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Influence of L-type activated carbons on photocatalytic activity of TiO_2 in 4-chlorophenol photodegradation

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Abstract

The main objective of this work is to study the influence of inorganic compounds employed in the synthesis of L-type activated carbons on photocatalytic activity of TiO_2 in 4-chlorophenol photodegradation. Different activated carbons were prepared from *Tabebuia pentaphyla* wood impregnated with $ZnCl_2$, H_3PO_4 and KOH. Activation was performed under N_2 flow at 450 °C by 1 h. Results clearly indicate differences in the photoactivity of TiO_2 which depends of physicochemical properties of activated carbons that are influenced by the concentration of the chemical substance. Kinetic results of 4-chlorophenol photodegradation show a synergistic effect between both solids and in certain cases the inhibition of TiO_2 photoactivity. These effects have been attributed to differences in texture, topology and principally to the surface chemistry of activated carbons. Scanning electron microscopy has shown a massive aggregation of TiO_2 nanoparticles on activated carbons with very acid or basic surface pH. In conclusion, the control of synthesis parameters of L-type activated carbons introduces an important enhancement in Titania's photoactivity for 4-chlorophenol photodegradation when both solids work in conjunction.

Keywords: Photocatalysis; 4-Chlorophenol; Titania; Activated carbon; Synergy

1. Introduction

Commonly, waste water treatment is performed by governmental controlled techniques as flocculation, filtration, and sterilization and by methods characterized by the addition of some chemical compounds employed as precursors of hydroxyl radicals responsible of total oxidation of pollutant with their conversion to mineral products [1]. Studies related with treatment of water have been shown an increase in photochemistry procedures. This is particularly truth for the photo oxidative degradation of organic compounds both in aqueous as in gaseous phase. These methods are well-known as advanced oxidation processes [2,3] such as heterogeneous photocatalysis which is characterized by employ UV–visible photoactive semiconductors [3] as titanium dioxide TiO_2. It has shown to be the most efficient [4,5] photocatalyst for treatment and purification of water and air in most of cases studied [6]. Titania is non-expensive, non-toxic, and biocompatible material that shows high photoefficiency and activity. Several attempts have been made to increase the photoefficiency of TiO_2, either by noble metal deposition or by ion doping [7] but such modifications did not enhance its photocatalytic activity and were rather detrimental. A more commonly way to possibly increase the photocatalytic efficiency of TiO_2 consists of adding an inert co-adsorbent such as activated carbon (AC) [8,9]. A synergistic effect has been already observed by some of us [10–14] by using powdered TiO_2 and powdered AC in the photocatalytic degradation of model pollutants such as phenol, 4-chlorophenol and the common herbicide 2,4-dichlorophenoxyacetic acid (2,4-D). For example, we have found that some H-type activated carbons increased remarkably TiO_2 photoactivity [10,12,14] while some L-type activated carbons were detrimental [11,12]. Both effects have been ascribed to the presence of a common contact interface spontaneously created between both solids [10–12]

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that promotes not only an appropriated diffusion of pollutants from activated carbon to photoactive Titania [10] but also can introduce changes in surface properties of semiconductor [13], and therefore, playing an important role upon its photoactivity [10,13,15]. In addition, the influence of carbon doping or carbon doped TiO_2 have been recently studied [16–19] showing that carbon clearly influence Titania capability for photodegradation of pollutants in aqueous phase. Having this in mind, the main objective of this work is to verify the influence of activated carbons on the photocatalytic activity of TiO_2 in 4-chlorophenol degradation employing different types of L-type activated carbons prepared by impregnation of a lignocellulosic precursor with different types of chemical agents in order to introduce changes in textural, topological and surface chemistry properties of the support.

2. Experimental

High purity 4-chlorophenol (4CP) was purchased from Aldrich. The photocatalyst was TiO_2 P-25 from Degussa, and the activated carbons (AC) were prepared from *Tabebuia pentaphyla* wood impregnated with $ZnCl_2$, H_3PO_4 and KOH. Activation was performed under N_2 flow at 450 °C by 1 h. Samples were denoted as $AC_{ZnCl_2\text{-}i\%}$, $AC_{H_3PO_4-i\%}$ and $AC_{KOH\text{-}i\%}$, respectively, being *i*% the weight concentration (w/w) employed for chemical agents. Similar experimental conditions employed in the present study have been reported by us in a recent work [16] but they can be summarized as follows. The photocatalytic test was performed at room temperature (20 °C). Fifty milligrams TiO_2 and 10 mg AC were added under stirring in 25 mL of solution of 0.78×10^{-3} mol L^{-1} (about 100 ppm) of 4CP (initial concentration) and maintained in the dark during 80 min to reach a complete adsorption at equilibrium. This apparent high concentration of catalyst (TiO_2 + carbon, 2.4 g total solid powder L^{-1}) was chosen because in an earlier study [10] this concentration showed the best photocatalytic behaviour for phenol photodegradation under UV-irradiation. A batch photochemical reactor in aqueous phase was employed [16]. It consists of a cylindrical flask (Pyrex, ca. 60 mL) with a bottom optical window of ca. 3 cm diameter and open to air. Irradiation was provided by a high-pressure mercury lamp (Phillips HPK, 125 W) and was filtered by a circulating-water cell (thickness, 2.5 cm) equipped with a 340 nm cut-off filter (Corning 0.52). Photons flux emitted by light source was determined by Actinometry using Uranyle Oxalate as actinometer and software Logicien Photon version 1.6. Photon flux estimated was 2.9×10^{15} photons cm^{-2} s^{-1}. Millipore disks (0.45 μm) were used to remove particulate matter from each aliquot (0.3 mL) before the analysis by HPLC. A Varian 9010 series HPLC systems equipped with a Spectra Systems UV 2000 absorbance detector adjusted at 280 nm was used to determine 4CP concentrations as a function of UV-irradiation time. The column was Hypersil BDS C18, 5 μm, (125 mm × 4 mm, 5 μm). The flow-rate was 0.8 mL min^{-1} and the injection volume 200 μL. Mobile phase consisted of 45% methanol and 55% water (v/v), whose pH was adjusted to 3 using acetic acid. From kinetic curves of 4CP photodegradation the apparent first-order rate constant were obtained as the best kinetic parameter to compare the photoactivity of the different systems. Textural characterization of TiO_2 and the activated carbons was performed by means of N_2 adsorption at 77 K in order to obtain the B.E.T. surface areas (S_{BET}). The full isotherms in the range of 0.03–30 Torr were measured employing a Micromeritics ASAP-2010 apparatus. Surface pH (pH_{PZC}) of AC and Titania were obtained by the drift method [20]. Scanning electron microscopy (SEM) was employed to detect morphological changes in the mixtures TiO_2-AC. Samples were obtained by mixing TiO_2 with AC at the same work conditions in 5 mL of water continuously stirred for 80 min. After this, the mixture was filtered and dried for around 12 h. Scanning electron microscopy (SEM) experiments were performed on palladium–gold-coated samples in a Hitachi apparatus (S-800). Fourier transform infra-red (FTIR) experiments were made on a spectrophotometer Magna-IR 560 from Nicolette. The powders were mixed with KBr in a 5% (w/w) mixture. The mixed powder was pressed to tablets of 1 cm diameter at 10 t for 1 min. The transparent tablets were inserted in the apparatus and the spectra were recorded from 4000 to 400 cm^{-1} with a resolution of 5 cm^{-1}. KBr reference spectrum and CO_2 from ambient have been subtracted to every spectrum in order to verify the functional surface groups presented on activated carbons.

3. Results and discussion

3.1. Characterization of activated carbons

BET surface areas and pH_{PZC} of AC are presented in Table 1. As expected, the higher the concentration of chemical compounds employed prior to the activation of AC, the lower pH_{PZC} values of AC. Table 1 showed that this is a general trend for all types of AC studied. For all concentrations, AC prepared with H_3PO_4 showed lower pH_{PZC} values than those AC prepared with $ZnCl_2$. For example, it can be noted from Table 1 that AC prepared with 1% (w/w) H_3PO_4 is clearly lower that that obtained for the same concentration of $ZnCl_2$ (4.7 against 6.4). This is the consequence of H_3PO_4 is a strong Brönsted acid while $ZnCl_2$ is a Lewis acid. Therefore, the first one should introduce more acidic groups in AC surface. In spite of AC were

Table 1
Summary of BET surface areas (S_{BET}) and surface pH (pH_{PZC}) of AC studied

System	S_{BET} (m^2 g^{-1})	pH_{PZC}
TiO_2	50	6.5
$AC_{ZnCl_2\text{-}65\%}$	2001	4.5
$AC_{ZnCl_2\text{-}35\%}$	2485	4.8
$AC_{ZnCl_2\text{-}5\%}$	561	6.0
$AC_{ZnCl_2\text{-}1\%}$	30	6.4
$AC_{H_3PO_4\text{-}65\%}$	1569	3.1
$AC_{H_3PO_4\text{-}35\%}$	1987	3.5
$AC_{H_3PO_4\text{-}5\%}$	414	4.0
$AC_{H_3PO_4\text{-}1\%}$	188	4.7
$AC_{KOH\text{-}65\%}$	309	6.1
$AC_{KOH\text{-}50\%}$	476	6.5
$AC_{KOH\text{-}5\%}$	17	7.5
$AC_{KOH\text{-}1\%}$	5	7.7

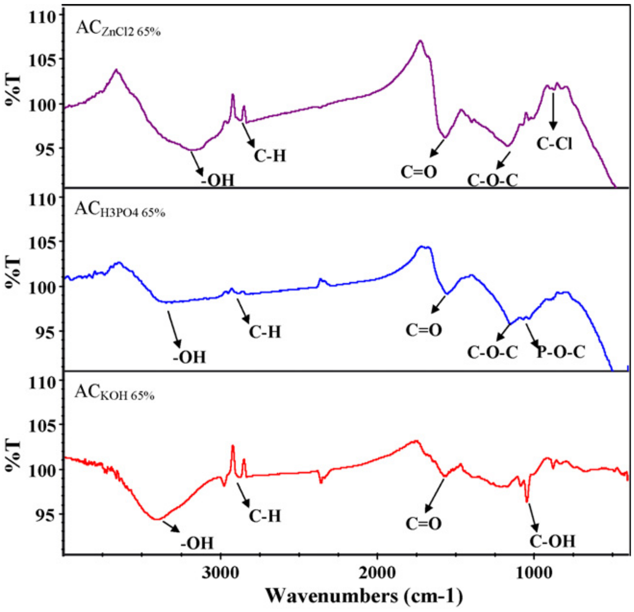

Fig. 1. FTIR spectra of some selected activated carbons.

washed extensively with hot water (around 80 °C), some remnant phosphorus and chloride remains on AC forming functional groups on its surface. This can be seen from FTIR showed in Fig. 1 that will be explained below. Also, it must to be note that activated carbons prepared with KOH showed an apparent unexpected behaviour. That is, thought KOH is a strong Lewis base, Table 1 show 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 can be explained by previous results of some of us [21,22] that showed that AC prepared with KOH develop a high structural disorder in their graphene sheets in comparison of H-type AC that commonly are carbon with basic surface nature and topologically more similar to graphite [16,21,22]. Structural chaos in the border of graphene sheets favors the reaction of carbon atoms with hydroxyl groups from KOH with concomitant formation of carboxylic acid groups [23-26]. These groups were detected by FTIR spectroscopy as we pointed above for the cases of phosphorous and chloride surface compounds (Fig. 1). Different types of acid, basic and other functional groups on AC surface were also detected in agreement with previous results [24,26]. For example, the presence of the main acid group, carboxylic acid, was detected in all AC but with less intensity in those prepared with KOH in concordance with pH_{PZC} values presented in Table 1. Phenol, another important acid was also detected in all AC but the comparison between AC_{ZnCl_2} against $AC_{H_3PO_4}$ clearly show a more important peak of such group in $AC_{H_3PO_4}$ in agree with lower pH_{PZC} (Table 1) for all concentration range studied. On the other hand, the most important basic group presented in AC [24,26] as cyclic ethers, was poorly detected in all AC. This is in agreeing with the acid surface nature detected in practically all AC of the present work. Finally, it must to be remarked the presence of cyclic peroxides and fundamental stretching mode of C–Cl bonds in AC_{ZnCl_2} and phosphates in $AC_{H_3PO_4}$ (Fig. 1). In short, FTIR analysis of the functional groups on surface of AC is in concordance with values of surface pH detected by the drift method. Regarding to BET surface areas (S_{BET}), it can be seen from Table 1 that the higher the concentration of impregnation compounds the higher the surface BET areas having a maxima of about 2485, 1987, and 476 $m^2 g^{-1}$ 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 concentration than those indicated above a clear decrease in S_{BET} is observed in all different types of AC prepared (Table 1). This experimental fact has been already reported by some of us for the activation of other carbonaceous precursors of activated carbon as Saccharose [21] and *Hymenaea courbaril* wood [25]. In these works, the decrease in S_{BET} was explained by the presence of a high concentration of steam produced during the thermal decomposition of the impregnated compounds. In another work [22] we have proposed that water molecules are responsible of the activation of the carbonaceous precursor by means of the gasification reaction: $C + H_2O \rightarrow H_2 + CO$. In short, from characterization results both of S_{BET} as pH_{PZC} in Table 1, it can be concluded that AC prepared in the present study are of L-type. This was expected because the presence of chemical impregnation compounds and the low activation temperature commonly leads to L-type AC [24], characterized by very high surface areas (Table 1) and high oxygen content forming oxygenated functional groups on the surface of AC (Fig. 1) principally of acid chemical nature giving therefore, AC with low surface pH as those indicated by pH_{PZC} in Table 1. This preliminary conclusion is very important because it would permits to understand the surface interaction between AC and TiO_2.

3.2. *Kinetics of 4CP adsorption in the dark*

Preliminary studies of 4-chlorophenol adsorption at 20 °C were performed on Titania (50 mg), AC (10 mg), and the suspended mixture TiO_2/AC with the same respective masses. These weights were performed because in a previous study of phenol degradation they showed the maxima photoactivity [10]. Kinetics of adsorption in the dark was followed by 80 min under stirring for different initial concentrations between 0.78×10^{-3} and 7.80×10^{-3} mol L^{-1}. In all cases, most of adsorption occurred within 20 min but to ensure a proper equilibrium of adsorption a longer period (80 min) of adsorption in the dark was considered in the photodegradation experiments. The kinetics of 4CP adsorption in the dark for some selected systems are given in Fig. 2 for an initial concentration $C_o = 0.78 \times 10^{-3}$ mol L^{-1} (100 ppm) and the Fig. 3 show the adsorption isotherms $n_{ads} = f(C_{eq})$ of systems from Fig. 2. Assuming the conventional Langmuir isotherm model with a surface coverage θ varying as

$$\theta = \left(\frac{n_{ads}}{n_T}\right) = \left[\frac{K_{ads} C_{eq}}{(1 + K_{ads} C_{eq})}\right] \qquad (1)$$

the total number of adsorption sites n_T and the adsorption constants K_{ads} were obtained from the linear transform $(1/n_{ads}) = f(1/C_{eq})$, obtaining correlation coefficients in most of cases close or higher than 0.99. The corresponding values for

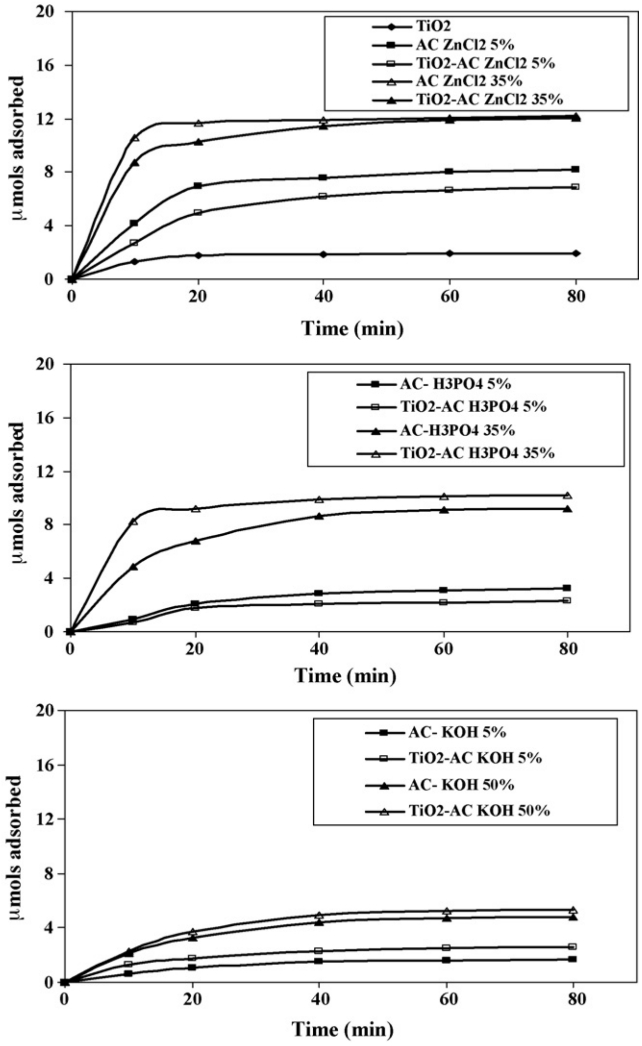

Fig. 2. Kinetics of adsorption in the dark of 4CP with some chemically AC.

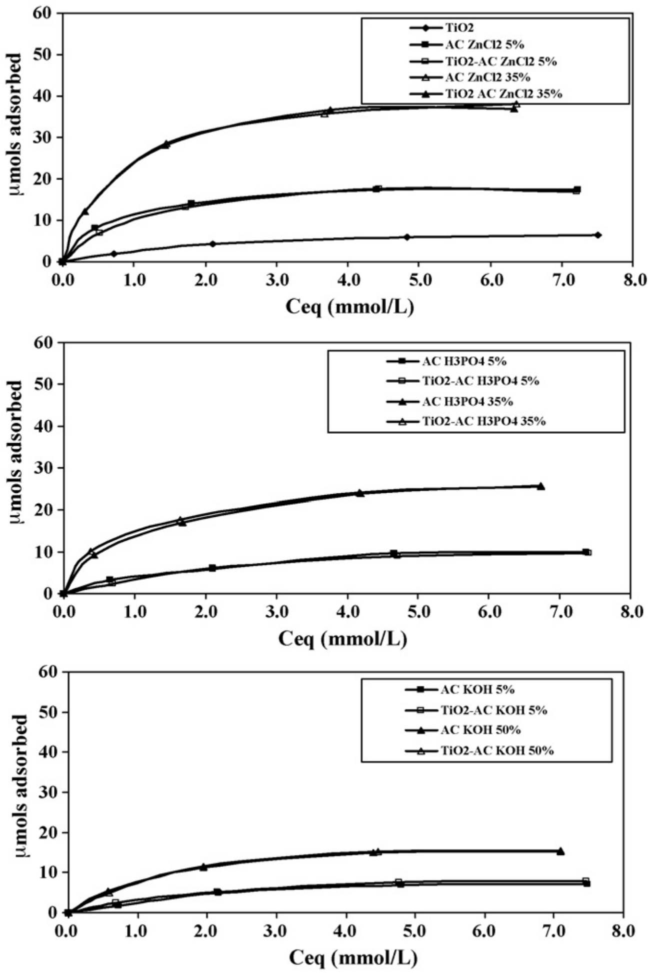

Fig. 3. Adsorption isotherms in the dark of 4CP of catalysts from Fig. 2.

these photocatalytic systems are given in Table 2. Remarkable differences were detected when 4CP adsorption parameters (K_{ads} and n_T) obtained on the mixed system are compared against those of TiO_2 and AC separately. For example, it can be seen from Fig. 2 that micromoles of 4CP adsorbed in the dark on the mixed system is slightly but significantly higher than on pure AC. However, considering n_T values from Table 2 it can be clearly observed that total number sites of 4CP adsorption on TiO_2-AC are smaller than theoretical ones indicating that there are no additive effects in 4CP adsorption between both solids. Comparing TiO_2-$AC_{ZnCl_2\text{-}35\%}$ with TiO_2 and $AC_{ZnCl_2\text{-}35\%}$, the total number of adsorption sites decreased by 22% and the adsorption constant decreased by ca. 24%. Also, if compared TiO_2-$AC_{ZnCl_2\text{-}5\%}$ against TiO_2 and $AC_{ZnCl_2\text{-}5\%}$, this fact is more pronounced being of about 31and 29% for the decrease in n_T and K_{ads}. In general, this behaviour is reproducible in the other systems included in Table 2. This fact have been already reported by some of us [10,12] for other TiO_2-AC systems and has been ascribed to a strong interaction between Titania particles and AC, which creates an intimate interface non-accessible to phenol molecules from the solutions. It is physically logical to think that as consequence of this common interface created during homogenization of the mixture of both solids, some of total number sites of adsorption would be lost in agree with results described above. From the study of adsorption in the dark we select $0.78 \times 10^{-3}\ \text{mol L}^{-1}$ as initial concentration of 4CP for the study of photodegradation that will be discussed in the fol-

Table 2
Langmuir Parameters: adsorption constant (K_{ads}) and total adsorption sites (n_T) for activated carbons chemically activated

System	K_{ads} (L/mol)	n_T (mol)	R^2
TiO_2	384	0.913E-05	0.9961
$AC_{ZnCl_2(35\%)}$	1281	4.33E-05	0.9717
TiO_2-$AC_{ZnCl_2(35\%)}$	1274	4.09E-05	0.9806
$AC_{ZnCl_2(5\%)}$	1185	1.93E-05	0.9868
TiO_2-$AC_{ZnCl_2(5\%)}$	1121	1.96E-05	0.9807
$AC_{H_3PO_4\,(35\%)}$	1161	2.76E-05	0.9842
TiO_2-$AC_{H_3PO_4\,(35\%)}$	1577	2.66E-05	0.9921
$AC_{H_3PO_4\,(5\%)}$	521	1.24E-05	0.9876
TiO_2-$AC_{H_3PO_4\,(5\%)}$	360	1.27E-05	0.9937
$AC_{KOH\,(50\%)}$	664	1.96E-05	0.9985
TiO_2-$AC_{KOH\,(50\%)}$	527	2.04E-05	0.9887
$AC_{KOH\,(5\%)}$	229	1.28E-05	0.9985
TiO_2-$AC_{KOH\,(5\%)}$	214	1.18E-05	0.9887

lowing section. Also, the above study permits us to conclude that employing 80 min for the kinetic of 4CP adsorption in the dark we ensure a proper equilibrium. This fact can be easily inferred from Fig. 2 which showed that practically 4CP reached the equilibrium in the adsorption process after this time.

Finally, when the 4CP adsorbed in the dark was compared versus BET surface area of AC a straight line was found. This behaviour was expected because the Langmuir mechanism of adsorption of gases and liquids on solids clearly permits to infer that the higher surface area of a solid the higher active sites that can be employed to adsorption processes, in this case of 4CP. Moreover, taking into account that L-type AC developed a very similar chaotic topology [22,25] in the shaped of closed structure, the above comparison is perfectly valid.

3.3. Kinetics of 4CP photodegradation

Fig. 4A and B show the kinetic results of 4CP photodegradation ($C_o = 0.78 \times 10^{-3}$ mol L^{-1}) as a function of reaction time for neat TiO_2, $AC_{ZnCl_2\text{-}65\%}$, and different TiO_2-AC_{ZnCl_2} mixed systems. For comparative purposes the degradation of 4CP by direct photolysis (in the same experimental conditions described in Section 2) is also showed in Fig. 4. The first point to be remarked corresponds to the fact that as a period of adsorption in the dark of 80 min for 4CP onto the different materials was performed previous to UV-irradiation. As indicated above, this preliminary stage permit us to estimate appropriately the apparent-constant rate values taking into account only the photocatalytic process. The second point to be noted is that the direct photolysis was negligible compared to the photocatalytic degradation (Fig. 4A) in concordance with the fact that the lamp flux was cut-off only to near-UV and visible light. Also, the disappearance of 4CP under UV-irradiated AC is negligible (Fig. 4A), which confirms that activated carbons are photoinactive in 4CP photodegradation in agree with previous results [12]. In addition, from the kinetic trends of 4CP disappearance (Fig. 4) it can be inferred that most of mixed systems, either TiO_2 or TiO_2 with AC prepared after impregnation with different concentration of $ZnCl_2$ follow an apparent first-order rate. This fact was also observed for AC prepared with H_3PO_4 or KOH (not shown). In concordance with this, linear transformation of kinetic results, $\mathrm{Ln}(C_o/C_t) = f(t)$, were employed to estimate apparent-constant rate of first-order (k_{app}) as the best kinetic parameter for the comparison between photocatalysts. The linear regression from kinetic data of Fig. 4 is shown closed inset Fig. 4A. A summary of kinetic results of 4CP adsorption and disappearance detected on different systems studied in this work is presented in Table 3. This treatment showed linear regression factors closely to unity that permits us to infer that reaction kinetics follows a first-order mechanism. After compare data from Table 1 against those in Table 3, it can be seen as a general trend that the higher is BET surface areas the higher the 4CP adsorbed in the dark. Moreover, it can be noted that maxima quantities of 4CP adsorbed in the dark on the mixed systems (Table 3) corresponds to the samples with maxima BET surface area (Table 1). This is particularly truth for the AC prepared after impregnation with $ZnCl_2 \cdot yH_3PO_4$. On the contrary, after comparison of values of S_{BET} or pH_{PZC} in Table 1 and k_{app} from Table 3, it is evident that there is no linear correlation between these parameters. For example, the mixed systems that adsorbed more quantities of 4CP in the dark were not the systems with the best photoefficiency in the degradation of 4CP. However, in terms of the surface coverage, it looks clear that for the cases of high values of θ, the mixed systems showed an increase in the photocatalytic activity represented by the factor F in Table 3. In other words, BET surface area is an important parameter that permits to improve the photoactivity of TiO_2 because it can improve the tendency to adsorb higher quantities of the pollutant but it is not the only important parameter and the present results seems to suggest that surface chemistry of AC, that means, their chemical composition on the surface, play the most important role on the photocatalytic activity of the semiconductor. For example, contrary to previous results [11,12], the present study clearly show that some L-type AC induces a beneficial effect on the photoactivity of TiO_2, thought their pH_{PZC} are lower than that of the semiconductor (Table 1). In short, as AC is photoinactive, it can be inferred that this cooperative influence is a synergistic effect which is represented by $F > 1$ values in Table 3, giving a maxima of 2.22 for the TiO_2-$AC_{ZnCl_2\text{-}5\%}$ photocatalyst. On the contrary, those systems where the interaction between AC with TiO_2 inhibits the photoactivity of the semiconductor show $F < 1$ giving a minimum of 0.26 for TiO_2-$AC_{KOH\text{-}1\%}$ (Table 3). The different types of interaction between both are discussed more

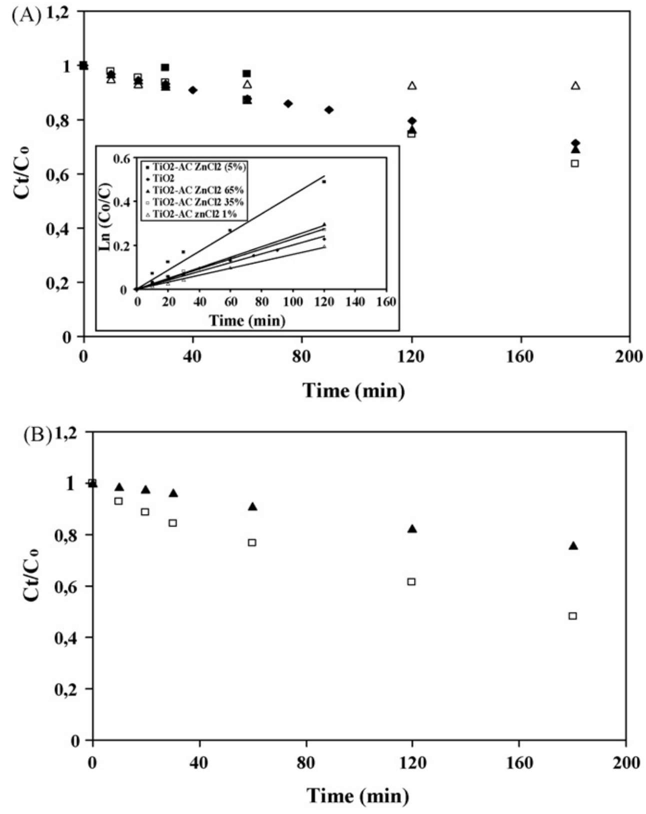

Fig. 4. Kinetics of disappearance of 4CP with AC prepared after impregnation with $ZnCl_2$. (A) (♦)TiO_2; (△) Photolysis; (■) $AC_{ZnCl_2-65\%}$; (□) $TiO_2 - AC_{ZnCl_2-65\%}$; (▲) $TiO_2 - AC_{ZnCl_2-35\%}$. (B) (□) TiO_2-$AC_{ZnCl_2-5\%}$; (▲) $TiO_2 - AC_{ZnCl_2-1\%}$.

Table 3
Kinetic results of adsorption at equilibrium in the dark of 4-chlorophenol ($4CP_{\text{ads-dark}}$) and apparent first-order constant rate (k_{app})

System	$4CP_{\text{ads-dark}}$ (%)[a]	$\Theta = (n_{\text{ads}}/n_{\text{T}})$[a]	$k_{\text{app}} \times 10^{-3}$ (min^{-1})	F[c]
TiO_2	9.8	0.21	2.02	1.00
TiO_2-$AC_{ZnCl_2\ 65\%}$	48.4	–[b]	1.98	0.98
TiO_2-$AC_{ZnCl_2\ 35\%}$	61.2	0.17	2.29	1.13
TiO_2-$AC_{ZnCl_2\ 5\%}$	34.8	0.62	4.49	2.22
TiO_2-$AC_{ZnCl_2\ 1\%}$	6.5	–[b]	1.59	0.79
TiO_2-$AC_{H_3PO_4\ 65\%}$	44.1	–[b]	1.25	0.62
TiO_2-$AC_{H_3PO_4\ 35\%}$	51.5	0.09	2.09	1.03
TiO_2-$AC_{H_3PO_4\ 5\%}$	11.6	0.86	3.36	1.66
TiO_2-$AC_{H_3PO_4\ 1\%}$	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

[a] Estimated from an initial 4CP concentration of about 0.78×10^{-3} mol L^{-1}.
[b] Not estimated in this study.
[c] Synergy or inhibition defined by: $F = [k_{\text{app}(TiO_2+AC)}/k_{\text{app}(TiO_2)}]$.

appropriately as follow. It is well-known that if aqueous pH is lower than that of Titania's pH_{PZC} (about 6.5) this fact clearly could introduce a massive protonation of hydroxyls groups on TiO_2 crystalline net inhibiting its photoactivity [3]. The fact that some AC are able to improved k_{app} for the 4CP photodegradation in comparison of TiO_2 alone, and the fact that some of them (particularly those prepared at low concentrations of $ZnCl_2$ and H_3PO_4 with representative lower values of pH_{PZC} in comparison of that for TiO_2) introduce a beneficial cooperative effect is in agreement with recently results obtained by other authors [27,28]. Those studies show that the addition of low concentrations of organic acids as ascorbic [27] or acetic [28] to aqueous suspensions with TiO_2 introduce modifications on the surface of semiconductor. For example, they showed that after dissociation in aqueous phase, carboxylic or acetic acid can coordinate to Ti^{+4} metallic centre of TiO_2, inhibiting the recombination of the photogenerated species in the semiconductor (e^-, h+). In addition, it is very well-known [3] that the inhibition of recombination of such species permits a higher concentration of hydroxyls ($^{\bullet}OH$) and superoxydes ($O_2^{\bullet -}$) radicals with a concomitant increase in the photoactivity of TiO_2, particularly in the photomineralization of aromatic organic molecules as 4CP. Now, in a previous work [25] we have shown that activated carbons prepared after impregnation with Lewis and/or Brönsted acids leads to the formation of oxygenated functional groups on the surface of AC. This is in agreement with results discussed in Section 3.1 in which, the present AC also have such kind of groups (Fig. 1). Therefore, if the surface concentration of such groups is enough low in the present AC, which is perfectly valid to consider in the present case of AC prepared at low impregnation concentrations of acids, in the case of the best photocatalytic results obtained employing TiO_2-$AC_{ZnCl_2\text{-}5\%}$ and TiO_2-$AC_{H_3PO_4\text{-}5\%}$ (Table 3), it can be suggested that we are in presence of a similar behaviour than that noted above. In other words, for the case of the mixed system that employs L-type AC, the synergy effect detected could be also attributed to the presence of low surface concentration of acidic oxygenated groups, particularly carboxylic acids that by means of the contact interface created between both solids, it would induce modifications on TiO_2 surface. The analogy is perfectly valid because once dissociated in aqueous phase, the carboxylic acid produce carboxylate anions (–COO^-) clearly stabilized by the possibility of transfer their electrons to the aromatic ring of the planar AC.

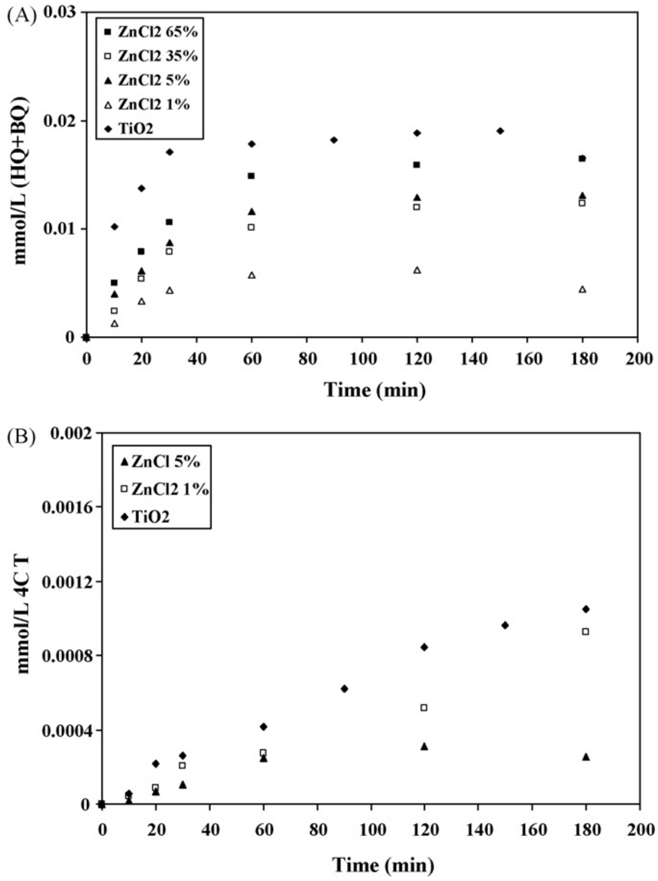

Fig. 5. Kinetics of appearance and disappearance of main intermediates in 4CP photodegradation in presence of activated carbons prepared after impregnation with $ZnCl_2$. (A) Hydroquinone (HQ) and benzoquinone (BQ). (B) 4-Chlorocathecol (4CT).

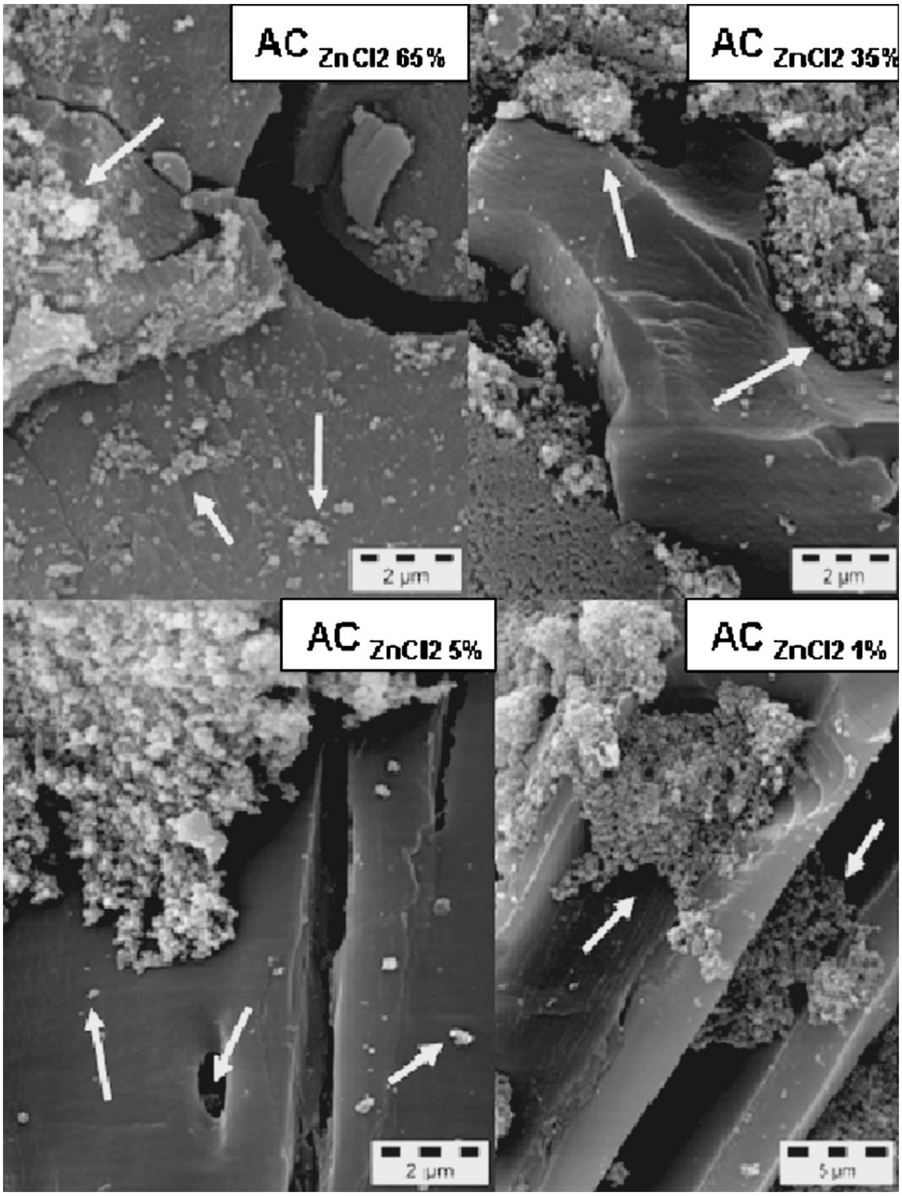

Fig. 6. SEM images from different TiO_2-AC_{ZnCl_2} photocatalysts.

Therefore, similar to the behaviour in aqueous phase noted above [27,28], the carboxylate anions on AC surface would be responsible of the synergy effect detected in the present work by means of a spontaneous contact interface created between both solids as we have reported [10]. This transfer of electronic density from AC to Titania is in agreement with recent works reported by us for the case of phenol photodegradation employing TiO_2 in conjunction with a commercial H-type AC [13] and in 4-CP photomineralization in presence of UV-irradiated Titania mixed with made-in-home H-type AC [16]. In those works, H-type AC are characterized by the presence of basic groups on its surface, as for example cyclic ethers and pirones and FTIR studies clearly showed that interaction between both solids occurs by means of oxygenated surface groups of AC. In short, not only the pH_{PZC} influence remarkably the surface properties of TiO_2 but also surface area of AC strongly influence the capability, selectivity and shape of 4CP adsorption in the dark on the mixed systems. As we discuss as follow, during the photocatalytic degradation of 4CP different intermediate product distributions were detected confirming this suggestion.

3.4. Kinetics of appearance and disappearance of intermediate products

The influence of physical and chemical properties of AC on the kinetics of adsorption in the dark (Table 2) and photodegradation of 4CP (Table 3) is confirmed by the fact that thought intermediate products generated during the degradation of 4CP are not quit different, according to the type of carbon materials employed, the proportion of the intermediate 4-chlorocathecol detected is clearly increased. This indicate that different surface sites governed by pH_{PZC} more than by

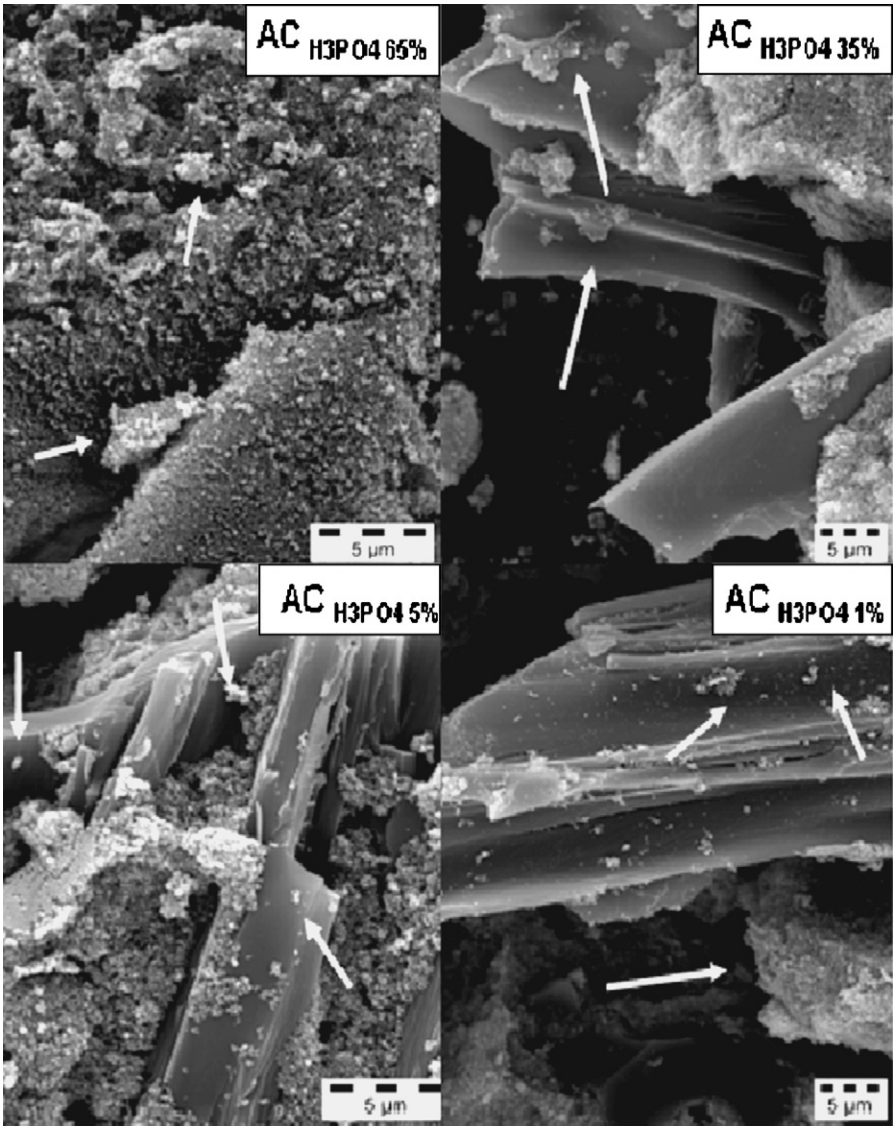

Fig. 7. SEM images from different TiO_2-$AC_{H_3PO_4}$ photocatalysts.

texture characteristics leads to different types of 4CP adsorption mechanism and therefore influence its photodegradation. These results are discussed as follow. The kinetics of appearance and disappearance of the main intermediate products detected on UV-irradiated TiO_2-AC_{ZnCl_2} photocatalysts during the 4CP photodegradation are showed in Fig. 5. The kinetic trends corresponding to the sum of HQ + BQ and 4CT are shown in Fig. 5A and B, respectively. In general, it can be seen from 5 that for TiO_2 alone and most of TiO_2-AC photocatalysts the main intermediate products are HQ + BQ, which at the present experimental conditions, are commonly in chemical equilibrium and for that reason are presented as a sum of both intermediates in Fig. 4A. This is a general trend that was also observed for the other mixed systems studied. However, from the quantitative comparison of 4CT detected it can be inferred that mechanism of photodegradation is influenced by a parallel oxidation (hydroxilation) reaction. For example, the maxima quantity of 4CT detected on TiO_2-$AC_{H_3PO_4\text{-}5\%}$ (not shown) was about 20 times higher than that detected on TiO_2-$AC_{ZnCl_2\text{-}5\%}$ (Fig. 5B). Therefore, it looks reasonable that a different type of mechanism adsorption of 4CP on TiO_2-$AC_{H_3PO_4}$ should be occurring that clearly influence the photoactivity of TiO_2 because synergy effect is clearly lower ($F = 1.66$ against 2.22 in Table 3). This result is totally in agree with previous ones [10,12,14] obtained during the photodegradation of phenol, 4-chlorophenol and 2,4-dichlorophenoxyacetic acid. In those works we found that employing L-type AC prepared by the activation at low temperature and after impregnation with 34% (w/w) phosphoric acid the photodegradation of such pollutants ocurred preferentially by means of ortho hydroxylated intermediates products yielding cathecol or 4-chlorocathecol as in the present case. In a recent publication, some of us [13] have demonstrated that if the quantities of the intermediates main products is enough high in the aqueous phase, they can compete with the pollutant by the original ones sites of adsorption with a concomitant less or inhibition of Titania's photoactivity. This fact is perfectly valid

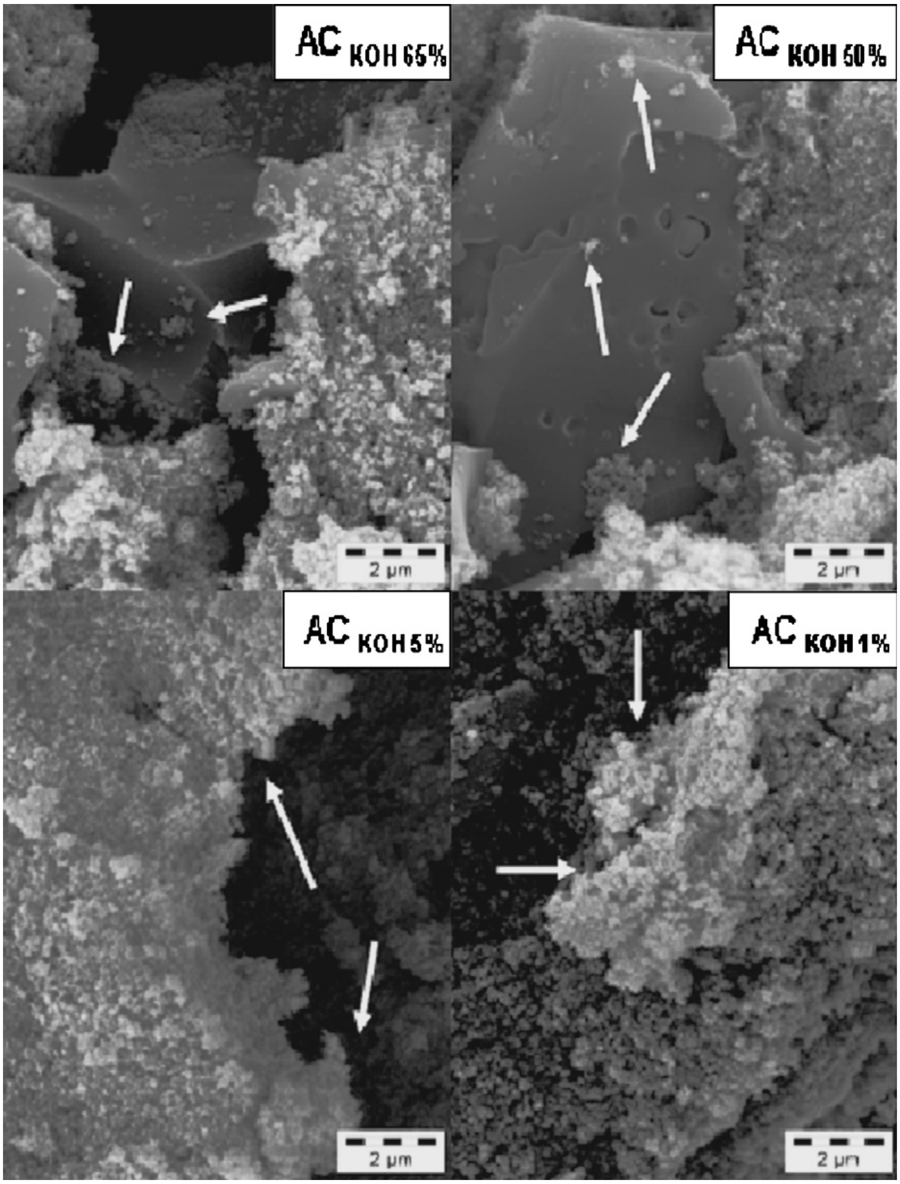

Fig. 8. SEM images from different TiO_2-AC_{KOH} photocatalysts.

to explain the very low values of k_{app} (Table 3) obtained for the very acid AC employed that yield the highest intermediated products concentrations.

3.5. *Surface nano-aggregation of TiO_2*

Figs. 6–8 show a composition of scanning electronic microscopy (SEM) images of the mixed photocatalytic systems TiO_2-AC_{ZnCl_2}, TiO_2-$AC_{H_3PO_4}$ and TiO_2-AC_{KOH}, respectively, for different concentration of the impregnation compounds. These samples were prepared at least by triplicate and important changes in morphologies of the different SEM images were not detected indicating that this characterization permit us to propose that pH_{PZC} play an important role upon the common interface created between both solids. In a general way, all images presented in Figs. 6–8 suggest that the higher the concentration of the impregnation compound and therefore more acid the pH_{PZC} of the AC, the more the TiO_2-AC mixtures present aggregations of Titania particles. As pointed above, the presence of more acid functional groups on AC surface could be responsible of the transfer of electronic density from AC to Titania by means of a common surface interface. Thus, if surface pH of AC is lowering for the case of more acidic concentration of impregnating agents, therefore it results reasonable to suggest that if high quantities of acid surface groups are presented on AC, the contact interface should be so high that it promotes the conglomerates of TiO_2 particles. For example, in a previous work [10] we have shown that this contact interface spontaneously created between both solids can reach up to half of the surface BET area of TiO_2. Therefore, the above suggestion seems to be reasonable because in the case of less acid mixed systems, as for example TiO_2 with $AC_{ZnCl_2\text{-}5\%}$ or $AC_{H_3PO_4\text{-}1\%}$, in Figs. 6 and 7, respectively, Titania particles show a higher level of dispersion on those AC surfaces. We employ the term nano-aggregation because the mean size of primary particles of TiO_2-P25 is about 30 nm [10] while the micro scale of SEM images is between 2 and 5 μm. Therefore, aggregates observed in Figs. 6–8 are clearly several hundred nanometres in size higher than that of TiO_2 primary particles, and the magnitude of aggregation depends of pH_{PZC} of AC. As we discussed in Section 3.3 and listed in Table 3, the influence of AC on Titania (synergism or inhibition) is principally controlled by the pH_{PZC} of the support. In other words, if the surface of AC is more acid, the nano-aggregation of TiO_2 particles is therefore clearly promoted with a concomitant decrease in the common contact interface between both solids. This fact, not only affect the driving force of diffusion of the pollutant adsorbed preferentially on AC to the semiconductor, but also in the nano-agregation of Titania particles, most of them would not be photoexcited by UV-irradiation which clearly affect the photoefficiency of the system. Thus, on the base of these results it can be suggested that for some L-types AC the presence of an effective common contact interface created between AC and TiO_2, some electronic density would be transferred from the AC to the semiconductor, principally if the carbonaceous support is characterized by the presence of some kinds of functional oxygenated groups on its surface as carboxylic acids.

4. Conclusions

Present results show that L-type AC can induce both beneficial as detrimental effects on the TiO_2 activity in the photocatalytic degradation of 4CP. A synergy effect between both solids was quantified by a factor of 2.22 (TiO_2-$AC_{ZnCl_2-5\%}$), 1.66 (TiO_2-$AC_{H_3PO_4\text{-}5\%}$) and 1.44 (TiO_2-$AC_{KOH\text{-}50\%}$). This effect has been attributed to low concentrations of carboxylic acid groups presented on AC surface that were detected by FTIR spectroscopy. This kind of organic functional groups would permit a proper transfer electronic density from AC to TiO_2 by means of a common contact interface that inhibits the recombination of photogenerated couple in agree with previous works of us and other groups. In short, present results show that it is possible to obtain clean water in a shorter period of time employing TiO_2 in conjunction with well designed AC. In a near future we will present a comparison between the present results against immobilized semiconductor particles on carbon films (prototype of solar collector).

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