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Optimisation of the photocatalytic activity of TiO_2 and mixtures of TiO_2 + *activated carbon* through dosage processes

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Abstract

The present paper shows the behaviour of TiO_2 and mixtures of TiO_2 + *activated carbon* when the organic to be degraded is progressively dosed in an aqueous catalyst suspension. Thus, we have studied *phenol*, *salicylic acid* and *p-aminophenol* degradation, observing that it is possible to obtain a ten times faster degradation when the compound is dosed in comparison to the direct treatment of the concentrated solution (>100 ppm). The highest concentration to be effectively treated by dosification and without saturation problems has been established for the different organics tested. Also, FTIR studies on the interaction of these molecules with the surface of these catalysts have been carried out. Degradation mechanisms under the experimental conditions employed and the effect of the organic molecules interaction with the catalysts surface has been proposed. In addition to this, catalyst reactivation processes through adsorbed intermediates have been noticed.

Introduction

Photocatalysis, as an advanced oxidation treatment, is considered nowadays as one of the most promising technique (1-4). However, photocatalytic studies have mainly been focused on studies of individual molecules more than on the treatment of real wastes (5-8). This is basically due to the catalyst activity loss with time. The deactivation is both of chemical and physical nature and occurs simultaneosly with the main reaction (9). In fact, photocatalysis is efficient at degrading organic pollutants at low concentrations at which processes such as coagulation, catalyst poisoning, pores blockage, etc, are minimised. The application

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*To whom correspondence should be addressed of photocatalysis to highly concentrated solutions has been constrained by the slowing down of the process, probably because of the mentioned processes.

Taking into account these facts our research group has tried to solve this problems by the dosification of the contaminant to be degraded. The experimental procedure has the following steps:

- In a 250 mL glass vessel TiO_2 or an AC + TiO_2 mixture has been suspended in 200 mL of water at pH 5.
- Then, the UV lamp was switched on and the solution containing the organic pollutant was progressively added to the reactor.
- Different dosing rates between 1 and 8 ppm/min were tested during 90 min. of reaction time. The process was monitored by measuring the TOC evolution every 15 min.

In the present paper the results obtained from *phenol, salicylic acid* and *p-aminophenol* aqueous solutions degradation are discussed and compared with the degradation of the concentrated samples (100 ppm).

Experimental

TiO_2 was *Degussa P-25* (80 % anatase). Catalysts with *activated carbon* (640 m^2/g) were obtained by mixing TiO_2 with *the carbon* at different proportions in an aqueous suspension continuously stirred for 1 h. After this, the mixture was filtered. The unmixed TiO_2 is denoted as bare-TiO_2 and that containing a 13 % w/w *activated carbon* as AC-TiO_2 (130 m^2/g).

Experimental conditions:

The following experimental conditions were employed for all experiments: 250 mL glass vessels reactors, 200 ml water at pH 5, and different doses of *phenol, salicylic acid* or *p-aminophenol* depending on the experiment (1, 2, 3... ppm/min). TiO_2 and AC-TiO_2 concentration were alwasys 2 g/L. Catalysts suspensions were continuously stirred and air-bubbled (100 ml/min). For FTIR analysis catalysts were impregnated with a saturated *phenol, salicylic acid* or *p-aminophenol* water solution and placed after 15 min. between two CaF_2 for spectra acquisition.

Equipments:

The concentrations of the remaining *phenol, salicylic acid,* 4-amino*phenol* and reaction intermediates at different reaction times were HPLC-measured by using a reverse phase column (C18) Zorbax ODS 5μ (Jones Chromatography) and a 0.2 M phosphoric acid mobile phase, using an UV detector (λ= 210 nm). TOC (total organic carbon), TC (total carbon) and IC (inorganic carbon) were measured by using a TOC Shimadzu 5000-A.

For FTIR experiments a FTIR spectrophotometer model RS/1 (UNICAM) was used. An internal reflection device (Standard Circle Liquid Analyzer, Spectra-tech, Inc.) has been employed for solution samples. Intervals of 2000 to 1000 cm^{-1}, a resolution of 2 cm^{-1} and a forward and reverse moving mirrors speed of 10 and 6.2 kHz, respectively were used. Water reference spectrum has been subtracted to every spectra.

Results

Phenol

Figures 1 and 2 show the results of the 100

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ppm *phenol* solution degradation by the catalysts TiO_2 and AC-TiO_2 and those when the organic is added by dosification (1, 2, 3 and 5 ppm/min).

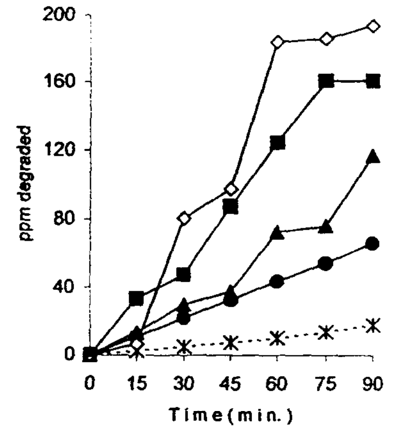

Figure 1. ppm degraded during *phenol* degradation with bare-TiO_2 catalyst. ✱ 100 ppm at t= 0 min, • 1 ppm/min, ▲ 2 ppm/min, ■ 3 ppm/min, ◇ 5 ppm/min.

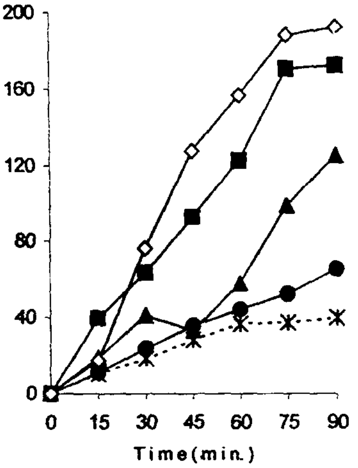

Figure 2. ppm degraded during *phenol* degradation with AC-TiO_2 catalyst. ✱ 100 ppm at t= 0 min, • 1 ppm/min, ▲ 2 ppm/min, ■ 3 ppm/min, ◇ 5 ppm/min.

As it can be osbserved, after 90 min. of reaction time only about 20 ppm have been degraded from the concentrated solution. On the contrary, when *phenol* is dosified about 200 ppm are degraded in the same time.

During dosification experiments catalyst reactivation processes seemed to occur, since in some cases periods of fast and slow kinetics were observed. In fact, it has been already indicated that some *phenol* degradation intermediates can improve the catalytic by

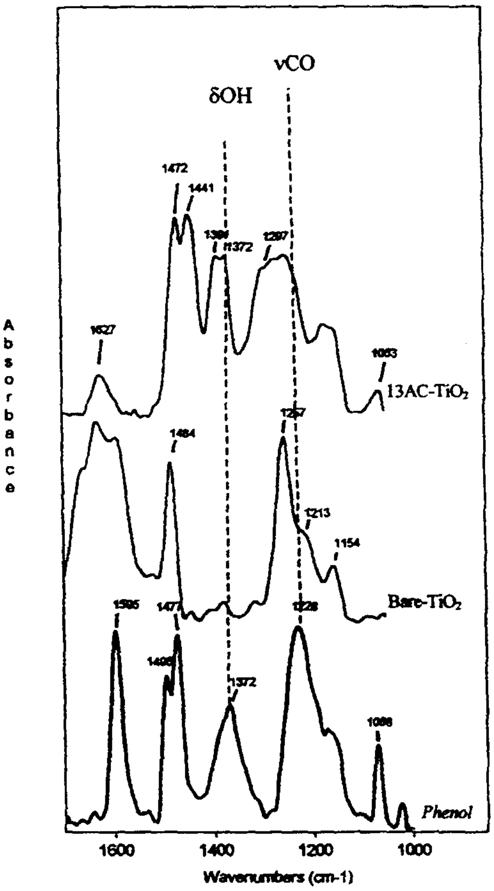

Figure 3. IR spectra from the interaction of satured *phenol*/H_2O solution with the different catalysts.

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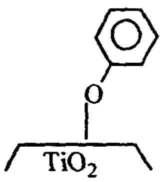
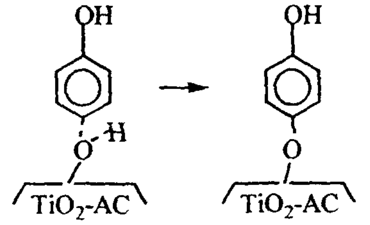
means of their adsorption onto the catalyst surface (6). Doses higher than 5 ppm/min are not effective because of the possible catalyst surface saturation, resulting in the process rate reduction.

The interaction of *phenol* molecules with the catalysts surface has already been studied by FTIR (10). Figure 3 shows the FTIR spectra obtained from the *phenol* interaction with the indicated catalysts and the molecule reference spectrum.

In the spectrum from the molecule interaction with the bare-TiO_2 catalyst the disappearance of the δOH vibration can be clearly observed, in addition to the νCO and νC=C vibrations shifts. These changes in the *phenol* spectrum have been attributed to the formation of a phenoxo compound, as it has been described (11, 12):



Nonetheless, in the spectra from the *phenol* interaction with the catalyst 13AC-TiO_2 the δOH vibration does not disappear, contrary to this, it seems that this band and that from the νC-O vibration tend to grow wider. Also, the intensity reduction and shift to higher wavenumbers of one of the νC=C vibrations (the one located at higher wavenumbers) is observed. These changes are proper of symmetric substitutions in the aromatic ring. In addition to this, a new band at 1441 cm^{-1} is observable. This band has also been noticed in FTIR studies carried out by our research group with hydroquinone and TiO_2. As a conclusion it seems that the *phenol* interaction with these catalysts can be giving species like:



This change in the *phenol* interaction with the catalyst AC-TiO_2 could be the cause of the slightly better catalytic behaviour observed for this catalyst.

Salicylic acid

Figures 4 and 5 show the *salicylic acid* degradation results by the catalysts TiO_2 and AC-TiO_2 when the organic is added by dosage (1, 2, 5 y 6 ppm/min) and the concentrated 100 ppm *salicylic acid* solution is treated.

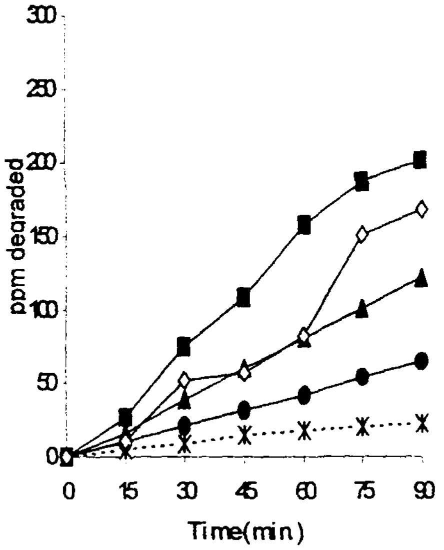


Figure 4. ppm degraded during *salicylic acid* degradation with bare-TiO_2 catalyst. ✱ 100 ppm at t= 0 min, • 1 ppm/min, ▲ 2 ppm/min, ■ 5 ppm/min, ◇ 6 ppm/min.

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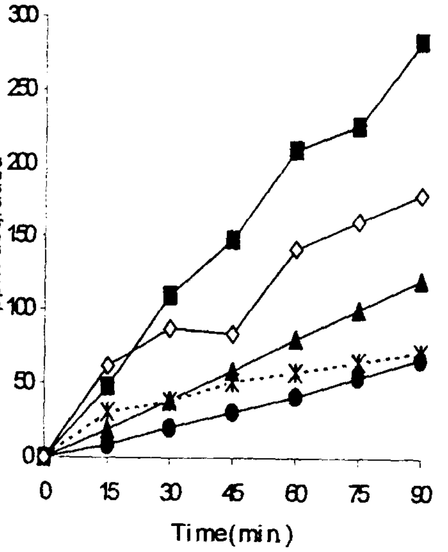

Figure 5. ppm degraded during *salicylic acid* degradation with AC-TiO_2 catalyst. ✱ 100 ppm at t= 0 min, • 1 ppm/min, ▲ 2 ppm/min, ■ 5 ppm/min, ◇ 6 ppm/min.

Similarly to the obtained with *phenol*, the *salicylic acid* dosage achieves stronger degradations being the 5 ppm/min dosage the most adequate. *Salicylic acid* shows a remarkable faster degradation rate than phenol, since under the same conditions (5 ppm/min) 190 ppm of *phenol* have been degraded while almost 280 ppm of *salicylic acid* have been eliminated by the catalyst TiO_2+AC.

Oppositely to the observed in the *phenol* degradation, the addition of AC significantly improves the TiO_2 catalytic behaviour. With the goal of determining if these changes can be associated with modifications of the molecule interaction with the catalyst surface FTIR studies of the catalyst impregnated with the compound were carried out.

Figure 6 shows the *salicylic acid* interaction with the catalyst and the nolecule reference FTIR spectra.

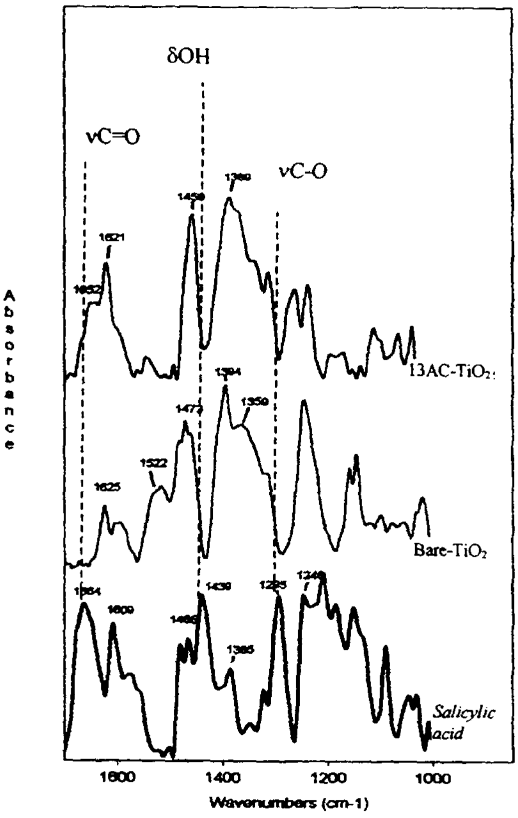

Figure 6. IR spectra from the interaction of satured *salicylic acid*/H_2O solution with the different catalysts. *salicylic acid* reference spectrum is also shown (10).

If the spectrum from the acid interaction with the bare-TiO_2 catalyst is compared with the reference spectrum the disappearance of the *salicylic acid* characteristic bands at 1295, 1439 and 1664 cm^{-1} can be observed (13). Also, a new band at 1522 cm^{-1}, attributable to the formation of the corresponding salt is noticed. On the other hand, in the spectrum from the molecule interaction with the catalysts containing AC the νC-O and δOH vibrations are not present, however the band at

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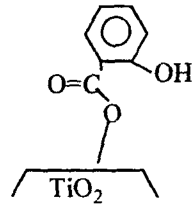
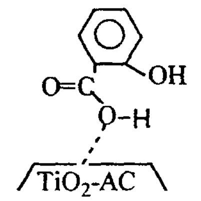
1525 cm^{-1} is not observable and the $\nu C{=}O$ at 1652 cm^{-1} is visible but shifted from its original position. Taking into account these results the following possible coordinations can be found:





The weak coordination of the *salicylic acid* with the catalyst TiO_2-AC could be the cause of its better catalytic behaviour during dosage.

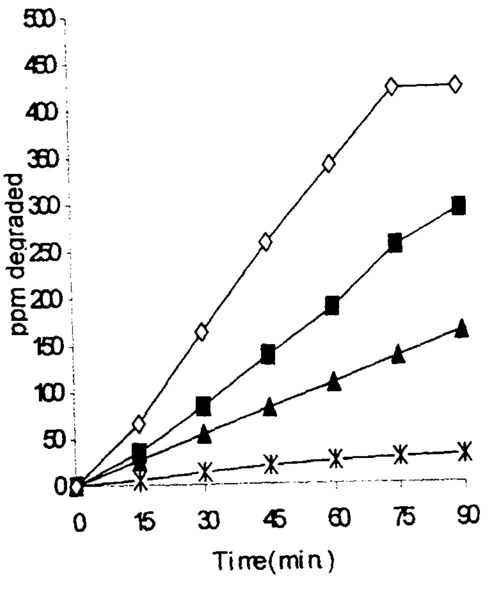


Figure 7. ppm degraded during *p-aminophenol* degradation with bare-TiO_2 catalyst. ✱ 100 ppm at t= 0 min, ▲ 2 ppm/min, ■ 5 ppm/min, ◇ 8 ppm/min.

p-aminophenol

Figures 7 and 8 show the *p*-amino*phenol* degradation results by the catalysts TiO_2 and AC-TiO_2 when the organic is added by dosage (2, 5 y 8 ppm/min) and the concentrated 100 ppm *salicylic acid* solution is treated.

Similarly to the obtained with *phenol* and *salicylic acid* the *p*-amino*phenol* dosage degradation is significantly faster than that of the concentrated solution. Also, the fastest *p-aminophenol* degradation if compared with those of *phenol* and *salicylic acids* must be pointed out. While about 190 and 280 ppm of these compounds are degraded (respectively with AC-TiO_2 catalyst, 5 ppm/min), up to 330 ppm of *p-aminophenol* have been eliminated in 90 min. Additionally, *p-aminophenol* can achieve a 8 ppm/min dosage without any noticeable saturation process. Also, significantly differences between both catalysts have been observed.

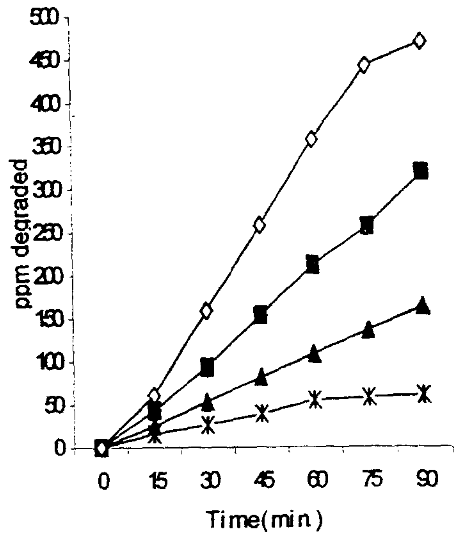


Figure 8. ppm degraded during *p-aminophenol* degradation with AC-TiO_2 catalyst. ✱ 100 ppm at t= 0 min, ▲ 2 ppm/min, ■ 5 ppm/min, ◇ 8 ppm/min.

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Similarly to the other tested compounds FTIR studies have been carried out in order to determine the organic interaction with the catalysts surfaces.

Figure 9 shows the FTIR spectra obtained from the amino*phenol* interaction with the catalysts bare-TiO_2 and AC-TiO_2, and the molecule reference spectrum.

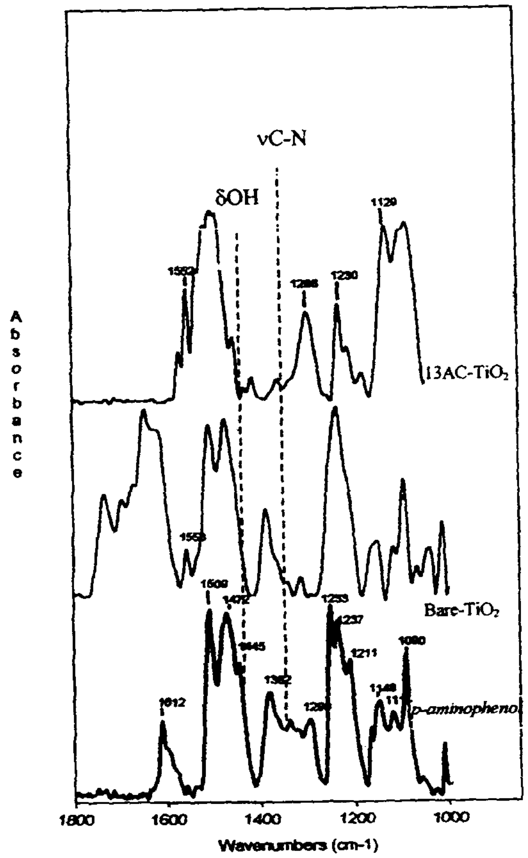
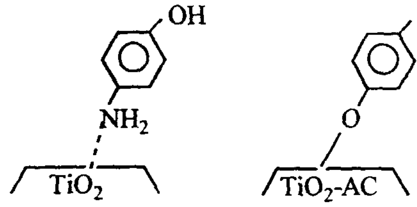


Figure 9. IR spectra from the interaction of satured *p-aminophenol*/H_2O solution with the different catalysts. *P-aminophenol* reference spectrum is also shown (10).

In the amino*phenol* interaction with bare-TiO_2 spectrum the disappearance of the νC-N vibration is clearly observed. This is characteristic of the formation of an aniline salt. However, in this molecule interaction with the catalyst AC-TiO_2 spectrum this band remains and the δOH vibration bands disappears. Since the –OH group in the amino*phenol* is more alkaline than the -NH_2 group, and the hydroxylic groups in the catalyst with AC seem to be more acidic than those in the bare-TiO_2, it seems plausible to consider that the interaction in the AC catalysts takes place by means of the hydroxylic group. Consequently, the species present in these catalyst could be the following:



As it has been observed the molecule interaction with the AC-TiO_2 catalyst by means of the hydroxylic group seems to favour the degradation.

Conclusions

Dosification is an efficient method to enhance the photocatalytic degradation of the studied molecules: *phenol*, *salicylic acid* and *p-aminophenol*. The obtained results show that applying the pollutant solution dosification it is possible to achieve a 10 times faster degradation in comparison to the obtained with the concentrated solution containing 100 ppm of more.

FTIR studies suggest important changes in the interaction of the studied molecules with the

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catalysts surfaces due to the presence of *activated carbon*. These interaction changes can be responsible of the better catalytic activity of AC-TiO_2, specially at the degradation of *p-aminophenol* and *salicylic acid* during the dosage process.

The optimum dosification rates for *phenol* and *salicylic acids* are about 5 ppm/min while for *p-aminophenol* it can be increased up to 8 ppm/min. However, different faster and slower steps have been observed during the dosification experiments with *phenol* and *salicylic acid*. This can be attributed to reactivation processes due to the adsorption of certain intermediates onto the catalysts surface.

When the degradation experiment has been carried out at a higher initial concentration (100 ppm) of any of these compounds the reaction becomes much more slower. In these cases stronger adsorption proceeses could be blocking the active centres of the catalyst and then reducing the rate of the possible degradation mechanisms.

We have successfully applied the dosification to the photocatalytic degradation of real wastes. This process may open new ways to the application of photocatalysis as an efficient waste treatment.

Acknowledgement

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