

## FTIR study of the photocatalytic degradation of $\text{NH}_4^+$ determination wastes

J. Araña, E. Tello Rendón, J.M. Doña Rodríguez,  
J.A. Herrera Melián\*, O. González Díaz, J. Pérez Peña

Departamento de Química, Universidad de Las Palmas de Gran Canaria, Campus de Tafira, E-35017 Gran Canaria, Spain

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### Abstract

In this work we present the results of the application of photocatalytic techniques to organic pollutants in water. Such aqueous wastes are produced during the UV–Vis spectrophotometric determination of the  $\text{NH}_4^+$  ion in water. Processes taking place during the photocatalytic degradation of such organics have been studied by using FTIR, HPLC and TOC measurements.

The obtained results suggest that in the presence of light, air and a catalyst ( $\text{TiO}_2$  or  $\text{Fe}^{2+}$ ) one of the existing organics, nitroprusside is decomposed to  $\text{C}\equiv\text{N}^-$ ,  $\text{NO}_2^-$  and  $\text{NO}_3^-$ . Free  $\text{C}\equiv\text{N}^-$  ions react with other intermediates yielding nitrogen-containing compounds such as acetaloximes and acetamides. The photocatalytic degradation of this kind of N-containing compounds seems to be more complicated than the corresponding alcohols and carboxylic groups generated during the individual degradation of phenol, citrate or ethanol.

A remarkable affinity of those nitrogenated species in adsorbing onto the  $\text{TiO}_2$  surface has been observed. This may be the cause of the reduced catalyst activity observed in the process. It has been also determined that  $\text{C}\equiv\text{N}^-$  ions tend to react with  $\text{Fe}^{3+}$  ions to give complexes like  $[\text{C}\equiv\text{N}-\text{Fe}]^{2+}$  and  $[\text{R}-\text{C}\equiv\text{N}-\text{Fe}]^{2+}$  inhibiting this way the photo-Fenton reaction. In fact, no organic carbon reduction was observed during the application of the photo-Fenton reaction or  $\text{TiO}_2$  photocatalysis.

Toxicity of the samples was determined before and after the application of the photo-Fenton reaction and  $\text{TiO}_2$  photocatalysis. Toxicity as determined by using the algal species *Phaedactylum tricorutum* after the photocatalytic treatment was higher. This suggests the possible above mentioned recombination of chemical species during the degradation of the samples. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** FTIR; Photocatalysis; Photo-Fenton; Aqueous wastes

### 1. Introduction

The application of photocatalytic techniques for the degradation of organic pollutants has been widely investigated in the last years. Many of these studies have been focused on individual molecules. For instance, degradation of phenol has been performed at different pH, different catalyst or phenol concentrations, by the photo-Fenton reaction, etc. [1–6]. However, few works have attended the degradation of mixtures and in these cases results have been very different from those obtained by using individual compounds. In some cases non-degradable products have been obtained that had not been produced when treating individual compounds [7]. Our research group is involved in the treatment of real lab wastes such as those from the spectrophotometric determination of ammonia by different oxidation tech-

niques [8]. In those wastes phenol, citrate, nitroprusside and ethanol are found as reagents.

The obtained results suggest the existence of inhibition processes of the photocatalytic mechanisms that did not appear when the components were individually degraded. In order to degrade the wastes by means of photocatalytic techniques it was necessary to pre-treat them with permanganate. FTIR studies have been undertaken in order to identify the intermediates that inhibit the photocatalytic process during the degradation of ammonia wastes and to determine why the permanganate pre-treatment favors their photocatalytic degradation.

### 2. Experimental

#### 2.1. Chemicals

Reagents were Aldrich products: phenol (99.0%), ethanol (96%), sodium citrate solution (3.8%), nitroprusside (pure), hydrogen peroxide (33%) and dihydrated ferrous sulfate.

\* Corresponding author. Tel.: +349-284-572-99; fax: +349-284-529-22.

E-mail addresses: jaranaesp@hotmail.com (J. Araña),

jalberto@cicei.ulpgc.es (J.A. Herrera Melián).

## 2.2. Experimental conditions

The following experimental conditions were employed: 250 ml glass vessels reactors containing waste-catalysts suspensions were continuously stirred and air-bubbled (100 ml/min). Concentration of catalyst  $\text{TiO}_2$  and  $0.15\text{Fe-TiO}_2$  was 2 g/l. The concentration of  $\text{Fe}^{2+}$  ions for photo-Fenton experiments was 0.02 g/l. The preparation and characterization of the doped catalyst has been already described [9].

Before switching the UV-lamp on the suspension was air-bubbled and stirred for 15 min in order to favor the organics chemisorption onto the catalyst surface.

## 2.3. Equipments

An 800 W xenon UV-lamp (Solarium Facial UV-A HPA 8068, with maximum emission around 385 nm, ENCO) was employed as a UV light source. Remaining phenol and citrate concentrations at different reaction times were HPLC-measured by using a reverse phase column (C18) Zorbax ODS  $5\mu$  (Jones Chromatography) and a 0.2 M phosphoric acid mobile phase, using a UV detector ( $\lambda = 210$  nm). TOC (total organic carbon), TC (total carbon) and IC (inorganic carbon) were made by using a TOC Shimadzu 5000-A.

FTIR studies of the catalysts were made by placing them between two  $\text{CaF}_2$  windows. Spectra were obtained by using an FTIR spectrophotometer model RS/1 (UNICAM). Every spectrum was analyzed using a resolution of  $2\text{ cm}^{-1}$ , forward and reverse moving mirrors speed of 10 and 6.2 kHz, respectively. Water reference spectrum has been subtracted to every spectra. An internal reflection device (Standard Circle Liquid Analyzer, Spectra-tech) has been employed for the determination of water dissolved substances. Kubelka–Munk

units have been employed for water dissolved substances and absorbance units have been employed for solids.

## 3. Results and discussion

The composition of the ammonia determination wastes is shown in Table 1. As it has been indicated in previous works [8] ammonia wastes contain a large concentration of volatiles and consequently air-bubbling will result in their transfer to the atmosphere. Different reactors were disposed as gas-traps in order to collect volatiles (Fig. 1). Reactor 1 was filled with 200 ml of ammonia wastes and reactors 2–4 were each filled with 200 ml of distilled water.

A first experiment was made by air-bubbling a waste sample placed in reactor 1 and collecting volatiles in reactors 2–4. Results after 7, 24 and 48 h are shown in Table 2.

Table 1  
Composition of ammonia determination wastes (% w/w)

	Phenol	Nitroprusside	Citrate	Ethanol
Initial composition (% w/w)	10.8	0.2	18.7	70.2

Table 2  
TOC measurements, in the different reactors, during air-bubbling a waste sample placed in reactor 1

Time (h)	TOC (ppm)				
	Reactor 1	Reactor 2	Reactor 3	Reactor 4	Total
0	16550	0	0	0	16550
7	15180	1023	204	15	16422
24	11278	3842	1100	201	16421
48	7593	3885	3014	1456	15948

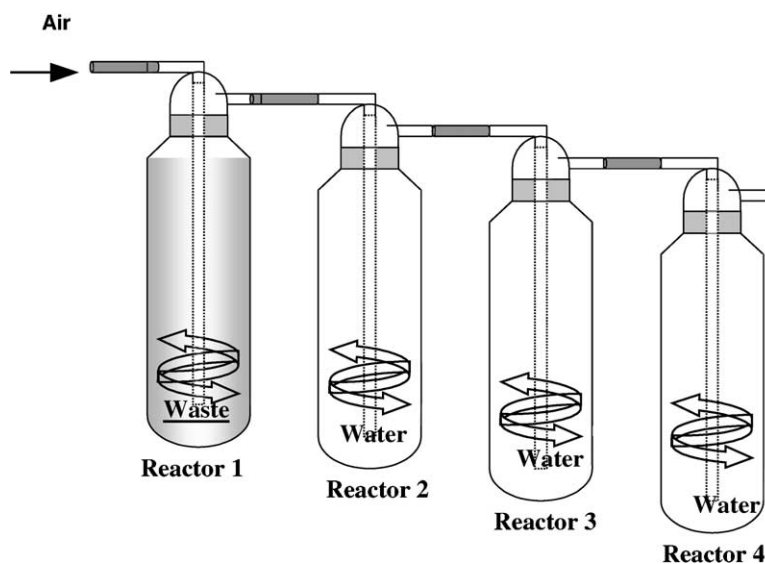


Fig. 1. Arrangement of reactors used in this study.

Table 3  
TOC measurements, in the different reactors, during the degradation of a waste water (the same initial sample used in Table 2) with TiO<sub>2</sub> (2 g/l)

Time (h)	TOC (ppm)			
	Reactor 1 (TiO <sub>2</sub> + hν)	Reactor 2 (TiO <sub>2</sub> + hν)	Reactor 3	Reactor 4
0	16550	0	0	0
7	14512	1625	203	84
14	— <sup>a</sup>	1214	549	141

<sup>a</sup> Reactor 1 disconnected.

After 48 h the waste sample TOC (in reactor 1) was reduced by a 54%. HPLC analyses of this sample (reactor 1) show that phenol and citrate concentrations remain constant. Since ethanol is the most volatile component of the initial sample it can be considered that the organic carbon loss in this reactor, is mainly due to ethanol volatilization. It is important to indicate that only a 3.64% is transferred to the atmosphere the rest was collected in reactors 2–4.

Later, the same experiment was repeated but adding TiO<sub>2</sub> (2 g/l) and UV-irradiating reactors 1 and 2. Reactors 3 and 4 were kept in the dark. Results are shown in Table 3.

After this, reactor 1 was disconnected and the experiment was resumed with reactor 2 and collecting volatiles with reactors 3 and 4 (Table 3). Results obtained after seven more hours of reaction (14 h in total) indicate that TOC reduction observed in reactor 2 coincide with TOC collected in reactors 3 and 4. In previous experiments made under the same conditions with only ethanol a 50% TOC reduction was achieved after 7 h. The fact that the obtained TOC reduction is not of the same extent of that achieved during the first 7 h of the experiment with the waste sample indicates that in addition to ethanol other substances are being collected in reactor 2 that inhibit the degradation process.

Also, individual degradation studies of citrate and phenol at the same concentrations of those found in the waste sample have been performed. Larger degradations than those obtained in previous studies have been achieved [8]. But when these experiments were repeated with nitroprusside no degradation was observed. Consequently, an FTIR individual study of this compound was accomplished.

### 3.1. Nitroprusside + TiO<sub>2</sub>

TiO<sub>2</sub> was impregnated with a water–nitroprusside solution (1:5 w/w) and then UV-irradiated and aired. Fig. 2 shows the FTIR spectrum from the so-treated catalyst after impregnation ( $t = 0$ ) (a), and at different reaction times (b)–(d). The nitroprusside spectrum is dominated in the region between 2300 and 1000 cm<sup>-1</sup> by three bands at

2145, 1937 and 1619 cm<sup>-1</sup>. The band at 2145 cm<sup>-1</sup> is attributed to the vibration of the [C≡N]<sup>-</sup> group, while bands at 1937 and 1619 cm<sup>-1</sup> are attributed to the [N≡O]<sup>+</sup> group co-ordinated or covalent bonded with Fe, respectively [10]. The spectrum obtained after impregnation (Fig. 2a) shows a change in the relative intensity of the present bands. But when the sample is aired and irradiated new bands at 2060, 1560 and 1374 cm<sup>-1</sup> are observed. Also the band at 1937 cm<sup>-1</sup> is doubled in two new bands at 1952 and 1924 cm<sup>-1</sup>. After 30 min of aeration and irradiation the intensity of the band at 2145 cm<sup>-1</sup> becomes notably reduced, the intensity of band at 2060 cm<sup>-1</sup> is enhanced and the band at 1374 cm<sup>-1</sup> becomes wider towards larger wavenumbers (about 1400 cm<sup>-1</sup>). After 1 h the spectrum is dominated by the wide band at 1400 cm<sup>-1</sup>. The band at 2060 cm<sup>-1</sup> is characteristic of the free cyanide ion [10], while bands at 1560, 1374 and 1400 cm<sup>-1</sup> may be attributed to NO<sub>2</sub><sup>-</sup> or NO<sub>3</sub><sup>-</sup> ions [10].

Consequently, it can be concluded that the combined interaction of nitroprusside with TiO<sub>2</sub>, O<sub>2</sub> and light results in the decomposition of the nitroprusside to give nitrate, nitrite and free cyanide ions. These could react with some of the radicals produced during the photocatalytic degradation of ethanol, phenol or citrate giving different intermediates from those produced during the individual degradation of these organics.

### 3.2. Nitroprusside + Fe<sup>2+</sup>

Also, the degradation of nitroprusside (50 ppm) in the presence of Fe<sup>2+</sup> ions was studied by FTIR. As it has been indicated in previous works [8] the nitroprusside degradation by the photo-Fenton reaction is scarcely effective (≈40% after 3 h). Fig. 3 shows the spectra from the solution of nitroprusside + Fe<sup>2+</sup> ions after 15 min in the dark and air-bubbled (a) and after being irradiated for 60 min (b). Important differences can be observed according to the initial nitroprusside FTIR spectrum (Fig. 2a).

The νC≡N vibration band at 2145 cm<sup>-1</sup> (Fig. 2) disappears and a new band is generated at 2341 cm<sup>-1</sup> that seems to be accompanied by other bands at 1389 and 1353 cm<sup>-1</sup>. After 60 min of nitroprusside interaction with Fe<sup>2+</sup> ions these three bands disappear (Fig. 3b). These bands can be attributed to the formation of a nitrile N-oxide (–C≡N → O) [11].

Also, a new band at 2100 cm<sup>-1</sup> is formed during interaction of nitroprusside with Fe<sup>2+</sup> ions (Fig. 3a and b). This band has a higher wavenumber than bands from free C≡N<sup>-</sup> ions (2060 cm<sup>-1</sup>). Different studies have indicated that Fe(CN)<sub>6</sub><sup>3-</sup> species absorb at 2114 cm<sup>-1</sup> [12]. Nonetheless, when the cyanide group C≡N<sup>-</sup> is parallel oriented to the metal surface and interact with the metal orbitals by means of the π systems more strongly than with the C atom shift towards lower wavenumbers takes place [12]. Consequently, the band observed at 2100 cm<sup>-1</sup> can be attributed to the formation of a ferricyanide ion

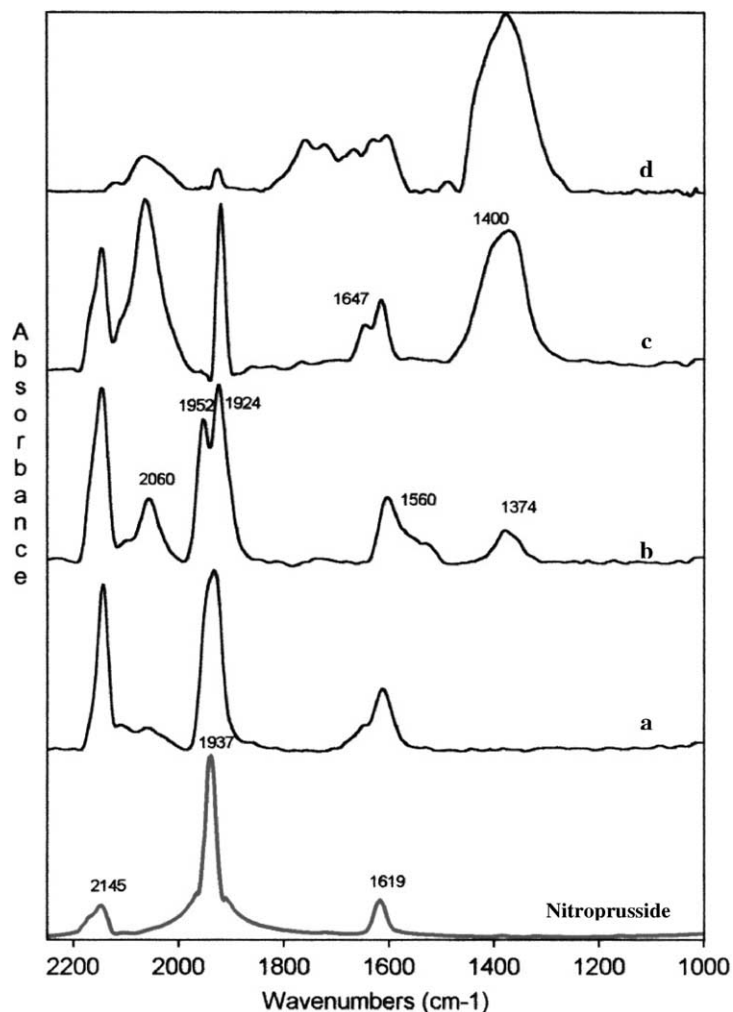


Fig. 2. IR spectra from the interaction of nitroprusside with  $\text{TiO}_2$ , air and light after: (a) 0 min (after catalyst impregnation), (b) 15 min, (c) 30 min and (d) 60 min.

$[\text{Fe}(\text{C}\equiv\text{N})_6]^{3-}$  in which groups  $\text{C}\equiv\text{N}$  are co-ordinated as shown [13]:



Also, the  $\nu\text{N-O}$  vibration band at  $1937 \text{ cm}^{-1}$  from nitroprusside disappears (Fig. 3a) and new bands at 1651, 1487, 1230 and  $1043 \text{ cm}^{-1}$  are now visible and attributed to different species such as  $\text{Fe-O-N=O}$  or  $\text{FeO}_2\text{-NO}$  [10].

### 3.3. Ammonia wastes + $\text{Fe}^{2+}$

The application of the photo-Fenton reaction to ammonia determination wastes gave the spectra shown in Fig. 3c and d, after 15 and 30 min of irradiation, respectively. After the first 15 min of irradiation the band at  $1940 \text{ cm}^{-1}$

attributable to the  $[\text{N}\equiv\text{O}]$  vibration is still visible though slightly shifted toward higher wavenumbers. The band at  $1619 \text{ cm}^{-1}$  is not observed. Also, it can be observed a small band at  $2076 \text{ cm}^{-1}$  increasing in intensity at the time that the band at  $1940 \text{ cm}^{-1}$  diminishes. In some papers it has been indicated that when the group  $\text{C}\equiv\text{N}^-$  is bound to a molecule in which the lower vacant orbital is antibonding with respect to carbon and nitrogen atoms the vibration  $\nu\text{C}\equiv\text{N}$  decreases down to  $2076 \text{ cm}^{-1}$  [14,15]. So free  $\text{C}\equiv\text{N}^-$  groups present in the solution from the nitroprusside decomposition seem to react with some of the olephinic groups from intermediates generated from the phenol degradation to give compounds such as  $[\text{R-C}\equiv\text{N-Fe}]^{2+}$ .

In addition to this, spectra obtained after 15 and 30 min or irradiation are mainly dominated by intense bands at 1120, 1076 and  $987 \text{ cm}^{-1}$ . These bands correlate quite well with those from orthoformates (Fig. 3e). In the literature it has been described that  $\text{C}\equiv\text{N}^-$  groups react in acidic media with primary alcohols to give orthoformates through the

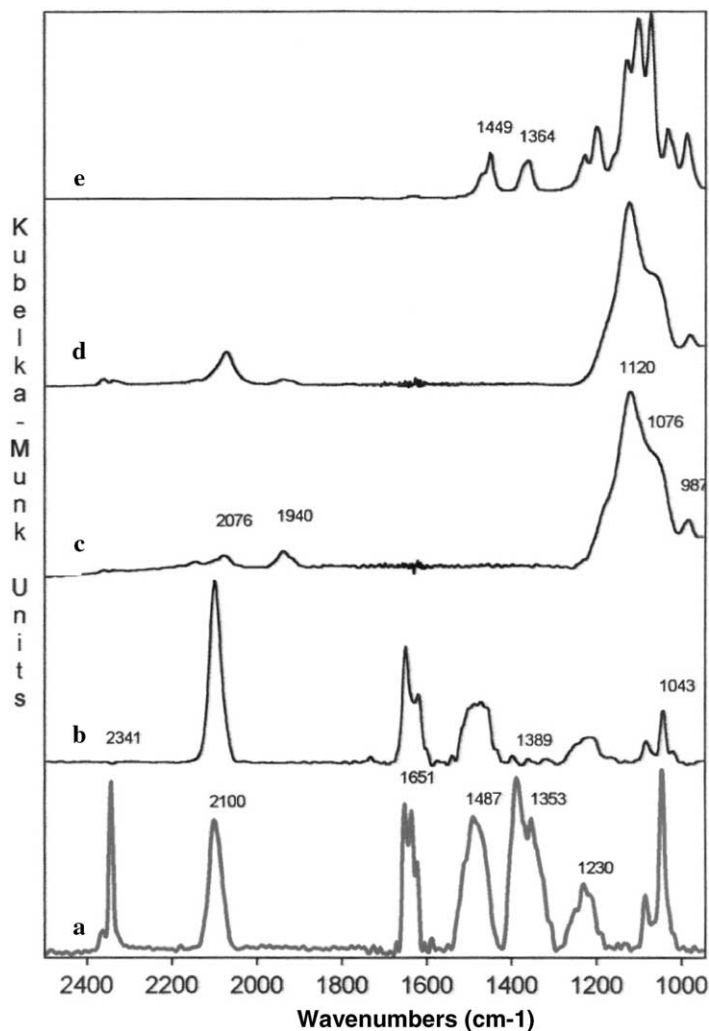
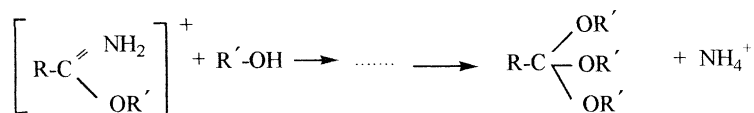
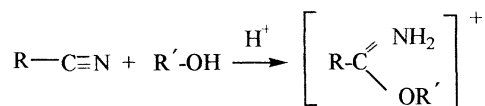


Fig. 3. IR spectra from the interaction of nitroprusside (50 ppm) with  $\text{Fe}^{2+}$  ions: (a) 15 min (in dark with air), (b) 60 min (with air and light). IR spectra from ammonia waste during photo-Fenton reaction: (c) 15 min, (d) 30 min. IR spectrum from orthoformate is also shown (e).

following mechanism [16]:



This way  $\text{C}\equiv\text{N}^-$  groups generated from the nitroprusside decomposition may tend to react with radicals or intermediates from the degradation of other organics and to coordinate  $\text{Fe}^{3+}$  ions.

Additionally, after 1 h of reaction of ammonia wastes with  $\text{Fe}^{2+}$  ions the presence of different suspended solids was observable (Fig. 4).

A blue solid was filtered from the solution and its FTIR spectra show an intense band at  $2076\text{ cm}^{-1}$  in addition to other bands of lower intensity at 1616, 1416 and  $1383\text{ cm}^{-1}$ . Also, an orange solid was separated from the solution. Its FTIR spectrum (Fig. 4b) is dominated by a band at  $1676\text{ cm}^{-1}$  with a shoulder centered at about  $1600\text{ cm}^{-1}$ . Three bands at 1422, 1383 and  $1284\text{ cm}^{-1}$  are also visible.

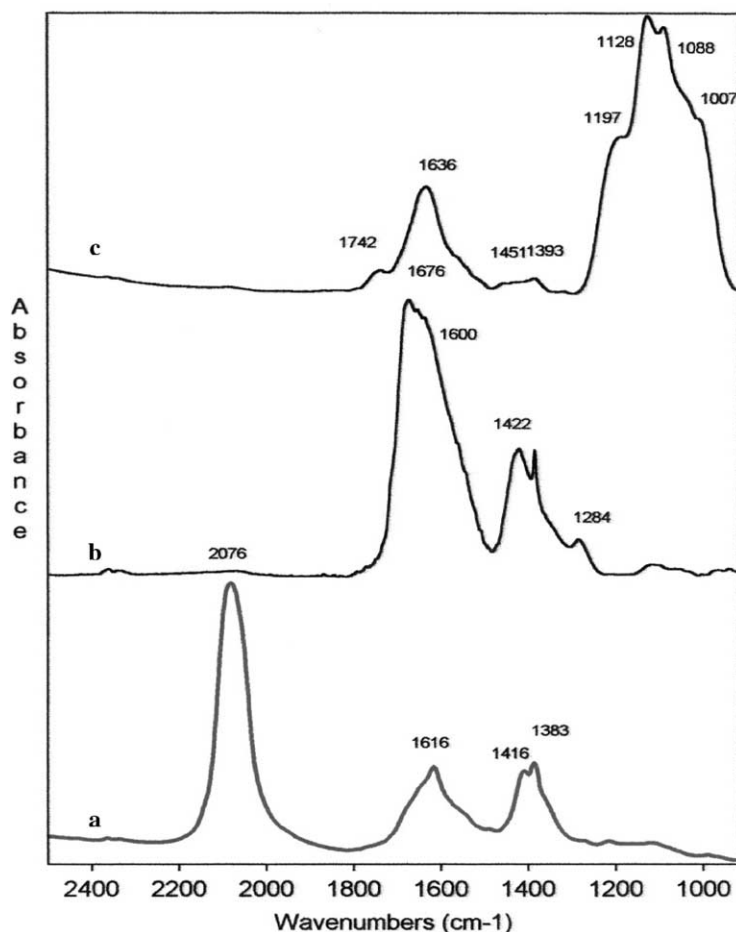


Fig. 4. FTIR spectra from solids precipitated during the application of the photo-Fenton to the ammonia wastes: (a) blue solid, (b) orange solid and (c) red solid.

Finally, a red precipitate was obtained and FTIR-analyzed (Fig. 4c). Three intense bands in the region between 1200 and  $1000\text{ cm}^{-1}$  are clearly visible in addition to other bands at 1742, 1636, 1451 and  $1393\text{ cm}^{-1}$ .

Considering the similarity of the red precipitate spectrum to the one of orthoformate (Fig. 3e) this red solid could be considered to be  $\text{Fe}^{3+}$  ions precipitated as ferric orthoformate. The orange precipitate shows a spectrum very similar to those described in the literature for acetoxime and acetamides. The subtraction of a H atom from a C–H group and the consequent addition of N atoms have already been described in studies of photocatalytic degradation [17]. The blue precipitate showing a band at  $2076\text{ cm}^{-1}$  could be due to an organic molecule containing a  $\text{C}\equiv\text{N}$  group co-ordinated to  $\text{Fe}^{3+}$ .

All these experiments have been performed in the reactor arrangement described in Fig. 1. No observable organic carbon reduction calculated from mass balances of the different reactors has been observed. Amines and amides according to what we have observed in different experiments (propanamide, propylamine, etc.) and to what is described

in the literature [18–20] are hardly degradable by means of photocatalytic mechanisms. This is due to the stability of N–H and C–N bonds which are stronger than the corresponding O–H and C–O. Consequently, the presence of this kind of species together with the ability of  $\text{C}\equiv\text{N}^-$  groups to complex  $\text{Fe}^{3+}$  ions and this way inhibiting the photo-Fenton reaction could be the reason why TOC was not reduced.

The application of the photo-Fenton reaction employing ozone instead of air gave similar results to those using air.

### 3.4. Ammonia wastes + $\text{TiO}_2$

Similar experiments to those described for the photo-Fenton reaction but using  $\text{TiO}_2$  or  $\text{TiO}_2$  doped with Fe (0.15%, w/w) instead of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  have been performed. In these experiments no TOC reduction was neither observed. After 7 h of reaction catalysts present in the different reactors were filtered and analyzed by FTIR (Fig. 5).

The spectrum of the non-doped catalyst from reactor 1 was similar to the one observed from the orange precipitate

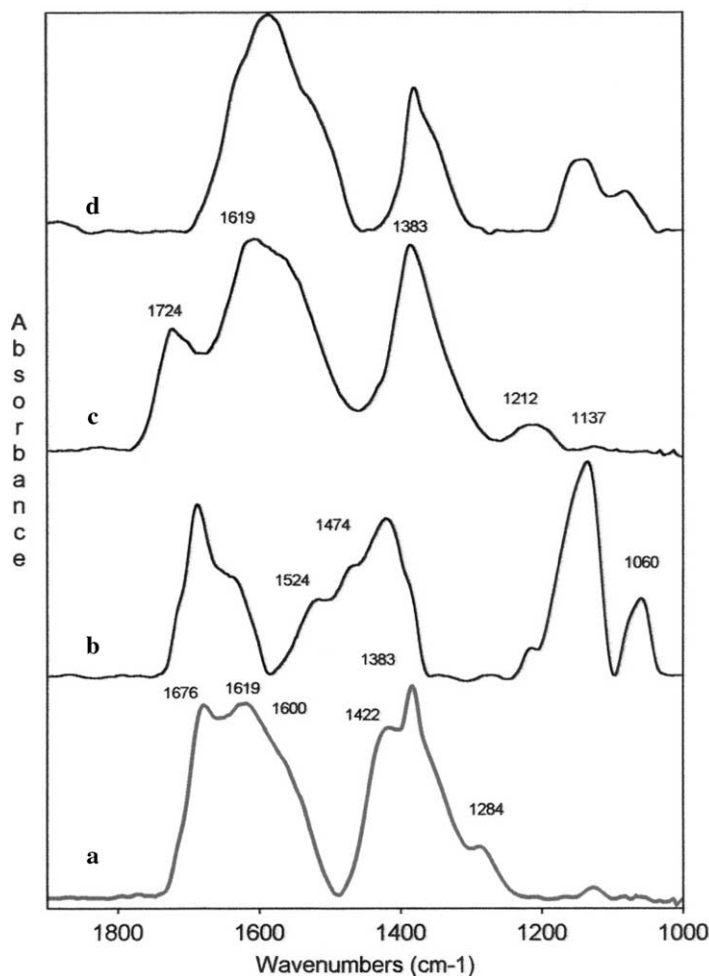


Fig. 5. IR spectra from the catalysts  $\text{TiO}_2$  and doped- $\text{TiO}_2$  after the photocatalytic degradation of ammonia wastes: (a)  $\text{TiO}_2$  reactor 1, (b)  $\text{TiO}_2$  reactor 2, (c) doped- $\text{TiO}_2$  reactor 1, and (d) doped- $\text{TiO}_2$  reactor 2.

during the photo-Fenton reaction, but with bands showing slightly different relative intensities probably due to adsorption effects. Oppositely, the spectrum from the non-doped catalyst in reactor 2 is dominated by bands at 1676, 1619, 1524, 1474, 1422, 1137 and  $1060\text{ cm}^{-1}$ . Spectrum from the doped catalyst in reactor 1 is formed by bands at 1724, 1619, 1600, 1384 and  $1212\text{ cm}^{-1}$ . Bands at 1724 and  $1210\text{ cm}^{-1}$  correlate well with those from formic acid. On the other hand, the spectrum obtained from this catalyst in reactor 2 has intermediate features between the one observed from the non-doped catalyst in this same reactor and the one obtained from the doped catalyst in reactor 1. Bands between  $1680$  and  $1300\text{ cm}^{-1}$  are similar to those obtained from the photo-Fenton reaction studies and are attributable to nitrogenated species such as acetaoximes and acetamides.

Consequently, it can be concluded that nitrogenated species could adsorb onto the catalyst surface this way poisoning active centers that would result in the inhibition of the photocatalytic process.

### 3.5. Toxicity studies

Toxicity of the samples before and after the application of different photocatalytic and conventional treatments has been measured. Toxicity tests were performed by determining the inhibition of luminescence from the marine bacteria *Vibrio fischeri* and the growth of the marine micro alga *Scenedesmun tricornutum*. Results show that samples may become more toxic after the treatments [21] evidencing the transformation toward of the initial compounds into more toxic substances.

## 4. Conclusions

The degradation of nitroprusside during ammonia determination wastes treatment gives free  $\text{C}\equiv\text{N}^-$  ions that react with intermediates or radicals. These nitrile groups evolve to give amines, amides or other nitro-compounds. The degradation of these compounds by means of photo-

catalytic processes seems to be very limited and is notably slower than that of alcohols and carboxylic acids with the same number of carbons. N–H and C–N bonds are stronger than the corresponding O–H and C–O. Consequently, the photocatalytic degradation of compounds containing these bonds will be harder.

Additionally,  $C\equiv N^-$  groups and nitrogenated compounds show a large tendency to react with  $Fe^{3+}$  ions or to adsorb onto the  $TiO_2$  surface, inhibiting this way the photocatalytic process. This is why previous treatments of these wastes with strongly cyanide oxidizing reagents such as permanganate [22] can enhance the elimination of these species and favor the later photocatalytic treatment.

Finally, generated nitrogenated compounds may be even more toxic than the initial compounds as it has been observed from the toxicity tests so it is necessary to determine how these techniques must be applied.

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### References

- [1] J. Araña, E. Tello-Rendón, J.M. Doña-Rodríguez, J.A. Herrera-Melián, O. González-Díaz, J. Pérez-Peña, *Appl. Catal. B* 30 (2001) 1.
- [2] J. Araña, E. Tello-Rendón, J.M. Doña-Rodríguez, J.A. Herrera-Melián, O. González-Díaz, J. Pérez-Peña, *Chemosphere* 44 (5) (2001) 1017.
- [3] C.K. Scheck, F.H. Frimmel, *Water Res.* 29 (10) (1999) 236.
- [4] G. Grabner, G. Li, R.M. Quint, R. Quint, N. Getoff, *J. Chem. Soc., Faraday Trans.* 87 (1991) 1097.
- [5] V. Augugliaro, E. Davi, L. Palmisano, M. Schiavello, A. Sclafani, *Appl. Catal.* 65 (1990) 101.
- [6] K. Okamoto, Y. Yamamoto, H. Tanaka, M. Tanaka, A. Itaya, *Bull. Chem. Soc. Jpn.* 58 (1985) 2015.
- [7] C.S. Turchi, D.F. Ollis, *J. Catal.* 119 (1989) 483.
- [8] J.A. Herrera Melián, E. Tello Rendón, A. Viera Suárez, J.M. Doña Rodríguez, C. Valdés, J. Araña, J. Pérez Peña, *Water Res.* 34 (2000) 3967.
- [9] J. Araña, O. González Díaz, M. Miranda Saracho, J.M. Doña Rodríguez, J.A. Herrera Melián, J. Pérez Peña, *Appl. Catal. B* 32 (1/2) (2001) 49.
- [10] N.B. Colthup, L.H. Daly, S.E. Wiberley, in: *Introduction to Infrared and Raman Spectroscopy*, Academic Press, New York, 1975.
- [11] R.H. Wiley, B.J. Wakefield, *J. Org. Chem.* 25 (1960) 546.
- [12] F.A. Miller, C.H. Wilkins, *Anal. Chem.* 24 (1952) 1253.
- [13] S. Pons, M. Datta, J.F. McAleer, A.S. Hinman, *J. Electroanal. Chem.* 160 (1984) 369.
- [14] M. Datta, A. Datta, *Spectrosc. Lett.* 19 (1986) 993–1037.
- [15] J.C. Moore, D. Smith, Y. Youhne, J.P. Devlin, *J. Phys. Chem.* 75 (1971) 325.
- [16] M.P. Cabildo Miranda, A. García Fraile, in: *Química Orgánica II*, Ministerio de Educación and Ciencia (UNED), 1981, p. 68.
- [17] A. Vidal, A. Dinya, F. Mogyorodi Jr., F. Modyorodi, *Appl. Catal. B* 21 (1999) 259.
- [18] M.A. Fox, J.N. Younathan, *Tetrahedron* 42 (1986) 6285.
- [19] G.K. Low, S.R. McEvoy, R.W. Mathews, *Environ. Sci. Technol.* 25 (1991) 460.
- [20] R.T. Morrison, R.N. Boyd, in: *Química Orgánica*, Addison-Wesley, Longmon, Mexico, 1985.
- [21] E. Tello Rendón, *Optimización de tecnologías fotocatalíticas de oxidación avanzada aplicadas al tratamiento de residuos líquidos de laboratorio*, Doctoral Thesis, Departamento de Química, Universidad de Las Palmas de Gran Canaria, Spain, 2001.
- [22] R. Stewart, *Oxidation by permanganate*, in: K.B. Wuberg (Ed.), *Oxidation in Organic Chemistry, Part A*, Academic Press, New York, 1965.