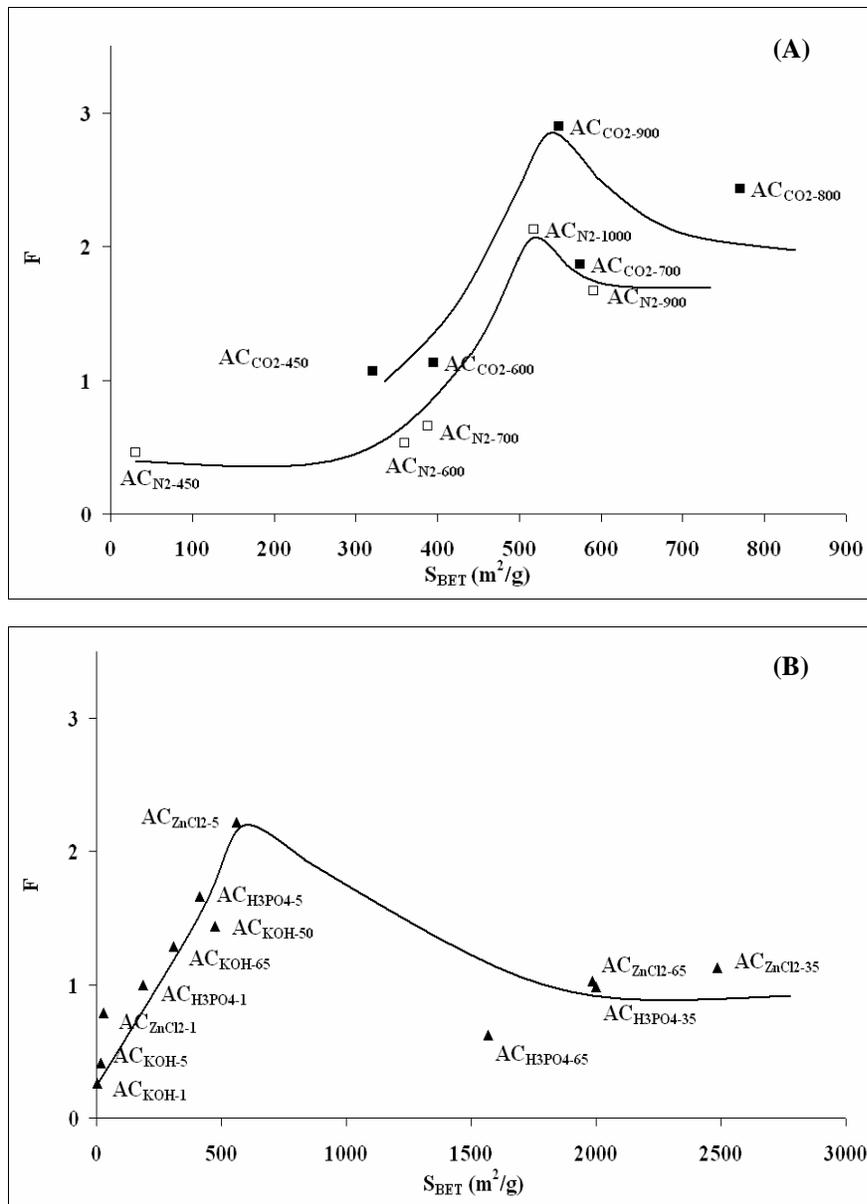


Fig. (1). Interaction factor (F) as a function of activated carbon's BET surface area (S_{BET}). (A): H-type. (B): L-type.

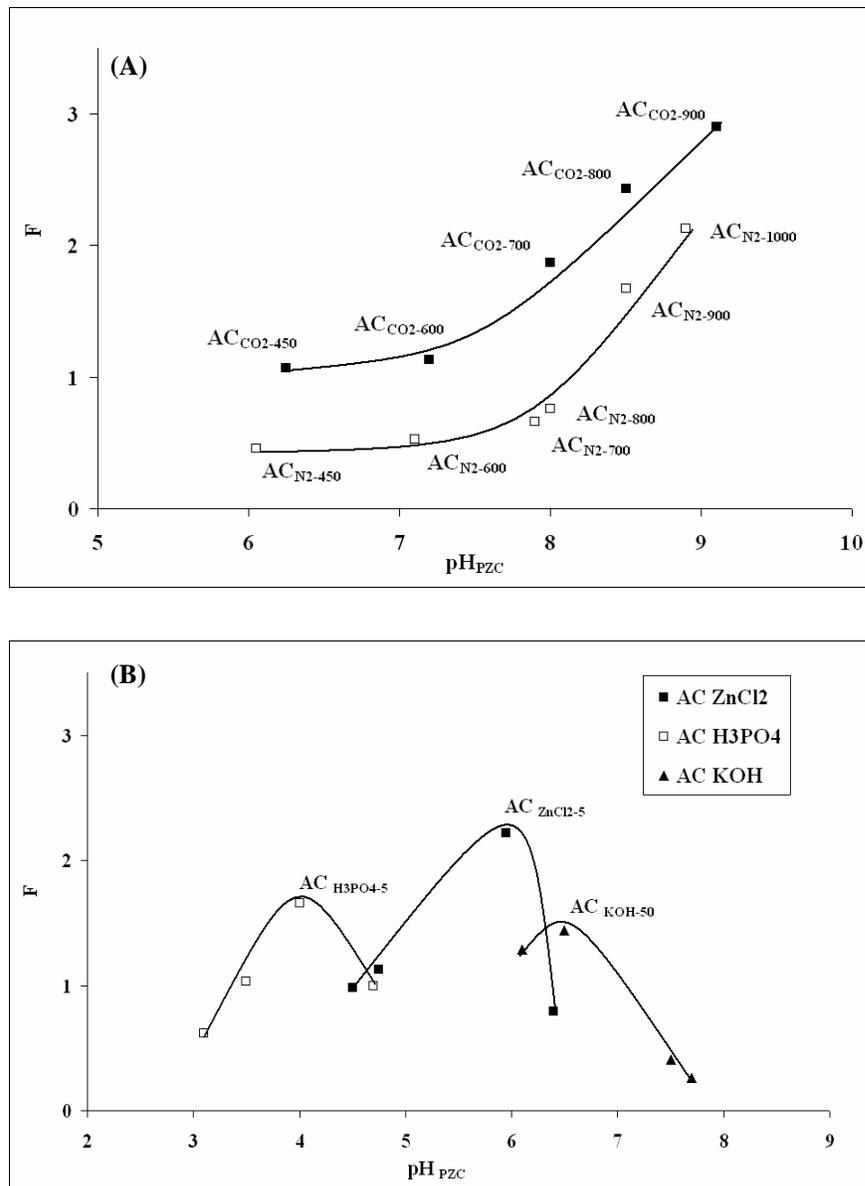


Fig. (2). Interaction factor (F) as a function of activated carbon's surface pH (pH_{PZC}). (A): H-type. (B): L-type.

ues in synergy were reached when S_{BET} was between 520 and $590 \text{ m}^2 \cdot \text{g}^{-1}$, and if S_{BET} of AC are higher than these values activities of TiO_2 clearly decrease. Figs. (1) show that BET surface area is an important parameter that permits to enhanced the photoactivity of TiO_2 because it can improve the tendency to adsorb higher quantities of the pollutant; however, another important parameter as surface chemistry of activated carbons must be considered. Trends of synergy effect as a function of AC's pH_{PZC} in Fig. (2) show that F factor increase proportionally as a function of pH_{PZC} for the case of H-type AC; however, for the case of L-type AC (Fig. 2B), F increase up to a maximum in all the cases studies suggesting that changes in electron density of L-type AC plays an important role that influence the interaction with Titania. As can be seen in Fig. (2A), a synergistic effect was found ($F > 1$) in most of cases of TiO_2 -H-type AC when pH_{PZC} is higher than that of TiO_2 alone (6.5, Table 1). However, it can be seen in Fig. (2B) that few specific TiO_2 -AC_L-type photocatalysts with pH_{PZC} lower than 6.5, develop syner-

gistic effects. If aqueous pH is lower than that of Titania's pH_{PZC} (about 6.5) a large protonation of hydroxyls groups on TiO_2 crystalline net can occur and this protonation cause an inhibition of TiO_2 photoactivity. However, the fact that some L-type AC with pH_{PZC} lower than 6.5 will be able to improved Titania photoactivity in 4CP photodegradation is in agreement with recently results obtained by other authors [17,18] that showed that addition of low quantities of organic acids as acetic acid can enhances TiO_2 photoactivity as consequence of a proper coordination of acetate groups in aqueous phase to Ti^{+4} . These and other kind of organic functional groups have been detected by us [14] in L-type AC and coordination to TiO_2 of different functional organic groups of AC surface as ethers or acetic acid and phenol have been also showed by us in previous studies [7,14]. Therefore, it can be proposed that coordination of organic groups to Ti^{+4} can be done by means of the contact interface between both solids.

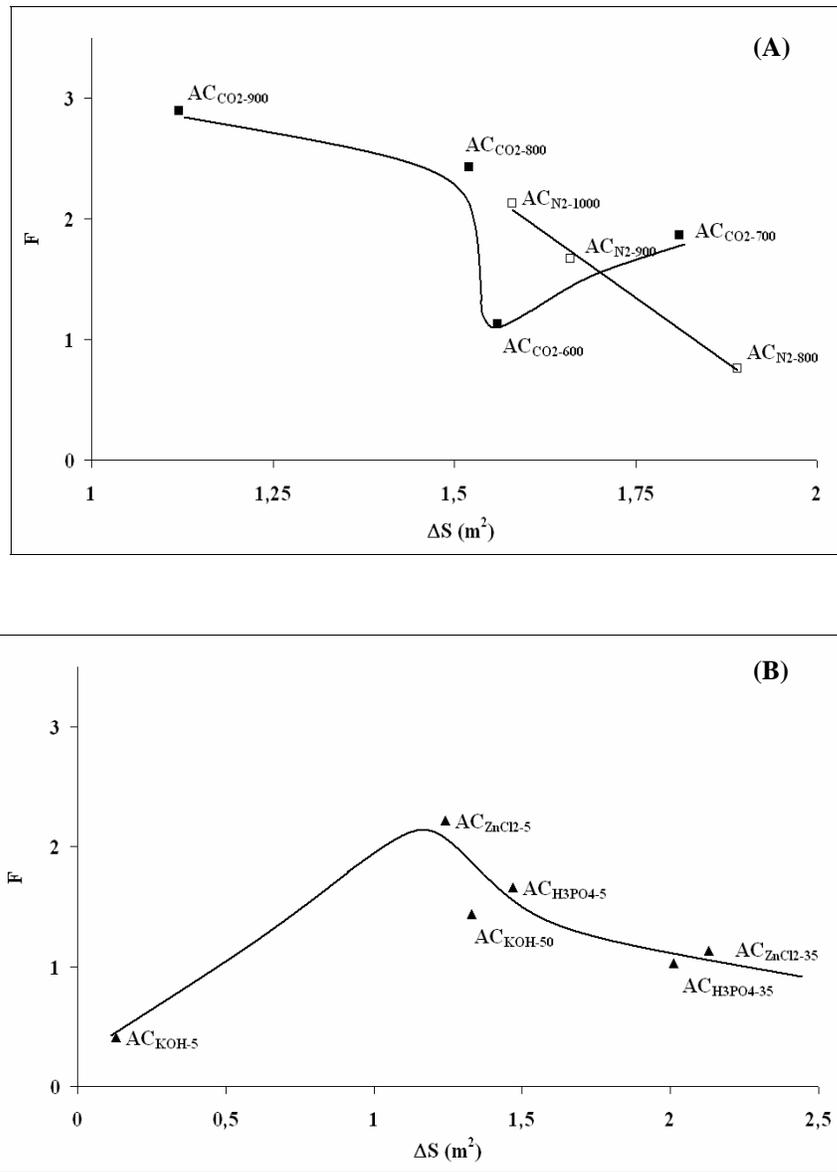


Fig. (3). Influence of contact interface (ΔS) on interaction factor. (A): TiO₂/H-type. (B) TiO₂/L-type.

3.4. Influence of Contact Interface

Beneficial influence of AC on photoactivity of Titania has been attributed to the formation of a common contact interface (ΔS) spontaneously created between both solids in aqueous suspension. This ΔS was proposed firstly by some us [3] from Langmuir's parameters obtained from phenol adsorption's isotherms in the dark and confirmed in more recently works [7,13,14]. It is estimated as follows [3]:

$$\Delta S = [\Delta n_T / d_{TiO_2} + d_{AC}] \tag{4}$$

Δn_T corresponds to the amount of 4CP in mol inhibited to be adsorbed by the presence of the contact interface and can be estimated [3] from the difference between the total number of adsorption sites n_T of TiO₂ and AC alone against that obtained on the mixture TiO₂/AC:

$$\Delta n_T = [(n_{T-TiO_2} + n_{T-AC}) - (n_{T-TiO_2/AC})] \tag{5}$$

d_i corresponds to surface concentration of adsorbed 4CP on each solid, obtained from:

$$d_i = (n_T / S_{BET} \cdot m) \tag{6}$$

where m is solid's weight. Fig. (3) shows the influence of contact interface on synergy effect for the case of TiO₂-AC_{H-type} (Fig. 4A) and TiO₂-AC_{L-type} (Fig. 4B). The best photoactivity behaviour corresponds to contact interfaces of about 1.12 and 1.25m² for TiO₂-AC_{H-type} and TiO₂-AC_{L-type}, respectively. These values are very similar and they correspond to those AC whom shown the maximums values of synergy as function of activated carbon's surface areas (S_{BET} in Fig. 1). Moreover, it was verified that this contact interface (1.12-1.25m²) is about 50% the specific total surface area of TiO₂. This value can be easily estimated from: 50m²·g⁻¹ × 0.05g = 2.50m² and therefore, contact interface for the best photoactivity of TiO₂ corresponds to 50% of total specific area. In other words, there is a combination of surface areas between AC (between 520-590m²·g⁻¹) and TiO₂ that leads to an

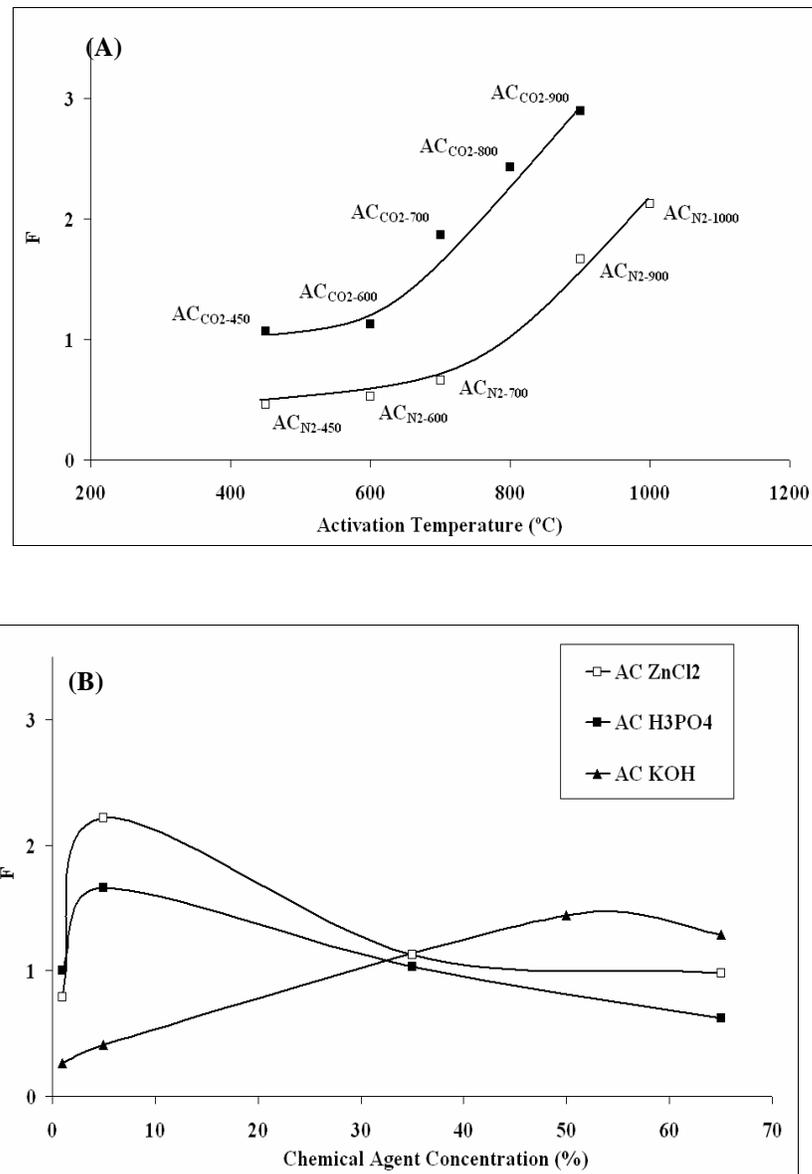


Fig. (4). Influence of activated carbon topology on interaction factor. (A): Activation temperature of H-type AC. (B): Chemical agent concentration in L-type AC.

optimal contact interface that permits the maxima synergy between both solids and this interface corresponds to half total surface area of TiO₂. This value was practically the same obtained for the case of phenol photodegradation [3]. We think this explanation is logical because the trends observed in Fig. (3) showed that if ΔS is higher than values between 1.12 to 1.25m² the synergy effect decrease remarkably. In short, if contact interface formed between solids is too high, then an important quantity of both adsorption sites and active sites in the semiconductor are lost with this interaction and concomitantly less sites will be available to produce OH radicals and a decrease in photoactivity should be expected.

3.5. Influence of Activated Carbon's Topology

In this part, we describe briefly the influence of another important, but commonly missed property of activated carbons like topology. For example, AC_{H-type} or close AC can

develop a topological structure lightly similar than that of graphite, a very well-known semiconductor, which graphene layers are ordered. This structural order influences the electronic density of AC. If topological structure of AC becomes lightly similar to that of graphite then the higher is electronic conductivity of AC. Having this in mind, it can be suggested a new parameter of correlation between AC properties and photoactivity of TiO₂. That means, if electron semiconductor of AC is good enough (in comparison of graphite) then AC will be able to behave as electron carriers, principally driving out photoelectrons excited by UV-irradiation from Titania's conduction band. Concomitantly, this electron carrier's effect contributes inhibiting the recombination of photogenerated species in semiconductor (h⁺, e⁻). This seems to suggest that the higher electron conductivity of AC the higher photoactivity of TiO₂. We do not have values of electron conductivity of AC, but this correlation can be inferred indirectly from trends of Fig. (4). In Fig. (4A) can be seen

that the higher activation temperature of preparation of AC_{H-type} the higher the cooperative effect F. This correlation is totally true for the case of AC_{H-type} prepared by activation under CO₂ flow because the higher temperature of activation the higher structural order [13] and therefore lightly similar to graphite and more basic the AC (Table 1). However, thought the photoactivity trend of TiO₂ with those AC prepared by extensive carbonization under N₂ flow follow a similar behaviour than in the previous case, it can be seen that some AC AC_{N₂-450}, AC_{N₂-600} and AC_{N₂-700}) inhibit the photoactivity (F < 1). This can be associated with the fact that AC prepared by extensive carbonization under N₂ flow develop a disordered structure in their graphene layers [19,20] and therefore, topology is completely different to that of graphite. Fig. (4B) show the influence of ZnCl₂, H₃PO₄ and KOH concentrations on TiO₂ photoactivity. Thus, the higher the oxidation condition employed to prepared L-type AC the higher the disorder of graphene layers and thought these AC commonly have higher S_{BET} that those prepared at lower concentrations of impregnation agents (Table 1) they will be not only more acidic but also less electron conductor carriers than H-type activated carbons and for that reason, AC_{L-type} or open AC behave as electron donors. Also, we have already reported [14] that some AC_{L-type} can be easily coordinated to Ti⁴⁺ as we indicated above in section 3.3, explaining the en-hancement of TiO₂ photoactivity for 4CP photodegradation.

4. CONCLUSIONS

Correlations between surface area and surface chemistry of AC with photocatalytic activity of TiO₂ for 4-chlorophenol degradation have been found. Surface area of AC has an important role because it is involved in the creation of a common contact interface between both solids; however, pH_{PZC} of AC seems to be the more important role because it remarkably affects Titania's photoactivity.

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