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On the recalcitrant nature of the triazinic ring species, cyanuric acid, to degradation in Fenton solutions and in UV-illuminated TiO_2 (naked) and fluorinated TiO_2 aqueous dispersions

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Abstract

Attempts to mineralize a variety of *s*-triazine herbicides and dyes containing the triazine ring by the photocatalytic TiO_2 method or by the Fenton process have typically terminated at cyanuric acid as the end product or at precursors such as ammelide, rather than at CO_2 for the carbons and NH_4^+ and/or NO_3^- ions for the nitrogens, when such triazines are subjected to $^{\bullet}OH$ radical (free or otherwise) oxidation. A recent study on the fate of triazoles (e.g. amitrole) in UV-illuminated titania dispersions [N. Watanabe, S. Horikoshi, A. Kawasaki, H. Hidaka, N. Serpone, Environ. Sci. Technol. 39 (2005) 2320] produced ring-expanded triazine intermediates that ultimately also terminated at cyanuric acid despite efforts to totally mineralize the triazole substrates. Another study [Y.-C. Oh, W.S. Jenks, J. Photochem. Photobiol. A: Chem. 162 (2004) 323] reported that the cyanuric acid ring is degraded by free $^{\bullet}OH$ radicals produced from the Fenton reagent and from UV-illuminated TiO_2 aqueous dispersions at various pHs (2–12) whose particle surface was fully fluorinated [C. Minero, G. Mariella, V. Maurino, E. Pelizzetti, Langmuir 16 (2000) 2632]. Our own studies have been unable to degrade cyanuric acid in Fenton solutions, in UV-irradiated naked TiO_2 and fluorinated TiO_2 dispersions, except in a hydrothermal/supercritical aqueous medium [S. Horikoshi, Y. Wada, N. Watanbe, H. Hidaka, N. Serpone, New J. Chem. 27 (2003) 1216] and as reported earlier by others on titania modified by metal complexes. Using various analytical methods (e.g. ESI-MS spectrometry, HPLC-ion chromatography, and UV/visible spectroscopy), we failed to detect any intermediates and mineralized end products that might have resulted from the degradation of this recalcitrant species. We also report ESR and electrochemical results for the characterization of naked TiO_2 and fluorinated TiO_2 specimens. Clearly, cyanuric acid remains a recalcitrant species where $^{\bullet}OH$ radicals are the oxidizing agents. The number of $^{\bullet}OH$ radicals produced from UV-irradiated TiO_2 (naked) and fluorinated TiO_2 depend on the incident light irradiance; at low light irradiance a greater number of $^{\bullet}OH$ radicals are formed on naked TiO_2, whereas at high light irradiance a greater number of $^{\bullet}OH$ radicals seems to form in fluorinated TiO_2 (F/TiO_2) than on naked TiO_2 dispersions owing to a rapid degradation of the DMPO spin trap by surface-bound $^{\bullet}OH$ radicals taking place on the naked particle surface.

Keywords: Cyanuric acid; Triazines; Naked titania; Fluorinated titania; $^{\bullet}OH$ radicals; Zero-zeta potentials

1. Introduction

Heavy usage of herbicides seems to be confined mostly to North America, Western Europe, Japan, and Australia. Farms are not the only users of herbicides, however, as they are also used extensively in industrial sites, roadsides, ditch banks, irrigation canals, fence lines, recreational areas, railroad embankments, and powerline rights-of-way. The two

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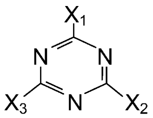
most popular classes of herbicides are the *s*-triazines and the phenoxyacetic acids [1].

s-Triazines are six-membered rings containing three nitrogen atoms and azine (a nitrogen-containing ring) that make up the heterocyclic nitrogens. The most familiar of the triazines are atrazine, simazine, cyanazine, prometon, and propazine. The U.S. Environmental Protection Agency estimates that atrazine is the most heavily used pesticide in the United States, primarily on corn. Triazines are strong inhibitors of photosynthetic electron transport. They inhibit the growth of all organs of intact plants, an effect attributed to a deficiency of photosynthate.



Atrazine: $X_1 = Cl$ $X_2 = NH\text{-}iPr$ $X_3 = NH\text{-}Et$

Cyanuric acid: $X_1 = X_2 = X_3 = OH$

In an early study of the TiO_2 photocatalyzed degradation of triazine herbicides (atrazine, simazine, tetrazine, prometon, and prometryn), Pelizzetti et al. [2] showed that these herbicides degrade rapidly in air-equilibrated titania (Degussa P25) dispersions under simulated sunlight irradiation even at trace (a few ppb) levels for atrazine, which decomposed in very short time to less than 0.1 ppb (0.1 $\mu g\,L^{-1}$). However, this herbicide did not fully mineralize to CO_2 and NH_3 (or NO_3^-), as was expected. Rather, degradation stopped at the refractory cyanuric acid undergoing no further degradation by the photocatalytic process even after 100 h of irradiation. No degradation occurred even by direct photolysis at $\lambda > 340$ nm in aqueous media or by treating a pure sample of cyanuric acid with Fenton's reagent [2]. Dechlorination accounted for ca. 10% loss of initial atrazine. Addition of IO_4^- or $S_2O_8^{2-}$ to the TiO_2 dispersion accelerated the degradation of atrazine [3] through (a) dechlorination by substitution with an OH group, (b) dealkylation of the alkylamino groups, and (c) deamination with formation of hydroxyl-substituted derivatives. The final degradation by-product of atrazine under conditions of a large decontamination solar plant [4] was again cyanuric acid. Further studies confirmed the pathways for the degradation of the *s*-triazines [5–8]. Others have also examined the degradation of *s*-triazine herbicides by photocatalytic methods among others.

Using natural sunlight, Lobedank et al. [9] degraded the *s*-triazine herbicide terbutryne using a photosensitization process with a ruthenium(II)-polypyridyl complex as the photosensitizer. No intermediates were identified and no attempts were made to ascertain whether cyanuric acid was also the end by-product of the degradation. In a more recent study, Chatterjee and Mahata [10] reported that atrazine degrades under visible-light irradiation in the presence of thionine and eosin-Y dyes yielding carbon dioxide. Although the herbicide did degrade partially under these conditions, the source of CO_2 is not evident since dyes also undergo degradation under otherwise identical conditions. A study by Konstantinou et al. [11] on the TiO_2 (Degussa P25) photocatalyzed degradation of other *s*-triazines (atrazine, propazine, cyanazine, prometryn and irgarol) under simulated sunlight provided no further insights into the fate of cyanuric acid, although several intermediates were identified by GC/MS methods. Even in a mixed pollutant feed consisting of atrazine, salicylic acid and phenol, the photocatalytic degradation of atrazine is delayed until the other substrates are degraded as a result of competitive adsorption on the TiO_2 surface [12].

Several workers have investigated the degradation of various *s*-triazines using Fenton's reagent Fe^{2+}/H_2O_2 [13], UV/H_2O_2 [14,15], $UV/TiO_2/H_2O_2$ [16], ozonation [17–19], O_3/H_2O_2 treatment [20] in aqueous Fe^{3+} media by the photo-Fenton process [21], in aqueous hypochlorite solutions [22,23], and dye photosensitization [24], while others examined the (photo)degradation of *s*-triazines, triazine-containing dyes, and triazole herbicides (e.g. amitrole) in UV/TiO_2 aqueous dispersions [25–28]. Some of these methods involve free $^{\bullet}OH$ radicals that should have led to complete oxidation of the triazine herbicides, in general, and cyanuric acid, in particular. Yet, in none of these studies was cleavage of the triazine ring ever observed, as ascertained by a search for intermediates and products. Indeed, even as long ago as 1971, Plimmer et al. [29] remarked that $^{\bullet}OH$ radicals generated by chemical systems dealkylate *s*-triazine herbicides, but that ring cleavage does not occur. Evidently, the TiO_2 photocatalytic process and even (free) $^{\bullet}OH$ radicals are unable to mineralize cyanuric acid, and by extrapolation mineralization of *s*-triazines to carbon dioxide.

Contrasting the above findings and based on work of Minero et al. [30,31], Oh and Jenks [32] investigated the photodegradation of cyanuric acid (0.3 mM) in aqueous suspensions of fluorinated Degussa P25 TiO_2 at low pHs (pH 2). The earlier Minero studies showed that addition of NaF (e.g. 10 or 40 mM) to an aqueous dispersion of TiO_2 (e.g. 0.1 or 1 $g\,L^{-1}$) completely fluorinates the surface of the TiO_2 particles by displacing the terminal $\equiv Ti–OH_2^+$ groups and replacing them by $\equiv Ti–F$ groups at pH ca. 3.5. In neutral media (pH ca. 7), the particle surface consists of Ti–OH groups, whereas in alkaline media (pH > 9) the surface is covered with $Ti–O^-$ functions. Consequently, the events in the photocatalytic process occurring on fluorinated TiO_2 are expected to be significantly different from those taking place on naked (non-fluorinated) titania. In their study, Oh and Jenks [32] concluded that cyanuric acid degraded (albeit partially) through involvement of free $^{\bullet}OH$ radicals in the bulk aqueous phase produced either by UV-irradiated F/TiO_2 dispersions or by the Fenton reaction which had earlier been found to be deficient in degrading this refractory substrate [2]. These inferences were based [32] on the quantity of cyanuric acid remaining after a 6-h treatment at three different pHs (pH 2 with HCl; pH 7 with phosphate buffer; and pH 12 with NaOH) involving irradiated aqueous dispersions of TiO_2 with and without surface fluorination, and the Fenton reagent known to produce free $^{\bullet}OH$ radicals through reaction 1. As noted by others,

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad (1)$$

cyanuric acid remained refractory to oxidation on naked TiO_2 at all three pHs. By contrast, in the F/TiO_2 system, loss of cyanuric acid was nearly 65% at pH 2, about 20% at pH 7, and 0% at pH 12; the Fenton reagent accounted for ca. 30–45% loss of initial cyanuric acid in homogeneous phase at all three pHs [32]. The drop in efficiency at the higher pHs was attributed to the lack of adsorption of cyanuric acid on the titania surface (fluorinated or otherwise) and to a lower reactivity of this otherwise refractory substrate.

Using a different approach, viz. solvothermal processes (pressure, 23 MPa; heating rate, 2 °K min^{-1} up to 675 K) to mineralize atrazine and cyanuric acid, Horikoshi and Hidaka [33] decomposed (not mineralized) about 90% (at 573 K) of the herbicide converting the nitrogens into NH_4^+ and NO_3^- ions. Addition of ozone enhanced the dynamics of degradation and dechlorination of atrazine, along with the decomposition of cyanuric acid under UV irradiation. However, though addition of TiO_2 in the solvothermal process enhanced the degradation of atrazine, it inhibited the degradation of cyanuric acid. In a later more comprehensive study [34], the TiO_2 photocatalytic process was combined with process(es) occurring in hydrothermal (hyH_2O) and supercritical water (scH_2O) under a fixed pressure of 23 MPa and a temperature of 623 °K (also 673 °K) in a batch reactor. Near quantitative dechlorination of atrazine occurred by the scH_2O and hyH_2O methods, becoming quantitative (100%) in the presence of TiO_2. The nitrogens in both atrazine and cyanuric acid were converted to NH_4^+ ions only; no NO_3^- ions were detected. TOC loss hovered around 84 and 51% with and without TiO_2, respectively, in the case of atrazine. For cyanuric acid, loss of TOC was significantly restricted to ca. 9 (no TiO_2) and 19% (with TiO_2), again indicating the recalcitrant nature of cyanuric acid to degrade. However, hydrolytic decomposition of cyanuric acid occurs catalytically at relatively high temperatures (240–450 °C) in the presence of active Al_2O_3 yielding NH_3 and CO_2 in a 1:1 ratio [35]. Mineralization of this recalcitrant species has also been achieved [36] on a proprietary immobilized TiO_2 membrane (PHOTOPERM CPP/313) and a proprietary irradiation module (PHOTOPERM WP), as attested by loss of organic nitrogen through direct hole (h^+) oxidation followed by reaction with the $O_2^{-\bullet}$ radical anions.

Hydrothermal-supercritical water (HY-SC) processes combined with ozonation (HY-SC/O_3) and UV/ozonation (HY-SC/UV/O_3) processes in a single-pass flow-through reactor led to partial mineralization of atrazine and cyanuric acid under hydrothermal conditions (23 MPa), and to almost quantitative mineralization in supercritical aqueous media [37] (Note that the hydrothermal process turns supercritical at ca. 260 °C at 23 MPa pressure.). The TOC results (i.e., evolution of CO_2) showed that mineralization was nearly complete for atrazine and cyanuric acid by the HY-SC method, and that addition of O_3 and UV/O_3 had a positive (albeit small) influence on the efficiency of degradation and on the cleavage of the triazine ring. All nitrogen atoms in atrazine and cyanuric acid were converted to NH_4^+ ions under HY-SC conditions with hardly any trace of NO_3^- ions. Unlike the HY-SC method, AOP processes and radiolytic methodologies are not practical in treating large volumes of a feed polluted by triazines and such other herbicides. By contrast, the HY-SC method can achieve significant mineralization, a feat that the TiO_2 photocatalytic process alone cannot achieve for atrazine, and definitely not for cyanuric acid.

Biodegradation of cyanuric acid through ring cleavage occurs in the presence of *Pseudomonas* sp. Strain D and other types of bacteria [17,38–40]. *s*-Triazines tend to biodegrade through pathways that converge to cyanuric acid, which is then subject to hydrolytic ring cleavage to CO_2 and NH_3 via hydrolysis of the intermediates biuret and urea [41]. Several other biodegradation studies have demonstrated successful cleavage of the triazinic ring and hydrolytic mineralization of the nitrogens and carbons to NH_3 and CO_2 [42–48].

As part of our comprehensive and systematic studies on the degradation of herbicides, we herein report on the refractory nature of cyanuric acid in homogeneous phase using Fenton's reagent ($Fe^{2+} + H_2O_2$), and in heterogeneous phase using naked TiO_2 and fluorinated TiO_2 dispersions under UV irradiation. The latter system has been reported to produce free $^{\bullet}OH$ radicals [30–32,49]. Monitoring the fate of cyanuric acid was achieved by electrospray mass spectroscopy in both positive- and negative-ion mode operation, and by HPLC-ion chromatography for detection of intermediates. DMPO spin-trapping ESR techniques were employed to assess the relative abundance of $^{\bullet}OH$ radicals photogenerated in naked and fluorinated TiO_2 suspensions.

2. Experimental section

2.1. The reagents

Reagent grade cyanuric acid was supplied by Wako Pure Chem. Co. Ltd. Degussa P-25 TiO_2 photocatalyst was used as naked particles (particle size, 20–30 nm by TEM microscopy; surface area, 53 $m^2 g^{-1}$ by BET methods; crystal structure 83% anatase and 17% rutile by X-ray diffraction analysis) and as fluorinated particles. For the latter, P25 TiO_2 (2 mg) was dispersed in a 1 L mixed solution of NaF (40 mM) and HF (20 mM) adjusted to pH 3.5 with HCl. The resulting dispersion was then mixed for 1 h under dark conditions. Fluorinated TiO_2 particles that settled out of the dispersion were centrifuged and separated; subsequently, the wet F/TiO_2 particles were heat-dried at 80 °C for 2 h.

2.2. Photodegradation procedure

To an aqueous solution of cyanuric acid (0.3 mM; 50 mL) was added either naked TiO_2 or F/TiO_2 (each 50 mg); the pH was adjusted to pH 3.5 with HCl. The resulting dispersion was placed in a 127 mL Pyrex vessel. The Fenton reagent in the cyanuric acid solution consisted of a mixed aqueous solution of $FeSO_4$ (8 mM) and H_2O_2 (80 mM). The respective solutions and dispersions were then thoroughly mixed by sonication for ca. 5 min. A magnet bar was introduced into the vessel after which it was sealed with an aluminum septum and a rubber stopper. The Fenton solutions and the titania dispersions were also purged by bubbling O_2 gas for 15 min. Finally, UV illumination was carried out with a 75 W mercury lamp (model Toshiba SHL-100UVQ2; light irradiance, 2.0 mW cm^{-2} at 360 nm) under continuous stirring. The dispersions containing naked TiO_2 and F/TiO_2 particulates were filtered through a suitable membrane filter (0.2 μm). To avoid any interference in the analytical methods, iron in the Fenton aqueous solution was removed by first bringing the pH to ca. 7 with NaOH, followed by filtering the sample through a membrane filter.

2.3. *Analytical methods*

The temporal loss of phenol and formation of catechol and hydroquinone intermediates were monitored using a HPLC chromatograph equipped with a JASCO MD2010 multi-wavelength detector and a JASCO Crestpak C18S column. Possible formation of NH_4^+, NO_3^- and NO_2^- ions was monitored by a JASCO HPLC system equipped with a CD-5 conductivity detector and either a Y-521 cationic column or an I-524 anionic column. The electrospray ionization mass spectrometer (ESI-MS; Agilent Technologies HP1100 series ESI-LC/MSD) was operated in both the negative-ion and positive-ion modes and used for detection and identification of intermediates that might have formed during the expected decomposition of cyanuric acid. In all cases, blank experiments were performed under otherwise identical conditions.

2.4. *ESR spectroscopy*

Air-equilibrated aqueous solutions (0.9 mL; pH 3.5) containing TiO_2 particles (loading, 1 mg) were sonicated for ca. 5 s in the dark, followed by addition of DMPO (5,5-dimethyl-1-pyrrolidine-*N*-oxide) spin-trap (0.1 mL) into the sample solution also under dark conditions, The solution was then introduced into the sample flat quartz cell of the ESR spectrometer, subsequent to which UV irradiation and scanning the spectra were initiated simultaneously. The UV irradiation source was an Ushio 250-W mercury lamp used at high light intensity (8.0 mW cm^{-2}) and at low light intensity (0.016 mW cm^{-2}). The ESR spectral peak intensities were calculated automatically relative to the standard Mn^{2+} marker using the appropriate software of the JEOL JES-TE200 ESR spectrometer. Fig. 1 shows the relevant times needed to record the full ESR spectral signature of the DMPO–$^{\bullet}$OH spin adduct; also shown is the signature of the Mn^{2+} standard marker inside the ESR cavity. Note that sonication of the aqueous dispersions caused formation of a slight quantity of $^{\bullet}$OH radicals for naked P25 TiO_2 and for the F/TiO_2 specimen—reported results in Fig. 3 have been corrected.

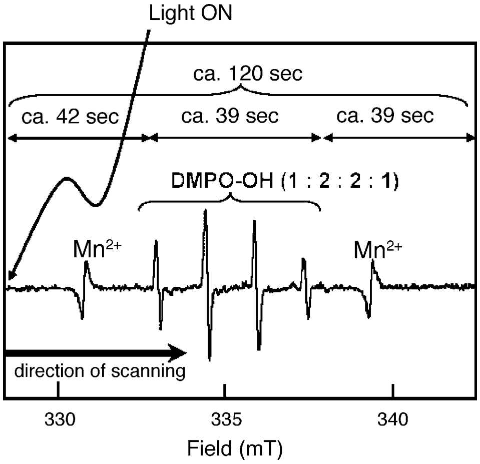


Fig. 1. Details of the method used to estimate the number of $^{\bullet}$OH radicals photogenerated from UV-irradiated TiO_2 and F/TiO_2 aqueous suspensions. Manganese(II) was the internal standard marker. The graphic also displays the time needed (39 s) to record the full DMPO–$^{\bullet}$OH spin-adduct signature from the time light irradiation of the system began (42 s). For more details, see text.

2.5. *Control experiment of naked TiO_2 versus F/TiO_2 using the photodegradation of phenol*

A phenol solution (0.1 mM; 50 mL) containing either 50 mg of naked TiO_2 (P25) or F/TiO_2 was adjusted to pH 3 with HCl, and then placed in the 127 mL Pyrex vessel. The dispersions were dispersed by ultrasonication for about 5 min and subsequently, treated under otherwise identical conditions as those of the cyanuric acid system above. The analyses were also carried out as above.

3. Results and discussion

In their original rather complex study, Minero et al. [30] examined the nature of the titania surface on addition of F^- ions which they followed by an examination of its effect on the photodegradation of phenol, a compound extensively investigated as a model substrate. Addition of fluoride led to substitution of the surface ≡Ti–OH hydroxyl groups, as attested by the displacement of chemisorbed catechol by fluoride ions to give strongly bound fluoride on the TiO_2 surface: ≡Ti–F. On UV illumination, the authors discarded the reaction (Eq. (2)) equivalent to formation of surface-bound $^{\bullet}$OH radicals for naked TiO_2 because the potential of the $F^{\bullet}/F^-$ redox couple is too high (E° = +3.6 V in homogeneous aqueous phase) to permit a similar situation to take place on a fully fluorinated TiO_2 surface.

$$h^+_{VB} + {\equiv}Ti\text{–}F \rightarrow {\equiv}Ti\text{–}F^{+\bullet} \qquad (2)$$

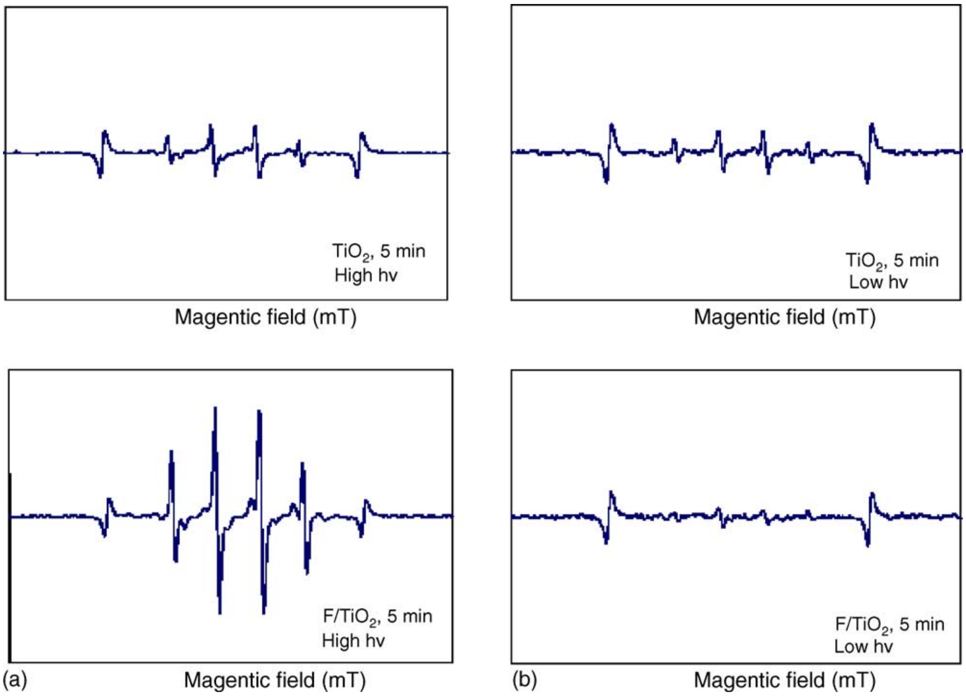


Fig. 2. . Results from ESR experiments recorded after 5 min of irradiation of the titania specimens at (a) high light irradiance of 8.0 mW cm^{-2} and (b) at low light irradiance of 0.016 mW cm^{-2} (see text). Upper panels refer to naked P25 TiO_2 specimens, and lower panels refer to fluorinated P25 TiO_2 specimens, F/TiO_2.

However, just as the potential for the $^\bullet OH/OH^-$ redox couple on the TiO_2 surface is decreased from $E^\circ = +2.8\,V$ in homogeneous aqueous phase [50] to ca. +1.5 V for the couple ($\equiv Ti–^\bullet OH/\equiv Ti–OH^-$) in aqueous titania dispersions [51], the same can occur for the analogous fluoride redox couple. Opposing this view, a recent study by Park and Choi [52] discarded this possibility, suggesting instead that the F in $\equiv$Ti–F acts as an electron trap owing to its large electronegativity. In their interesting work, however, they [52] failed to indicate how the free $^\bullet OH$ radicals formed in F/TiO_2 dispersions except to portray its formation as originating from reaction (3), which presumes that $^\bullet OH$ radicals are formed by oxidation of free OH^- ions in aqueous media, a rather unlikely event especially in acidic media.

$$h\nu/{\equiv}\mathrm{Ti{-}F} + \mathrm{OH}^- \rightarrow \mathrm{Ti(IV){-}F} + {}^\bullet\mathrm{OH}_{\mathrm{free}} \qquad (3)$$

In the range of pH 2–6, Minero et al. [31] noted that photodegradation of phenol in UV-irradiated F/TiO_2 dispersions occurred totally through involvement of free $^\bullet OH$ radicals in the bulk solution phase, whereas in naked TiO_2 dispersions the photocatalytic degradation of phenol involved less than ~10% direct hole transfer to the phenolic substrate and ca. 90% the surface-bound $^\bullet OH$ radicals, i.e., surface-trapped holes. If the surface-bound $\equiv Ti–F^{+\bullet}$ radicals were to behave as surface-bound $\equiv Ti–^\bullet OH$ radicals do, it would not be unreasonable to expect formation of fluorinated intermediates in photo-oxidations taking place in UV-irradiated F/TiO_2 suspensions for molecules that adsorb on the fluorinated TiO_2

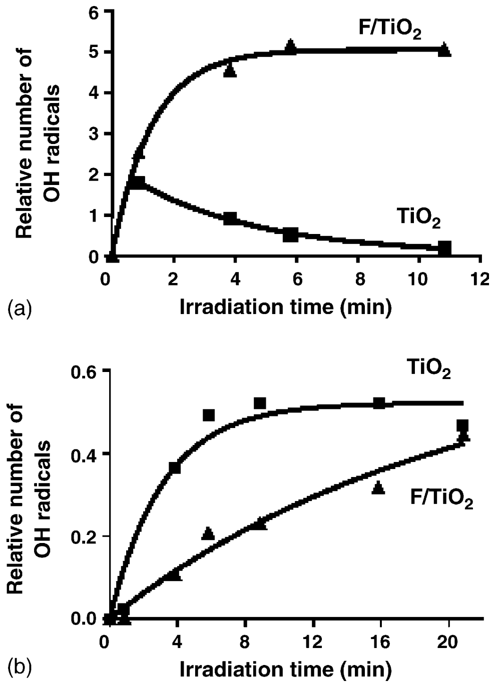


Fig. 3. Temporal behaviour of the photogeneration of $^\bullet OH$ radicals evidenced by DMPO spin trapping ESR techniques for naked P25 TiO_2 and fluorinated P25 TiO_2 (F/TiO_2) at (a) high light irradiance of 8.0 mW cm^{-2} and (b) at low light irradiance of 0.016 mW cm^{-2}.

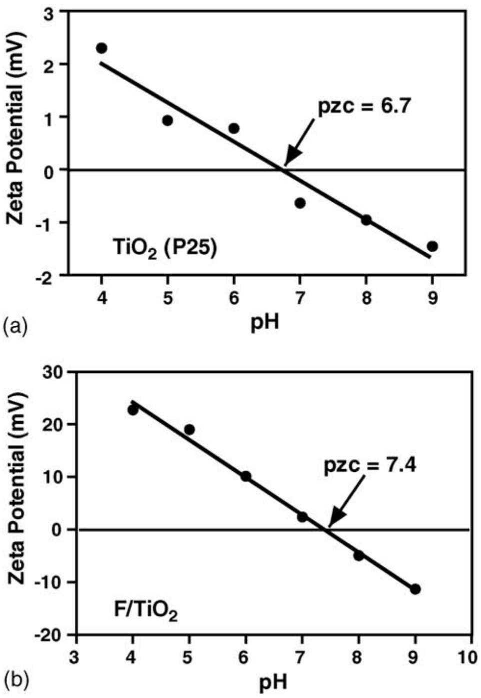


Fig. 4. Point of zero charge determination for (a) naked P25 TiO_2 and (b) fluorinated TiO_2 specimens.

surface (a similar assertion was implied by others [53]). We further presume that in aqueous media, reaction (4) is not unlikely yielding oxidized water:

$$\equiv\text{Ti–F}^{+\bullet} + H_2O \rightarrow \equiv\text{Ti–F} + \{H_2O^{+} \leftrightarrows H^{+} + {}^{\bullet}OH\} \tag{4}$$

viz. H_2O^+, which is nothing more than the protonated form of the ${}^{\bullet}OH$ radical that is then freed into the bulk solution. Accordingly, determination of the relative number of photogenerated ${}^{\bullet}OH$ radicals in UV-irradiated naked TiO_2 and fluorinated TiO_2 dispersions by DMPO-spin trap ESR techniques was undertaken to ascertain the veracity of the above inferences.

3.1. Characterization of F/TiO2 and test of methodology

Fig. 2 illustrates the relevant ESR spectra of the DMPO–${}^{\bullet}OH$ adducts (1:2:2:1 signature flanked by the Mn^{2+} marker) in the absence of any organic substrate other than DMPO recorded at high light irradiance (8.0 mW cm^{-2}; Fig. 2a), and at low light irradiance (0.016 mW cm^{-2}; Fig. 2b) after 5 min of irradiation. Fig. 3 displays the temporal behaviour of the photogeneration of ${}^{\bullet}OH$ radicals as the DMPO spin adducts at high (Fig. 3a) and low light irradiance (Fig. 3b) for both naked P25 TiO_2 and for the fluorinated P25 TiO_2

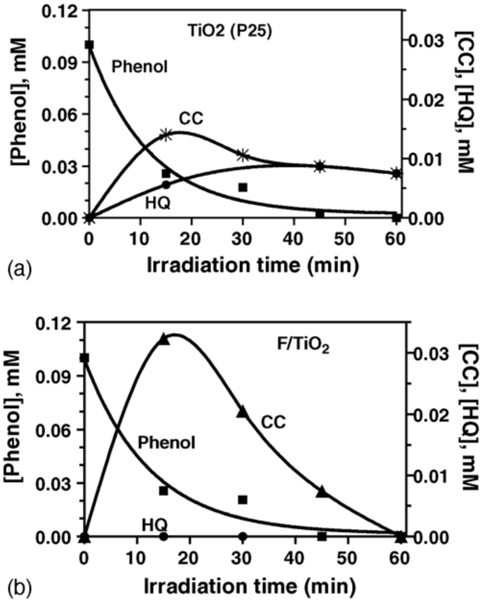


Fig. 5. Temporal distribution of intermediates during the photodegradation of phenol; initial concentration, 0.1 mM: (a) in aqueous naked P25 TiO_2 and (b) in aqueous F/TiO_2 dispersions.

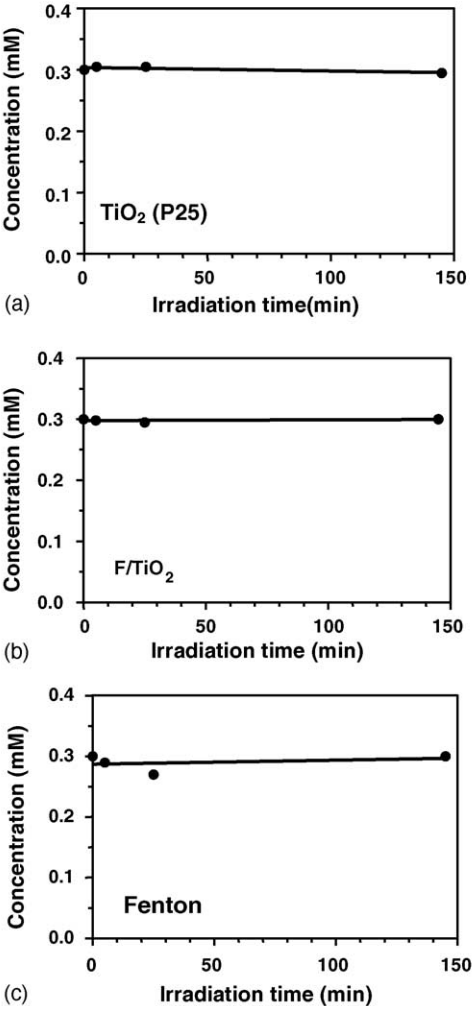


Fig. 6. Results from HPLC analyses of the fate of cyanuric acid present in (a) naked P25 TiO_2 dispersions and (b) in fluorinated TiO_2 dispersions subjected to UV irradiation for up to 150 min, and in (c) Fenton solutions.

specimen (F/TiO_2). The high light intensity observations (Fig. 3a) confirm results from Mrowetz and Selli [49] on F/TiO_2 samples (however, see below). Plots in Fig. 3 were corrected for a small quantity of $^{\bullet}OH$ radicals produced by the sonication of the specimens prior to the ESR runs. The above results show convincingly that at low light intensities a greater number of $^{\bullet}OH$ radicals are formed in naked TiO_2 dispersions than in the fluorinated TiO_2 suspensions. There is no doubt that a similar occurrence also takes place at high light intensities, though not evident experimentally owing to the rapid degradation of the surface-adsorbed DMPO spin trap caused by a larger number of $^{\bullet}OH$ radicals photogenerated that remain on the surface of the UV-irradiated naked TiO_2 particles (Fig. 3a). The DMPO spin trap is likely not adsorbed on F/TiO_2 [52], thus precluding such degradation.

To further characterize the fluorinated P25 TiO_2 specimen, we measured the point of zero charge (pzc) for this particular sample and for naked P25 TiO_2. The results are portrayed in Fig. 4. The pzc for naked TiO_2 particulates was 6.7; for the fluorinated specimen pzc was 7.4. Clearly, fluorination of the titania particle surface increases the pH range in which the surface of the fluorinated TiO_2 particles is positively charged. The band gap energy for the F/TiO_2 specimen was also determined to be 3.14 eV by diffuse reflectance spectroscopy compared to 3.11 eV for naked P-25 TiO_2 obtained under otherwise identical conditions.

As a further control of the methodology used herein, we re-examined the photodegradation of phenol in UV-irradiated P25 TiO_2 (naked) dispersions and in fluorinated P25 TiO_2 dispersions in oxygenated acidic aqueous media. Fig. 5 illustrates the temporal course of the degradation with first-order disappearance of phenol and first-order formation of intermediates. Under otherwise identical conditions, the degradation of phenol in naked TiO_2 suspensions yields both catechol and hydroquinone. By contrast, in fluorinated TiO_2 dispersions, only catechol was detected with traces of hydroquinone. Nonetheless, the results of Fig. 5 are fairly consistent with those reported earlier by Minero et al. [30,31].

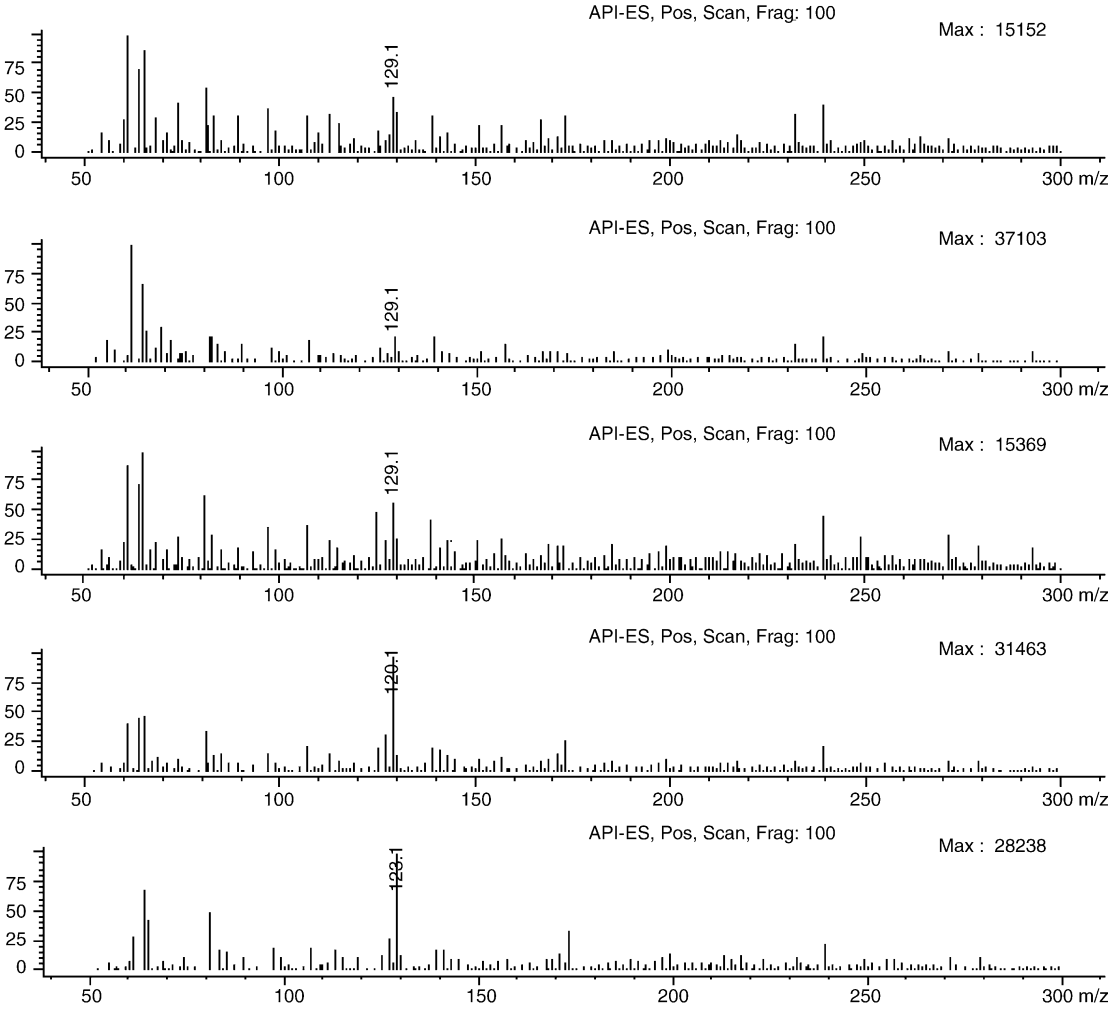


Fig. 7. Electrospray ionization mass spectra recorded in the positive-ion mode for solutions of cyanuric acid subjected to UV-irradiation in naked P25 TiO_2 dispersions: from the top, (Panel 1) mass spectra of a solution of cyanuric acid alone (0.3 mM); (Panel 2) mass spectra recorded at $t = 0$ h; (Panel 3) mass spectra at $t = 5$ h; (Panel 4) mass spectra at $t = 24$ h; and (Panel 5) mass spectra at $t = 72$ h.

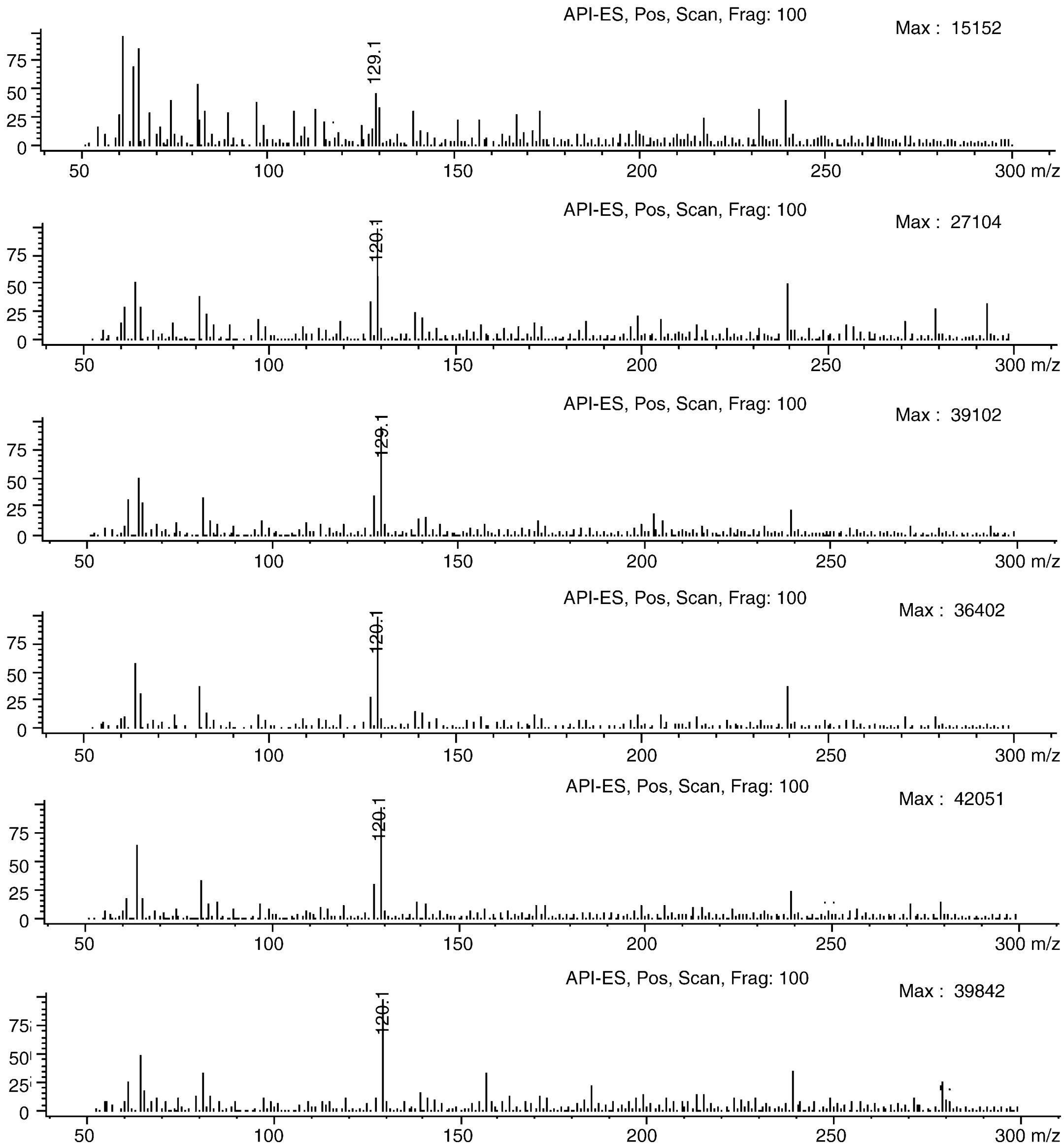


Fig. 8. Electrospray ionization mass spectra recorded in the positive-ion mode for solutions of cyanuric acid subjected to UV-irradiation in fluorinated P25 TiO_2 (F/TiO_2) dispersions: from the top, (Panel 1) mass spectra of a solution of cyanuric acid alone (0.3 mM); (Panel 2) mass spectra recorded at $t = 0$ h; (Panel 3) mass spectra at $t = 5$ h; (Panel 4) mass spectra at $t = 24$ h; (Panel 5) mass spectra at $t = 72$ h; and (Panel 6) mass spectra at $t = 144$ h.

Accordingly, we next examined the fate of cyanuric acid under conditions that paralleled those used for phenol.

3.2. *Photocatalyzed treatment of cyanuric acid with naked TiO_2 and fluorinated TiO_2*

The possible photodegradation of cyanuric acid was examined in UV-irradiated TiO_2 (naked) and fluorinated TiO_2 aqueous dispersions, as well as in a solution containing the Fenton reagent. In all cases, the initial pH of the solution/dispersions was kept at pH 3.5, a condition at which the surface of the TiO_2 particles is completely fluorinated in the presence of fluoride [30,31] and at which the Fenton reagent is most efficient at producing the largest number of $^{\bullet}OH$ radicals (Eq. (1)) [54]. Note that at pH ca. 7 and in more alkaline media, the Fenton reagent produces no $^{\bullet}OH$ radicals but does form gelatinous iron hydroxides. Analyses of the irradiated dispersions (UV light irradiance, $2.0\,\mathrm{mW\,cm^{-2}}$) and of the Fenton solution show that after 150 min, there was no degradation of cyanuric acid (Fig. 6). Further irradiation for up to 144 h of the naked and fluorinated TiO_2 dispersions containing cyanuric acid, and further treatment of this acid in the Fenton solution also up to 144 h showed no intermediates (e.g. biuret and urea) and no mineralized products, such as NH_4^+ and/or NO_3^- ions (nor nitrites) by HPLC ion chromatographic analyses.

Electrospray ionization mass spectral analyses of the UV-irradiated naked TiO_2 and fluorinated TiO_2 dispersions in both the positive-ion (Figs. 7 and 8) and in the negative-ion mode also revealed no degradation of cyanuric acid

($m/z = 129$, positive mode) even after an extensive period of UV illumination (up to 144 h). In the Fenton process, the mass spectral analyses also indicate that the cyanuric acid remains recalcitrant to degradation; however, we did observe a mass spectral signal at $m/z = 147$, which we attribute to a species (chlorodihydroxy triazine) in which an OH group on cyanuric acid is substituted by a Cl atom (note that the pH was adjusted by addition of HCl acid). It was not the scope of this study to further examine this observation.

4. Concluding remarks

This study confirms earlier observations that under conditions where $^{\bullet}OH$ radicals are the oxidizing agents in photocatalytic degradation or Fenton-type degradation processes, regardless of how such radicals are generated, the cyanuric acid remains a recalcitrant species to degrade. However, as discussed above (Section 1) under other conditions, such as biodegradation, hydrolytic methods at high temperatures on alumina, and in supercritical aqueous media, cyanuric acid is degraded as evidenced by an analysis of the ensuing end products (e.g. ammonia, nitrate ions, carbon dioxide, COD, and loss of TOC). In addition, Johnson et al. [55] have degraded cyanuric acid under anodic oxidation at a Pt electrode converting the triazine nitrogens into NO_3^- ions (ca. 70%) and traces of NO_2^- ions, whereas Macyk et al. [56] degraded cyanuric acid on TiO_2 anatase particles modified with 4% $H_2[PtCl_6]$ as evidenced by loss of TOC and formation of NO_3^- ions (ca. 60% degradation after 6 h on UV irradiation at $\lambda > 320$ nm and with visible light at $\lambda > 455$ nm). Hequet et al. [57] were able to degrade cyanuric acid by direct photolysis at 185 nm in aqueous media with formamide being the preponderant end product. This study calls attention to and re-emphasizes the need to identify the nature of intermediates and end products to ascertain the degradation/mineralization of substrates in advanced oxidation processes.

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