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TiO_2-photocatalysis as a tertiary treatment of naturally treated wastewater

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Abstract

Solar TiO_2-photocatalysis was applied to waters from a natural wastewater treatment plant located in the Universidad de Las Palmas de Gran Canaria. Degussa P-25 TiO_2 and its mixture with activated carbon (AC–TiO_2) were used as catalysts. The presence of ozone and certain ions such as phosphates on the photocatalytic degradation of organic matter was also studied.

Disinfection experiments have provided interesting results, particularly when using the catalyst AC–TiO_2 and ozone, since total disinfection was achieved in less than 60 min. No bacterial reappearance at 24 or 48 h was observed. Additionally, this catalyst gave important TOC and some ions concentrations reductions.

Studies in catalyst reuse revealed that the catalyst AC–TiO_2 showed almost no deactivation.

Keywords: Photocatalysis; FT-IR; TiO_2; Wastewater; Activated carbon

1. Introduction

Currently, one of the most significant environmental problems is wastewater treatment and depuration. This is not an easy task due to the high variety of contaminants present in such wastes [1–3].

Many wastewater treatment facilities rely on biological systems that tend to be cheap and easy to operate [4]. For instance, the dairy industry combines different steps of decantation in addition to aerobic and anaerobic biological treatments [5]. Even, the pharmaceutical industry has developed biocolumns containing activated sludge that is continuously aired to treat its wastewaters [6].

Another type of “natural” wastewater treatment takes advantage of chemical, physical and biological processes to eliminate water contaminants. Biological processes such as the metabolic activity of bacteriae and algae are key factors in these systems. Water macrophytes (helophytes) also play an important role in natural wastewater treatments since they consume nutrients released by the microbial degradation of organic matter and they are able to inject dissolved O_2 through their roots [7,8].

Ozonation is becoming more widely used for industrial wastewater treatment. Ozone can rapidly react with organic and inorganic contaminants [9,10] and shows a strong sterilizing and disinfecting effect. Also, it has proved useful in improving iron and manganese

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precipitation [11] and in eliminating organic traces in water [12].

Photocatalysis is considered an effective system for the mineralization of many organics through the generation of radicals such as $^{\bullet}OH$ and $O_2^{-\bullet}$. TiO_2 is the most widely used semiconductor for photocatalytic studies and applications, but in recent years efforts have been focused on developing new photocatalysts. Many experiments employ individual test molecules, but results from mixtures of different organics have not always been satisfactory [13,14]. The application of photocatalysis to municipal wastewaters has also been started to be studied [15,16]. We believe that the applicability of photocatalysis or its combination with other methods for the treatment of real wastes must be one of the main goals of future research.

In this paper we present the results obtained from combining natural wastewater treatment with TiO_2-photocatalysis and ozonation for the depuration of raw wastewater from the University of Las Palmas de Gran Canaria. The efficiency of the system has been determined by measuring total coliforms, biological oxygen demand (BDO), chemical oxygen demand (COD), organic carbon (total, inorganic and non-purgable) and inorganic ions such as nitrites, nitrates, phosphates, etc.

2. Experimental

2.1. Natural wastewater treatment

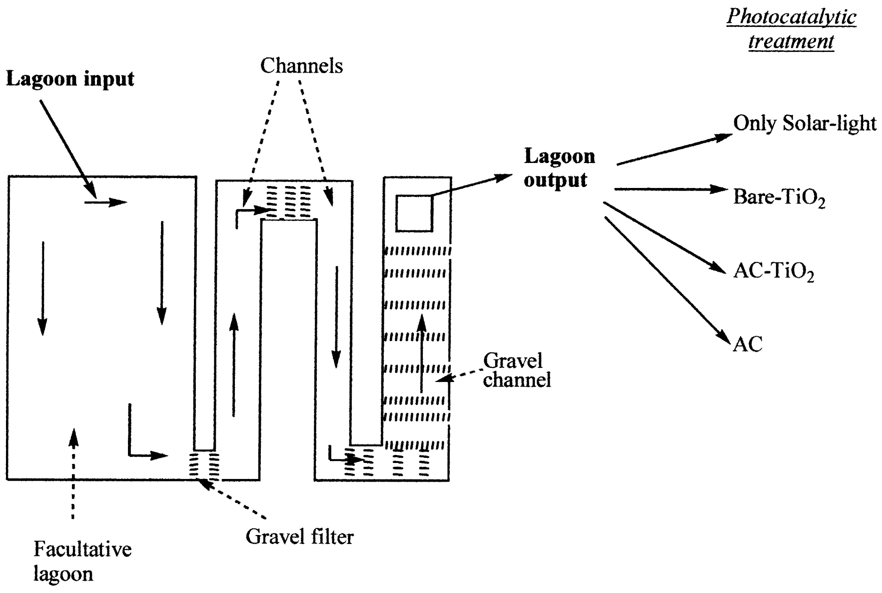
This system is loaded with about $3.8\,m^3$ per day of raw wastewater by a timer-controlled pump (Scheme 1). Wastewater is pumped into a 1.8 m facultative lagoon from which it flows through two channels separated by roots and gravel filters. A third gravel channel is used as a small subsurface flow system. Different wetland plants such as *Phragmites* spp., *Juncus* spp., *Pontederia* spp. and *Typha* spp. have been planted on the shores of the lagoon and channels. The system has been operating for about 1 year.

2.2. Catalysts

Degussa P-25 TiO_2 (80% anatase) (TiO_2), its (87% TiO_2–13% activated carbon, w/w) mixture (AC–TiO_2) and activated carbon (AC) alone have been tested as catalysts.

2.3. Microbiological analyses

Total coliforms have been determined by the membrane filter method. For total coliform determination,



Scheme 1.

Table 1
Total coliforms (CFU/100 ml) after the different treatments[a]

	Only air	Bacterial reappearance after only air	Air + ozone	Bacterial reappearance after air + ozone
Only solar light	3.5×10^3	2.8×10^6	2×10^2	2×10^3
TiO_2[b]	4.2×10^4	2.8×10^5	0	0
AC–TiO_2[b]	2.4×10^4	1.0×10^6	0	0
Ac[b]	1.9×10^4	1.1×10^7	1×10^1	0

[a] Lagoon input = 2.5×10^7 CFU/100 ml, lagoon output = 1.5×10^5 CFU/100 ml.

[b] Treatment was for 2 h.

endo agar base and 10% (w/v) in ethanol 96% (v/v) fuchsin basic (Cultimed, Panreac, Spain) were employed. These media were disposed in plastic sterile Petri dishes and preserved in a refrigerator at 13 °C until filtration. Water samples were filtered through 0.45 μm membranes (Millipore) and membranes disposed on the growing media. Total coliforms replicates with more than 80 CFUs (colony forming units) and less than 20 CFU were rejected (EPA, 1973). Petri dishes were oven heated at 37 ± 0.5 °C for 24 h.

By air-bubbling the treated samples for 48 h, bacterial reappearance experiments were carried out.

2.3.1. *Experimental conditions*

Reactors were 250 ml glass vessels. TiO_2 concentration was 2 g/l, AC–TiO_2 concentration was 2.3 g/l and AC concentration was 0.3 g/l. Samples were continuously stirred and air-bubbled (100 ml/min) or air–ozone bubbled (80–20 ml/min). All irradiation experiments were carried out between 10 and 14 h by employing solar light.

Data shown in Tables 1 and 2 were obtained after 2 h of reaction under the indicated conditions.

2.3.2. *Equipment*

TOC (total organic carbon), TC (total carbon) and IC (inorganic carbon) were made by using a TOC Shimadzu 5000-A.

FT-IR analyses were made using a spectrophotometer model RS/1 (UNICAM) equipped with two CaF_2 window devices in which the catalysts were placed. Intervals of 2000–1000 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. The ozone generator was an Azcozon HTC-500 ACPSE.

Table 2
Results from the analyses of the physico-chemical parameters after the different treatments

	TOC (ppm)	Alk. (ppm)[a]	pH	Cond. (mS/cm)[b]	WH (mg/l)[c]	PO_4^{3-} (mg/l)	COD (mg/l)	NO_2^- (mg/l)
Lagoon input	130.21	315.22	8.02	2.04	125.41	30.23	660.01	6.42
Lagoon output	22.63	64.53	8.43	2.81	632.73	19.62	97.08	0.19
Only								
Only solar light	22.63	62.57	7.58	2.76	632.78	19.64	96.03	0.55
Bare-TiO_2	16.92	57.30	7.9	2.62	456.94	5.63	56.42	0.51
AC–TiO_2	7.28	57.30	8.05	2.02	374.15	5.01	35.31	0.74
AC	10.71	57.30	8.06	2.66	616.85	19.81	85.42	0.34
Air + ozone								
Only solar light	22.66	64.24	8.21	2.70	307.90	18.52	96.05	0.17
Bare-TiO_2	22.66	57.95	8.16	2.50	270.64	7.95	86.00	0.17
AC–TiO_2	9.64	55.28	7.88	1.97	261.83	7.23	58.24	0.21
AC	15.76	55.26	7.94	3.17	291.67	10.39	69.8	0.15

[a] Alkalinity.

[b] Conductivity.

[c] Water hardness = $CaCO_2 + MgCO_3$.

2.3.3. *p-Nitrophenol and inorganic ions determinations*

p-Nitrophenol was directly determined by UV-Vis spectrophotometry ($\lambda = 400$ nm) in samples at pH higher than 10. Nitrites ($\lambda = 543$ nm) and phosphates ($\lambda = 885$ nm) have been also determined by UV-Vis after the formation of the proper colored complexes spectrophotometry [17]. Hardness was determined by titration through the formation of Ca^{2+} and Mg^{2+} etilendiaminetetracetic complexes and using murexide as indicator [17]. Alkalinity was determined by titration with H_2SO_4 and using phenolphthalein and methyl orange as indicator. COD was determined by the proper digestion of the samples (2 h at 150 °C) and later titration with an aqueous solution of $[Fe(NH_4)_2(SO_4)_2]^{\bullet}6H_2O$ [17]. $SO_4^{=}$ ions were analysed by turbidimetry (Hanna Instruments LP-2000-11) and Cl^- and NO_3^- by selective electrodes (Metrohm-LTD, Switzerland).

Results from the analyses shown in tables are the mean of five measurements. The variation coefficient was lower than 2% in all the cases.

3. Results

3.1. *Bacterial disinfection*

Mechanisms that explain the good levels of pathogen elimination in wetlands are not fully understood. Physical, chemical and biological processes and factors such as sedimentation, adsorption, natural UV light, pH, presence of oxygen, predation, competition and the antibiotic action of plants exudates are blamed for disinfection in wetlands [18–20]. However, in many cases the disinfections obtained are not high enough to meet the standards for reuse of the treated water.

Disinfection studies have been carried out by following the evolution of total coliforms in the different treatments. Table 1 shows the results obtained after treatments with air and ozone.

Raw wastewater gave a total coliforms concentration of 2.5×10^7 CFU/100 ml (typical values range). After the natural treatment a concentration of 1.5×10^5 CFU/100 ml was determined. This gives a reduction $((\text{in} - \text{out})/\text{in} \times 100)$ of 99.4%, which is of the same order of those shown by other natural systems [21,22]. However, when this sample was only irradiated with solar light the obtained reduction after 2 h was of 99.986%. The presence of the different catalysts (TiO_2, AC–TiO_2 and AC) gave lower reductions. After these treatments the samples were air-bubbled for 48 h in order to determine the bacterial reappearance that was lower in samples containing TiO_2.

Table 1 shows the results obtained when ozone is added to the treatment. As can be seen the combination of ozone and solar light gives a 17 times higher efficiency than that with only air. Additionally, total coliform concentrations in the samples containing TiO_2 and AC–TiO_2 were nil and reappearance was not observed either. Samples containing only AC almost reached total disinfection, since 10 CFU/100 ml were counted after 2 h of reaction. The catalyst AC–TiO_2 achieves total elimination in less than 60 min, while the catalyst TiO_2 obtains the same result after 120 min.

These results from the combination of photocatalysis and ozone are interesting because of the high efficiency obtained and the notable effect of the catalyst AC–TiO_2.

3.1.1. *Other parameters*

In order to determine the efficiency of the photocatalytic application to the naturally treated waters other parameters have been analyzed. These are TOC, pH, conductivity (mS/cm), COD and concentrations of HCO_3^-, PO_4^{3-}, Cl^-, NO_2^-, $SO_4^{=}$, NO_3^-, Ca^{2+} and Mg^{2+}. The concentration of $SO_4^{=}$ ions was not modified after any of the natural and photocatalytic treatments, while NO_3^- concentration increased from 16 to 40 ppm in the natural system and did not change after the photocatalytic treatments. Table 2 shows the concentrations of the different parameters in every treatment.

3.1.1.1. Organic matter. The organic matter present in the natural system is composed of organic wastes and new material synthesized by living organisms. Dissolved organic matter may be divided in two main groups:

(a) Nonhumic substances composed of carbohydrates, proteins, peptides, amino acids, and other low weight compounds that can be easily degraded by microorganisms.

(b) Humic substances of complex and diverse composition that give a characteristic brown-yellowish color to the water [23–25] than can complex metals [26,27] and act as precursors of the mutation of halogenated compounds [28,29].

Table 2 shows the TOC results after the different treatments. TOC has been measured as non-purgable organic carbon (NPOC) because of the high proportion of IC of the samples. The natural system obtains a notable reduction, from 130.21 to 22.63 ppm, attributable to nonhumic substances. In fact, water from the natural system shows a yellowish color probably due to the presence of humic substances. In the application of only solar light + air or only solar light + ozone no TOC reduction has been observed. In the experiment employing the catalyst bare-TiO_2 + air a TOC reduction of about 25% was obtained. The addition of ozone did not give any TOC reduction. In both the cases the yellowish color of the samples was slightly diminished. These results agree with those from the literature that indicate that TiO_2 is able to degrade humic substances, but is hardly able to mineralize them to CO_2 [30].

Moreover, in experiments carried out with the catalyst AC–TiO_2 + air or ozone, important TOC reductions have been obtained (68 and 57%, respectively). Catalyzing treatment has also led to total water discoloration.

Finally, the test carried out with AC reduced TOC but less than the reduction achieved with catalyst AC–TiO_2. Furthermore, in this latter case, almost no change was observed in water color. These catalysts were filtered after being used and then reused in the degradation of the same residual water. In the reuse tests carried out with catalyst AC–TiO_2 only limited variation was observed in the grade of degradation. With catalyst bare-TiO_2, however, no degradation was noted after reuse and with catalyst AC, reduction of TOC diminished 35% from its initial capacity.

Thus these results seem to indicate that the TOC reduction observed with catalyst AC could only be attributed to adsorption processes. Whereas in the case of catalyst AC–TiO_2 elimination of yellow-colored water, the greatest reduction of TOC compared to catalyst AC and its capacity to continue degrading after reuse, indicates existence of both combined degradation and adsorption process.

Subsequent degradation of humid acids was monitored by spectroscope. The capacity to absorb ranged from 254 to 400 nm [30]. In Fig. 1 the results obtained from these acids are shown for the different tests performed with air alone.

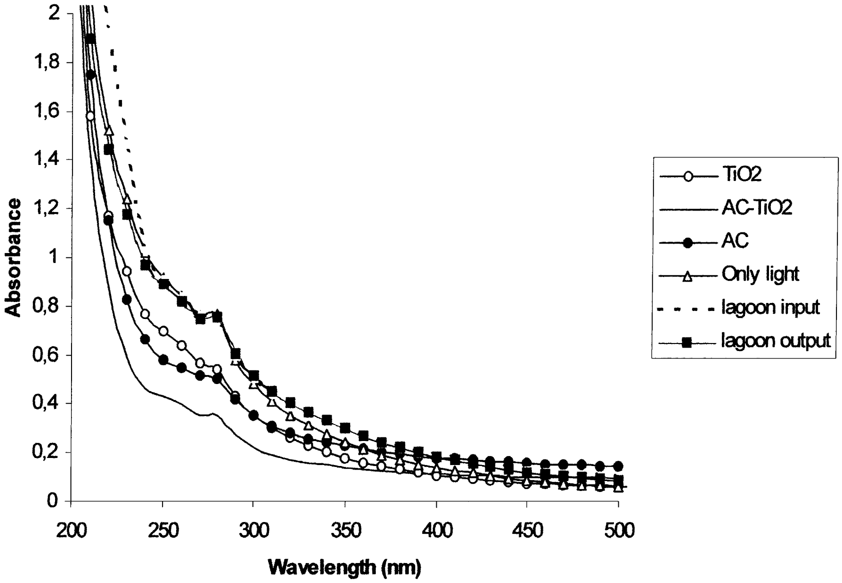


Fig. 1. Comparison of spectra UV-Vis adsorption of the residual water samples after different treatment processes.

The figure shows a significant peak in the 240 and 290 nm region. This longitudinal wavelength range indicates electronic transitions π–π^* of phenol substances, derived from aniline, benzoic acids, polyenes and aromatic polycycle hydrocarburates [31]. The 280 nm band is an important sign of the aromatic level of the substances present.

As we see in Fig. 1 the spectrum, in the indicated region, barely changes over the period in which the water is in the lagoon and after treatment with light only. The spectra obtained after catalyst bare-TiO_2 and AC–TiO_2 treatments show absorbance reduction in this region (especially with catalyst AC–TiO_2). In addition to the latter spectra, a reduction is also observed in band intensity to 280 nm (characteristic of the aromatic types) and a shoulder at 250–260 nm. The appearance of this shoulder may be related to the degradation products produced during the reaction. The spectrum obtained from the catalyst AC test shows a reduction in the intensity of the shoulder in the region between 240 and 290 nm but not the appearance of the shoulder centered between 250 and 260 nm since the reduction of organic material which takes place in this case, as indicated above, may only be attributed to adsorption processes.

3.1.2. *FT-IR study*

The catalysts' surface area was studied with an FT-IR spectroscope before and after photocatalytic degradation studies. In Fig. 2 we see the initial spectra of the catalysts bare-TiO_2 and AC–TiO_2 after being in a watery solution which is shaken and gasified with air bubbles for 30 min.

In the spectra of catalyst bare-TiO_2 we can clearly identify bands attributed to adsorbed water (1635 cm^{-1}) and to the presence of carbonates as described in the literature [32]. Furthermore, in catalyst AC–TiO_2, in addition to observing carbonate related bands, bands may be identified at 1690, 1408 and 1148 cm^{-1}. The band at 1690 cm^{-1} is typical of the νC=O vibration of a carboxylic group and a band at 1148 cm^{-1} it is found in the region of vibration νC–O. AC uses to have surfacial organic groups due to oxidation during the carbon lifetime, since the carbonization process, to the later cooling and storing. This happens when oxygen is present in the water or atmosphere around the carbon. Obviously, after the photocatalytic treatment these species can be degraded and eliminated from the surface. The spectra of the catalysts after degradation study are also shown in Fig. 2 (bare-TiO_2* and AC–TiO_2*). These spectra are similar and attributed to HCO_3^- presence adsorbed at the surface of the catalyst due to its similarity to the spectrum obtained in the carbonate hydrogen interaction with TiO_2 (Fig. 2). The bands observed over the catalyst formed only with active carbon are attributed to non-coordinated carbonate [32].

The presence of these types (HCO_3^- and $CO_3^=$) adsorbed at the surface of the catalysts may explain the slight decline in the alkalinity concentration determined in analyses of the samples after photocatalytic treatments (Table 2). Also the presence of carbonate hydrogen adsorbed on TiO_2 may cause the deactivation of the catalyst bare-TiO_2 when it is reused. The surface would be taken up by this type of species and not permit adsorption of the organic molecules present in the residues. In catalyst AC–TiO_2, however, although the TiO_2 surface is occupied by carbonate hydrogen, in the active carbon, active centers must continue to exist where the molecules can be adsorbed and attacked by radical oxidants to produce degradation so TOC reduction is observed after reusing the catalyst.

3.1.2.1. *Other parameters.*

Of the parameters and ions studied, we highlight the following results:

- The pH reduction after the different treatments, even in the studies with light only.
- Reduction of the conductivity and COD with catalyst AC–TiO_2 in comparison with other catalysts.
- Reduction of PO_4^{3-} in the photocatalytic studies with catalysts containing TiO_2 (bare-TiO_2 and AC–TiO_2).
- Increased hardness after coming out of the lagoon and its subsequent reduction after different photocatalytic treatments.
- A notable NO_2^- concentration increase in the tests carried out with air only, especially in those with the catalyst AC–TiO_2.

In these results, we did not anticipate the reduction of some ions present in media such as PO_4^{3-} or the subsequent hardening, which are related to the decrease in conductivity and COD, when the tests are carried out, especially in catalyst AC–TiO_2.

The presence of inorganic ions may influence the catalytic behavior of TiO_2. In fact, the notable increase

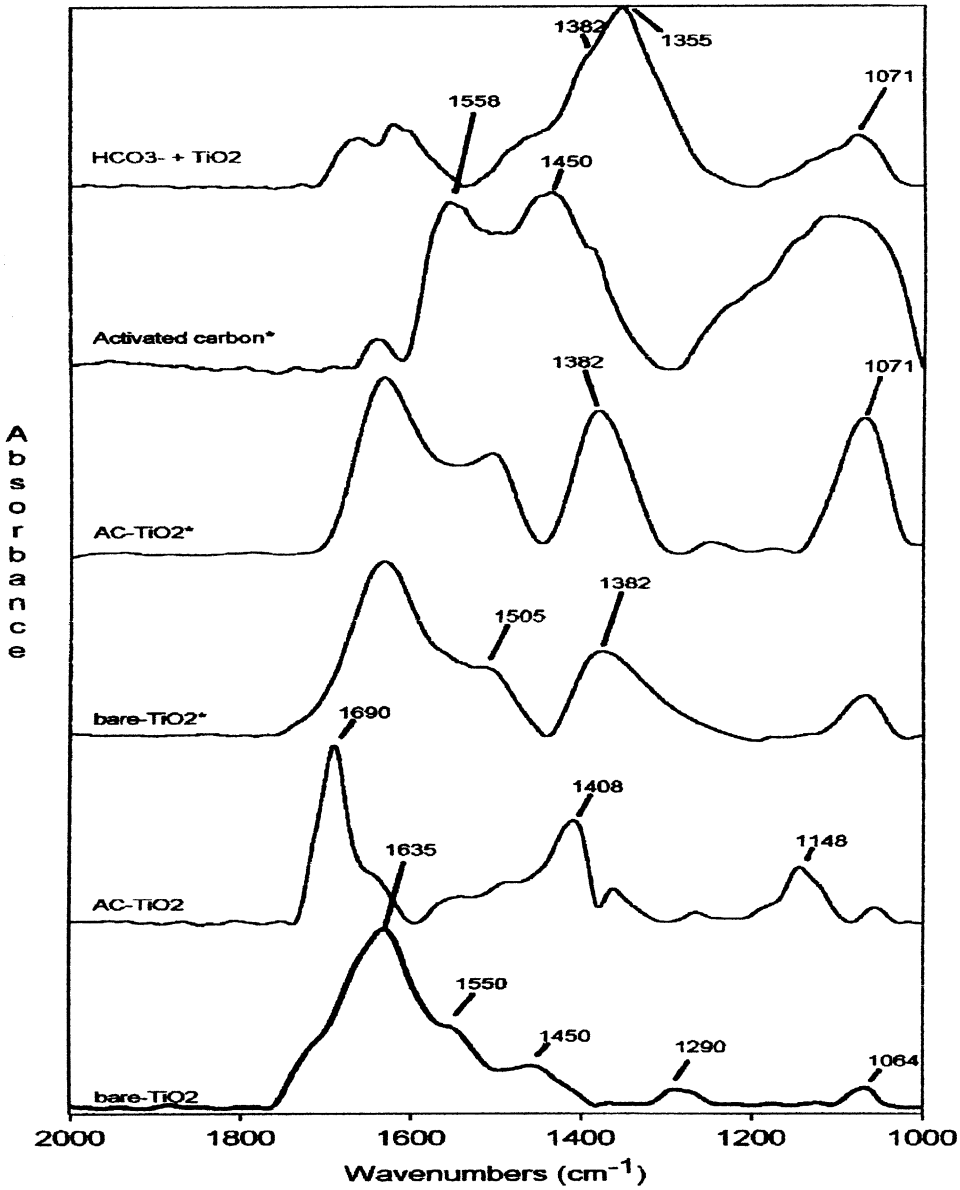


Fig. 2. IR spectra obtained from the catalysts before and after photocatalytic degradation studies are observed; also the spectrum obtained from the interaction of HCO_3^- with TiO_2. * Spectra obtained after photocatalytic studies.

of NO_2^- ion concentration could be due to the interaction of NH_4^+ ions with radical $^\bullet OH$ as described by other authors [33].

In a depuration of residual water process where different inorganic ions and organic molecules are present, it is difficult to determine how each one of them influences the degradation process. In this paper we have also begun to study the influence of inorganic ions on the photocatalytic degradation of organic material. Taking into account the significant reduction of phosphate ion concentration during the studies carried out with catalysts bare-TiO_2 and AC–TiO_2, we have chosen to experiment with those ions.

3.1.2.2. Studies with PO_4^{3-} ions. To consider how the presence of PO_4^{3-} ions influences the degradation of organic material and the catalytic behavior of the catalysts, we have chosen a molecule which is simple and easy to monitor with a molecular composition and characteristics similar to those of humic acids. The latter are substances containing carbon, hydrogen, nitrogen and oxygen as compounds and whose main functional groups are hydroxylic, carboxylic and carbonylic [3]. With this in mind, we chose *p*-nitrophenol (50 ppm) as a reference molecule. We studied degradation of this molecule with or without a set concentration of PO_4^{3-} (50 ppm). In Fig. 3 we show the results of *p*-nitrophenol (50 ppm) degradation with air only + ozone, and with or without PO_4^{3-} ions.

As shown in the studies with ozone, the presence of PO_4^{3-} ions encourages degradation of *p*-nitrophenol. Also, in the study with air only, with catalyst bare-TiO_2 the presence of these ions seems to worsen catalytic behavior, whereas with catalyst AC–TiO_2 hardly any difference was detected.

In Fig. 4 we show the PO_4^{3-} ions development during degradation. A rapid concentration reduction took place during the first hour in studies with air only, with very little variation in the rest of the reaction time. In the ozone studies an initial significant reduction in ion concentration occurred during the first hour of reaction, although less than the one observed in tests without ozone, with a subsequent tendency to stabilize also.

The same tests were carried out in darkness with and without catalysts. Hardly any reduction in phosphate concentration was observed. Also tests were performed with only phosphates (50 ppm), with catalysts and solar light without the presence of *p*-nitrophenol (Fig. 5).

In these studies we noted that phosphate elimination occurred, although this was less extensive than in the studies with *p*-nitrophenol and air. However, we continue to observe less elimination in ozone tests.

PO_4^{3-} ion elimination during the test reaction with only these ions (Fig. 5) could be occurring due to the direct interaction of phosphate ions with ${}^{\bullet}OH$ radicals, as indicated by some authors [12], favoring the ions adsorption during the irradiation.

Adsorbed ions PO_4^{3-} could be reduced:

$$PO_4^{3-} + 2H_2O + 2e^- \rightarrow 3OH^- + HPO_3^{2-} \qquad (1)$$

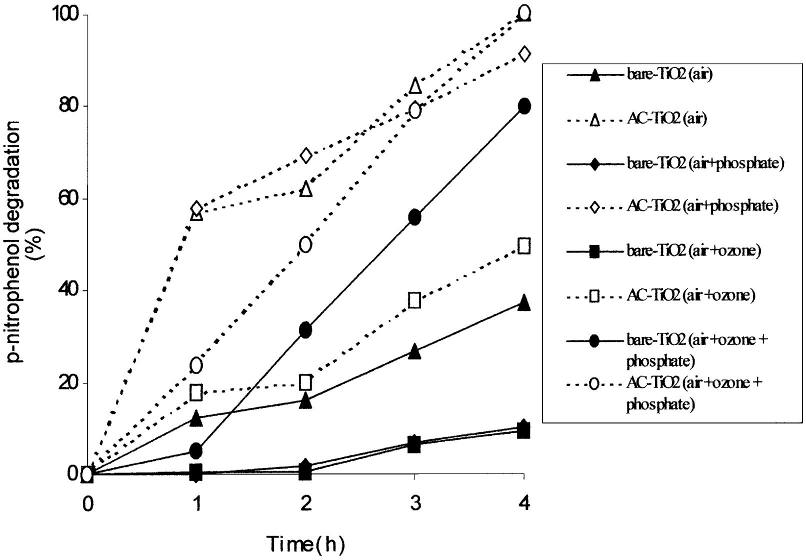


Fig. 3. Results of *p*-nitrophenol degradation with catalysts bare-TiO_2 and AC–TiO_2 with and without phosphate ions. These tests were carried out with a mixture of air and ozone.

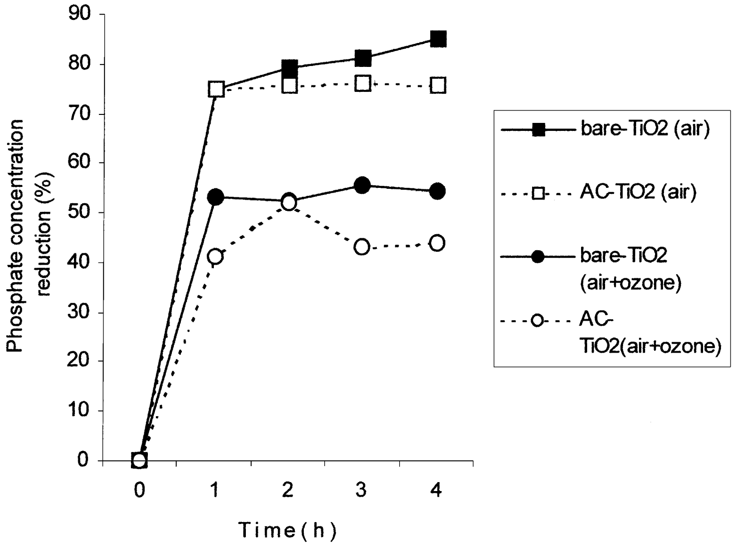


Fig. 4. Evolution of PO_4^{3-} (%) ion concentration during *p*-nitrophenol degradation (Fig. 3).

through the e^- generated by TiO_2:

$$TiO_2 \xrightarrow{h\nu} h^+ + e^- \quad (2)$$

The apparent redox potential of reaction (1) at the studied pH is −0.42 V, while the redox potential for the TiO_2 conduction band is −0.52 V. These potentials show the possibility of this process to happen.

Even the HPO_3^{2-} ions could be interacting with the holes created and oxidizing again the phosphate ions which would explain the increase and reduction

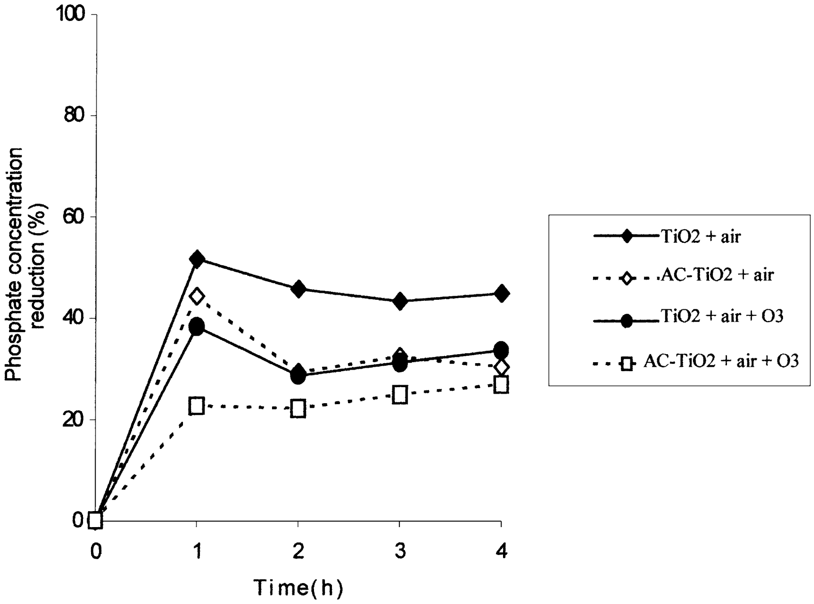


Fig. 5. Evolution of PO_4^{3-} (%) ion concentration with only phosphates (50 ppm), with catalysts and solar light without the presence of *p*-nitrophenol.

in phosphate ion concentration during some of these tests. When the *p*-nitrophenol degradation reaction was tested in the presence of phosphate ions with air only and the catalyst bare-TiO_2, the degradation observed worsened compared to the tests without phosphate ions. Thus the competence produced by the e^- and holes produced photocatalytically by TiO_2 between the phosphates and hydroxylic ions seems to be limited for the degradation of the *p*-nitrophenol.

When the reaction is carried out with ozone it is accompanied by significant improvement in *p*-nitrophenol degradation. Ozone could be reacting with e^- generated by TiO_2 and leading to the following reactions [9,10,34]:

$$O_3 + e^- \rightarrow O_3{}^{-\bullet} \tag{3}$$

$$H^+ + O_3{}^{-\bullet} \rightarrow HO_3{}^{\bullet} \tag{4}$$

$$HO_3{}^{\bullet} \rightarrow O_2 + {}^{\bullet}OH \tag{5}$$

The redox potential of reaction (3) is $-0.28\,V$, lower than that of reaction (1). This may indicate that ozone could be reacting most quickly with e^- than the phosphates ions favoring the formation of radical $^{\bullet}OH$ and thus *p*-nitrophenol degradation.

To better understand how these ions are interacting with the catalyst surface and inciting the catalytic behavior of the TiO_2 further, more detailed surface analyses are being carried out.

We should also emphasize also the increased capacity for degrading the *p*-nitrophenol of the catalyst AC–TiO_2 in all the conditions regarding bare-TiO_2 as well as observing in residual waters testing. Active carbon could be acting as an adsorption nucleus for certain ions so that they avoid contaminating TiO_2.

4. Conclusions

The results obtained in this study have demonstrated that combining biological and photocatalytic treatments could greatly improve the depuration of residual waters.

Catalysts formed by mixing TiO_2 with active carbon, as used in our tests seem to be the most efficient both in obtaining a high level of disinfection, as well as reducing organic material and even eliminating some inorganic ions.

We have also investigated how the presence of a certain ion such as phosphate affects the catalytic behavior of TiO_2 and mixes of TiO_2 with carbon. The latter mixture did not inhibit degradation capacity. On the contrary it seemed to encourage its capacity to eliminate organic material. In the catalyst bare-TiO_2, however, the presence of phosphate ions inhibited its capacity to degrade organic material. The reduction of phosphates by e^- produced photocatalytically by TiO_2 and its subsequent oxidation by means of the holes generated could impede the formation of radical $^{\bullet}OH$.

The study of how the presence of certain inorganic ions, typically found in urban wastewaters, influences the catalytic behavior of photocatalysts is a new research field. We believe these studies are of vital importance in the application of photocatalysis in real residue.

Acknowledgements

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References

[1] O. Hutzinger, The Handbook of Environmental Chemistry, vol. 1, Part C, Springer, Berlin, 1984.
[2] M. Schnitzer, S.U. Khan, Humic Substances in the Environment, Marcel Dekker, New York, 1972.
[3] N.M. Atherton, P.A. Cranwell, A.J. Floyd, R.D. Haworth, Humic acid—IESR spectra of humic acids, Tetrahedron 23 (1967) 1653.
[4] M. Lagrega, P. Buckingham, J. Evans, Gestion de Residuos Tóxicos-tratamiento, eliminación y recuperación de suelos, McGraw-Hill, New York, 1996.
[5] M. Espigares García, F. Sánchez Izquierdo, J. Moreno Carretero, R. Gávez Vargas, Tecnol. Del Agua 162 (1997) 47.
[6] J. Marti Duran, L. Leyda Escoruela, Ingen. Quím. (1996) 117.

[7] H. Brix, Use of subsurface flow constructed wetlands for waste water treatment—an overview, in: R. Ramadori, L. Cingolani, L. Cameroni (Eds.), Proceedings of the Conference on Natural Constructed Wetlands for Wastewater Treatment and Reuse—Experiences, Goal and Limits, Perugia, 1995, p. 103.

[8] R.M. Gersberg, B.V. Elkins, S.R. Lyon, C.R. Goldman, Water Res. 20 (1986) 363.

[9] J. Hoigne, H. Bader, Water Res. 17 (1983) 173.

[10] J. Hoigne, H. Bader, Water Res. 17 (1983) 185.

[11] H. Pillard, B. Legube, M.M. Boubigot, E. Lefevre, Ozone Sci. Eng. 11 (1989) 93.

[12] J. Staehelin, J. Hoigne, J. Environ. Sci. Technol. 19 (1985) 1206.

[13] J. Araña, E. Tello Rendón, J.M. Doña Rodríguez, J.A. Herrera Melián, O. González Díaz, J. Pérez Peña, J. Photochem. Photobiol. A 148 (2002) 215.

[14] C.S. Turchi, D.F. Ollis, J. Catal. 119 (1989) 483.

[15] R. Dillert, U. Siemon, D. Bahnemann, Chem. Eng. Technol. 21 (1998) 256.

[16] R. Dillert, U. Siemon, D. Bahnemann, J. Adv. Oxid. Technol. 4 (1999) 55.

[17] Standard Methods for the Examination of Water and Wastewater, Aphs-Awwa-Wpcf Ed., 1985.

[18] K. Seidel, Macrophytes and water purification in: J. Tourbier, R.W. Pierson (Eds.), Biological Control of Water Pollution, University of Pennsylvania Press, 1976.

[19] R.M. Gesberg, S.R. Lyon, R. Brenner, B.V. Elkins, Integrated wastewater treatment using artificial wetlands: a gravel marsh case study, in: D.A. Hammer (Ed.), Constructed Wetlands for Wastewater Treatment, vol. 145, Lewis Publications, 1990.

[20] H.K. Kadlec, R.L. Knight, Treatment Wetland, vol. 181, Lewis, Boca Ratón, 1996.

[21] M. García, E. Bécares, F. Soto, E. De Luis, Tecnol. Del Agua 185 (1999) 64.

[22] A. Moreno Carmona, R. Angulo Sánchez, Tecnol. Del Agua 160 (1997) 23.

[23] A.P. Black, R.F. Christman, J. Am. Water Works Assoc. 55 (1963) 753.

[24] R.F. Packham, Proc. Soc. Water Treat. Exam. 13 (1964) 316.

[25] L.E. Bennett, M. Drikas, Water Res. 27 (1993) 1209.

[26] J.H. Reuter, E.M. Perdue, Geochim. Cosmochim. Acta 41 (1977) 325.

[27] M. Hiraide, Y. Arima, A. Mizuike, Anal. Chim. Acta 200 (1987) 171.

[28] T.A. Bellar, J.J. Lichtengurg, R.C. Kroner, J. Am. Water Works Assoc. 66 (1974) 703.

[29] J.J. Rook, Environ. Sci. Technol. 11 (1977) 478.

[30] M. Bellouti, M.M. Alves, J.M. Novais, M. Mota, Water Res. 31 (5) (1997) 1227.

[31] S.J. Traina, J. Novak, N.E. Smeck, J. Environ. Sci. Technol. 19 (1990) 151.

[32] A.A. Davydov, Infrared Spectroscopy of Adsorbed Species on the Surface of Transition Metal Oxides, Wiley, New York, 1990.

[33] K.C. Low Gary, R. McEvoy Stephen, W. Matthews Ralph, Environ. Sci. Technol. 25 (1991) 460.

[34] J. Hart, I. Walker, D.C. Armstrong, Ozone Sci. Eng. 17 (1995) 485.