

Photocatalytic degradation of citric acid under different conditions: TiO₂ heterogeneous photocatalysis against homogeneous photolytic processes promoted by Fe(III) and H₂O₂

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Abstract

Degradation of citric acid (Cit) at relatively high concentrations by photocatalysis over TiO₂ under air bubbling and near UV-light was tested under different conditions. The reaction was improved by addition of H₂O₂, Fe(III) or both. Minor amounts of H₂O₂ were effective to enhance the oxidation and the mineralization. H₂O₂ addition impacts more on the initial rate, while the effect of Fe(III) is more important after prolonged irradiation. The kinetic profiles were analyzed and compared, and the best ratio of reagents was found (1:1:1 H₂O₂/Cit/Fe molar ratio). However, a lower amount of Fe (1:1:0.2 H₂O₂/Cit/Fe ratio) was also effective. Similar experiments under the optimal conditions in the absence of TiO₂ were performed for comparison. When both H₂O₂ and Fe(III) were present, the behavior with and without TiO₂ was very similar. So far, 3-oxoglutaric acid was detected as a reaction intermediate. A mechanistic analysis is initiated to explain some features of these complex systems.

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1. Introduction

Advanced oxidation technologies (AOTs) are innovative methods for water treatment, extremely useful in the case of substances resistant to conventional technologies [1,2]. From them, TiO₂ heterogeneous photocatalysis (HP) and photo-Fenton (PF) processes are the most investigated; there are already promising results for real applications in a near future [2,3].

Citric acid (C(OH)(COOH)(CH₂COOH)₂, 2-hydroxy-propane-1,2,3-tricarboxylic acid, Cit), is a model compound of several natural systems due to its presence in plants and soils. It

is an Fe(III) transport agent in biological systems [4], a frequent domestic and industrial chelating agent used in the food industry and in detergents [5], and it is often used as a reducing agent in photolytic and photocatalytic systems.

Fe(III) is easily complexed by citric acid; the Fe(II)-complex is rather much less stable [6]. There is some discrepancy in the literature concerning the ferric citrate species dominant in solution at different pHs [7,8] but, according to Field et al. [9], Hamm et al. [10] and Nansheng et al. ([11] and references therein), mononuclear FeCit (log *K* = 11.85) is the predominant species from pH 2 to 4, whereas Fe(OH)(Cit)[−] (log *K* = 9.40) appears to be the most abundant species between 4 and 6. Even though the absorption of 1:1 ferric complexes varies with pH, it remains roughly constant at 365 nm over a large pH range ($\epsilon \cong 900 \text{ M}^{-1} \text{ cm}^{-1}$ from pH 2 to 6) [12].

Early reports indicate that citric acid is relatively stable to near UV-light [13], but it is decomposed by photolysis below

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242 nm to products similar to those obtained under ionizing radiation [14–17]. Although thermally stable, iron(III) carboxylates are photochemically unstable: in the case of Fe(III)–Cit, UV- and blue-light promote an efficient photolysis with Fe(II) formation and oxidation of the ligand followed by decarboxylation [8,18,19]. The reported final products are acetone, carbon dioxide and acetonedicarboxylic acid (3-oxoglutaric acid, 3-OGA), while acetic and acetoacetic acids were found as intermediates [8].

AOTs studies on citric acid are scant. So far, only two reports on mineralization through UV/TiO₂ photocatalysis and no additives are informed [20,21]. Photocatalysis was proved to be efficient to degrade citric and other acids in relatively high concentrations, as representatives of wastewaters coming from cleaning of boilers in power plants. In those papers, no effect of the addition of oxidants other than O₂ is mentioned.

Other papers are related to the oxidative destruction of citric acid in conjunction with the reductive removal of heavy metals (Ag(I), Cr(VI), Hg(II) and Pt(IV)) via TiO₂ photocatalysis [5,22–24], pointing out the synergy between reduction and oxidation processes.

Iron species participate in a series of environmental processes (Fenton, photo-Fenton, etc.), whereby many compounds are transformed in natural waters or in the atmosphere [25]. On the other hand, Fe(III)-complexes such as Fe–NTA, Fe–EDTA or Fe–Cit can be used to induce photodegradation of pollutants [1,2,26]. For example, Fe(III)–Cit was found efficient to accelerate the photodegradation of dyes, especially under sunlight [19] and the oxidation of arsenic(III) into arsenic(V) [27].

Some years ago we initiated AOTs studies for the treatment of liquid wastes of decontamination and cleaning processes of nuclear power plants, which are composed of a mixture of oligocarboxylic acids (NTA, EDTA, oxalic acid, citric acid, etc. and their degradation derivatives) at relatively high concentrations. We have already analyzed the cases of EDTA, NTA and oxalic acid, and made some preliminary studies on citric acid [28–38]. We found that the degradation and the mineralization degree strongly depend on the chemical complexity of the compound. It was also found that the effect of oxidants such as H₂O₂ and Fe(III) also depends on the type of compound and on the photochemical redox process associated to the complex formed between Fe(III) and the organic acid.

In this work, 366 nm-photocatalytic degradation of citric acid at relatively high concentrations (5 g L⁻¹, 0.024 M) and pH 3.7 using TiO₂ heterogeneous photocatalysis (HP), photo-Fenton (PF) and their combination (HP-PF) is described. Concentration and pH conditions were chosen as representative of typical values found in liquid wastes coming from cleaning and decontamination processes of nuclear power plants.

2. Experimental

2.1. Chemicals

All chemicals were reagent grade and used without further purification. TiO₂ (Degussa P-25) was provided by Degussa AG

Germany and used as received. Citric acid (C₆H₈O₇·H₂O) was Riedel de Häen. Hydrogen peroxide (30%) was Merck. Water was purified with a Millipore Milli Q equipment (resistivity = 18 MΩ cm). Iron was added to the TiO₂ systems as Fe(III) in the form of NH₄Fe(SO₄)₂·12H₂O (Mallinckrodt), while Fe(II) (as Mohr salt, Fe(NH₄)₂(SO₄)₂·6H₂O, Mallinckrodt) was used in the Fenton systems. Both reagents were of the highest available purity.

2.2. Irradiation procedure

Irradiation experiments were performed in a recirculating system (1.5 L min⁻¹ flow rate) consisting of an annular reactor (415 mm length, 35 mm external diameter, 92 mL volume), a peristaltic pump and a thermostated (298 K) cylindrical reservoir (380 mL). The total volume of the circulating mixture was 350 mL, from which 100 mL were permanently kept in the reservoir to take samples and to measure pH. A black-light tubular UV lamp (Philips TLD/08, 15 W, 350 nm < λ < 410 nm, maximum transmission at 366 nm) was installed inside the annular reactor as the illumination source. Air was constantly bubbled in all experiments (2 L min⁻¹). A 0.024 M fresh solution of citric acid was daily prepared for the experiments. Actinometric measurements were performed by the ferrioxalate method [36]. A photon flow per unit volume of 8 μEinstein s⁻¹ L⁻¹ was calculated.

In all TiO₂ photocatalytic (HP) experiments, 1 g L⁻¹ of photocatalyst was used; the suspension containing 0.024 M citric acid was ultrasonicated before irradiation during 15 min for homogenization, pH was adjusted to pH 3.7 with NaOH, and the suspension stirred for 30 min in the dark to assure the adsorption equilibrium of citric acid onto TiO₂. However, due to the high concentrations, the amount of citric adsorbed on the catalyst was negligible, as calculated by measuring concentrations before and after stirring in the dark.

In PF experiments, the solution of the ferrous salt at a known concentration was added to the citric solution, and pH was adjusted at 3.7. In HP-PF, TiO₂ was added to the citric acid solution, the suspension was sonicated, iron(III) was then added and pH adjusted to 3.7.

In experiments with H₂O₂, the reagent was added just before irradiation, and to avoid its depletion, a volume similar to the initial quantity was periodically added. The additions were done every each 20 min during the first hour and then every hour.

In all experiments, pH was maintained constant throughout the irradiation time by periodical addition of concentrated HClO₄. Samples (0.25 mL) were taken at different times for analysis. All experiments were performed at least by duplicate and results averaged. The experimental error was never higher than 12%.

Reactions in the dark in the absence as well as in the presence of TiO₂ (O₂, no other oxidants) or under irradiation without TiO₂ gave negligible degradation, indicating clearly that transformations were due only to photocatalytic effects. Blanks in the dark (no TiO₂) in the presence of H₂O₂ (1:1 H₂O₂/Cit molar ratio) or in the presence of Fe(III) (1:1 Cit/Fe molar

ratio) yielded no detectable citric acid transformation. Reaction with both reagents (1:1:0.2 H₂O₂/Cit/Fe³⁺ molar ratio) in the absence of light (dark Fenton reaction) yielded some minor citric acid degradation (only 9% after 160 min).

2.3. Analysis of samples

Evolution of citric acid concentration with time was followed by HPLC using a Konik-500-A HPLC chromatograph, a UV/VIS Thermo Separation Products UV 100 detector and a Konikrom Chromatography Data System V.5.2. Initially, the following conditions were used: RP-C18 Prevail (Alltech), 5 μm, 4.6 mm × 150 mm column, pore size 110 Å; 25 mM KH₂PO₄ at pH 2.5 (H₃PO₄) as eluent; 1.2 mL min⁻¹ flow rate; UV-detection at 210 nm. During the experiments, 3-OGA was identified as an intermediate of the reaction, and then the pH of the eluent had to be changed to 2.3 to avoid interference with citric acid. Detection of acetone was attempted at 269 nm. Samples (0.25 mL) were periodically taken and diluted to 25 mL with the phosphate buffer for TOC and citric acid concentration analysis. In the case of experiments with H₂O₂, 0.1 mL of a quenching solution, composed of Na₃PO₄, KI and Na₂SO₃, all 0.1 M, was previously added to eliminate residual H₂O₂ and to quench the oxidation after sampling.

To eliminate Fe(III) and avoid precipitation by the phosphate buffer into the chromatographic column, Fe-containing samples (after addition of 0.1 mL of the quenching solution when needed) were alkalinized with 0.25 mL of 1.5 M NaOH. Fe(OH)₃ was filtered through a 0.2 μm Millipore membrane, the filter washed with diluted NaOH, 0.5 mL of concentrated H₃PO₄ added and the solution diluted to 25 mL with the eluent.

TOC was measured with a Shimadzu 5000-A TOC analyzer in the NPOC (non-purgeable organic carbon) mode.

3. Results

Evolution of citric acid concentration with time was followed under different conditions. Fig. 1 shows the time profiles (Cit/Cit₀) of selected experiments over TiO₂ under irradiation in the absence and in the presence of increasing H₂O₂ concentrations. An experiment in the 0.5:1 H₂O₂/Cit molar ratio has been also performed, giving results very similar to that of 0.1:1 H₂O₂/Cit ratio, but is not shown for clarity. While only around 30% of conversion was attained in the absence of H₂O₂ after 270 min together with a negligible TOC decrease, a remarkable increase in the extent of degradation was observed with only a minor amount of the oxidant: for example, almost 60% of Cit conversion and ca. 25% of TOC removal (not shown) were reached with the 0.01:1 H₂O₂/Cit molar ratio. However, after this initial increase, higher amounts of H₂O₂ did not improve very much the degradation; the highest ratio (5:1 H₂O₂/Cit) was even slightly detrimental at long irradiation times, although always better than in the absence of H₂O₂.

Analogous profiles but in the presence of Fe(III) are shown in Fig. 2. Low amounts of iron (for example, 1:0.1 Cit/Fe) cause almost no effect, but higher concentrations enhance degrada-

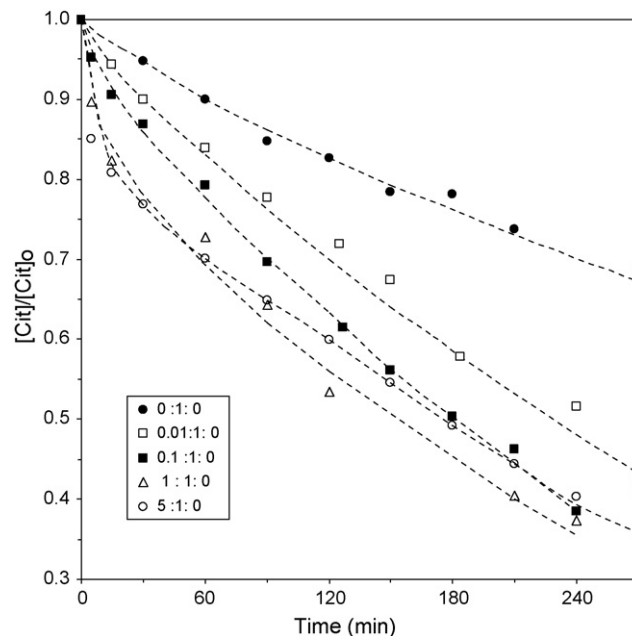


Fig. 1. Time profiles for the photocatalytic degradation of Cit in the absence and in the presence of H₂O₂ under continuous air bubbling. Conditions: [Cit] = 0.024 M; [TiO₂] = 1 g L⁻¹; pH 3.7; T = 298 K; P₀ = 8 μEinstein s⁻¹ L⁻¹. H₂O₂:Cit:Fe³⁺ molar ratio is indicated.

tion. The optimal ratio was Cit/Fe 1:1; under these conditions, around 70% of citric acid disappeared after 270 min of irradiation (cf. with 30% in the absence of Fe), from which ca. 30% was mineralized. A higher amount of iron resulted detrimental for the degradation as well as for the mineralization, being even worse with the 0:1:2 ratio, not shown for clarity. The kinetics looked very complicated in these cases;

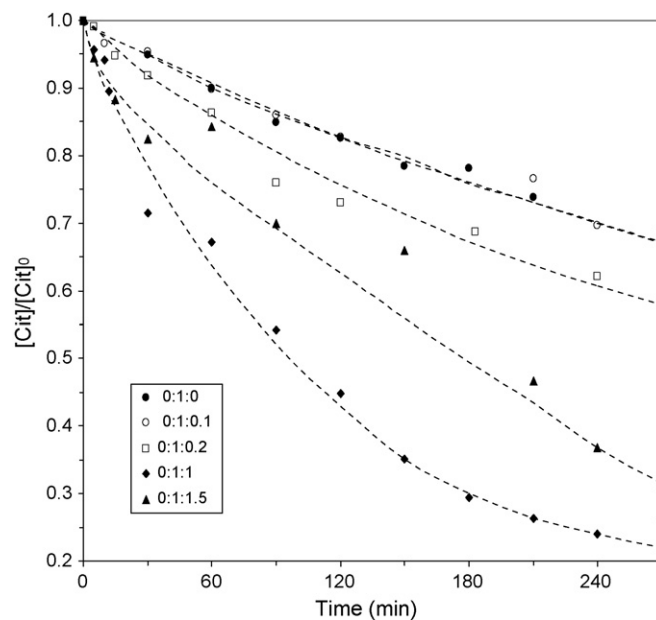


Fig. 2. Time profiles for the photocatalytic degradation of Cit in the absence and in the presence of Fe³⁺ under continuous air bubbling. Conditions: same as in Fig. 1. H₂O₂:Cit:Fe³⁺ molar ratio is indicated.

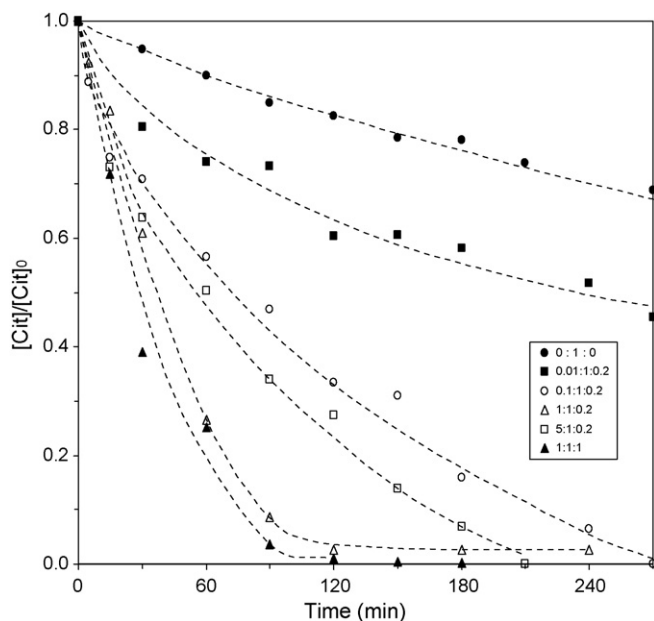


Fig. 3. Time profiles for the photocatalytic degradation of Cit in the absence and in the presence of Fe^{3+} and H_2O_2 under continuous air bubbling. Conditions: same as in Fig. 1. H_2O_2 :Cit: Fe^{3+} molar ratio is indicated.

however, the degradation extent was always higher than in the absence of iron.

A higher improvement of the degradation extent was obtained by adding Fe^{3+} and H_2O_2 simultaneously to the TiO_2/O_2 system (HP-PF) (Fig. 3). A low and constant amount of iron (Cit/Fe 1:0.2 ratio) was chosen initially to be combined with increasing amounts of H_2O_2 . Again, minor amounts of H_2O_2 caused an important increase in the rate. The optimal ratio was 1:1:0.2, higher H_2O_2 amounts being detrimental. Under the optimal conditions, 96% citric acid was degraded in 120 min together with ca. 60% of TOC decrease (and 80% after 240 min). A somewhat better result was obtained with a higher Fe(III) amount (1:1:1 ratio); however, this did not cause any relevant change and, on the contrary, it would represent a waste in iron.

Experiments in the absence of TiO_2 , with iron or with iron and H_2O_2 (i.e. photo-Fenton experiments), were also performed under the best conditions found in HP experiments and compared with them. The results are shown in Fig. 4. The slight degradation of citric acid taking place in the absence of iron and TiO_2 after prolonged irradiation (20% at 240 min) could be only attributed to the presence of some impurity (probably, iron or TiO_2 traces) in the reactor. For comparison, data from Fig. 1 with the same amount of H_2O_2 and TiO_2 were added to Fig. 4, and this shows the remarkable effect exerted by the catalyst (almost 65% of citric acid degraded after 240 min). With Fe(III) and no H_2O_2 , the kinetic behavior is similar with or without TiO_2 during the first 120 min, but then a deceleration takes place in the TiO_2 -containing system. A possible explanation is that some intermediates formed during the reaction adsorb onto the TiO_2 surface competing with Cit. In the presence of both H_2O_2 and Fe(III), the presence of TiO_2 is irrelevant. Addition of

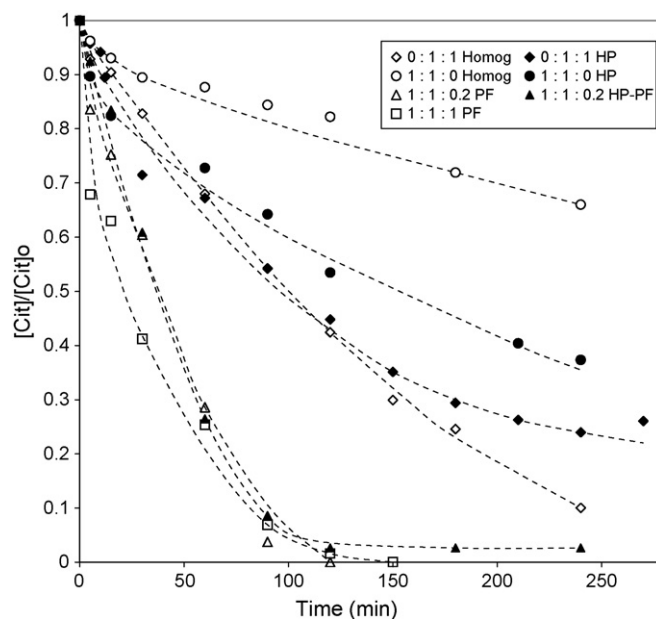


Fig. 4. Comparison of time profiles of Cit degradation in the absence and in the presence of TiO_2 under different conditions. Conditions: same as in Fig. 1. H_2O_2 :Cit: Fe^{3+} molar ratio is indicated.

a higher amount of Fe(III) causes an acceleration in the first stages, but only a very low enhancement at longer irradiation times.

Fig. 5 shows results of %Cit degradation and TOC decrease at 120 min together with initial apparent pseudo-first order rate constants (k_0) calculated from the time profiles in the best conditions. Parameters match each other in most of the cases. Analyzing the influence of the oxidants, addition of H_2O_2 causes more impact than Fe(III) addition on initial rates while the opposite occurs at prolonged irradiation regarding either Cit or TOC decrease. Another conclusion from Fig. 5 is that, under the optimized conditions, the presence of TiO_2 does not improve the removal process and even TOC removal is slightly higher in the absence of the catalyst.

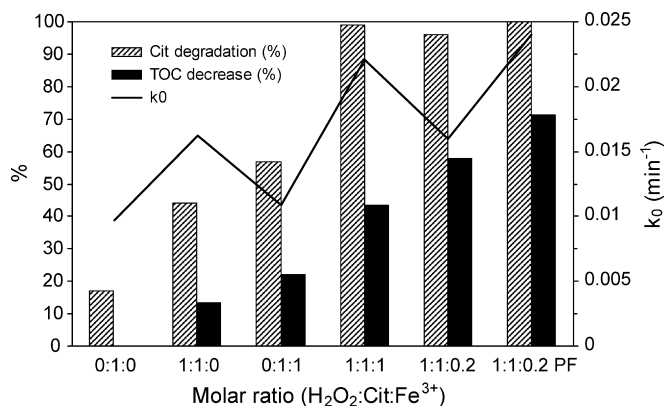


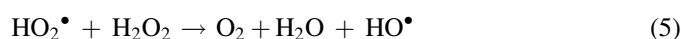
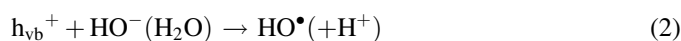
Fig. 5. Selected results of initial rate constants (k_0 , line, right axis), Cit degradation percentage (Cit degradation (%)) and TOC removal (TOC decrease (%)) at 120 min (bars, left axis). H_2O_2 :Cit: Fe^{3+} molar ratio is indicated.

In separate TiO₂ photocatalytic experiments, either in the absence or in the presence of Fe(III), we tried to detect and identify reaction products by HPLC in the first stages of the reaction (around 35 min). Oxalic, glyoxylic and formic acids, and formaldehyde were discarded by comparison with standards. Acetone or acetic acid was not detected even when air was not bubbled in the system, ruling out their possible volatilization. So far, the only identified product is 3-oxoglutaric acid. Some other peaks were present in the chromatograms indicating still not identified additional products. Experiments for identification and quantification of these compounds are underway.

4. Discussion

4.1. Pure UV/TiO₂ system

According to the very well-known mechanism of photocatalysis with TiO₂, the following set of equations can be written:

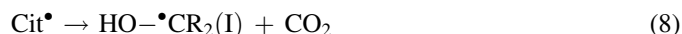


At the concentration and pH used in this work (3.7), citric acid is mainly in the monoanionic C₆H₇O₇⁻ form (pK_{a1} = 3.13, pK_{a2} = 4.76, pK_{a3} = 6.40) [40]. At this pH, the one-electron reduction potential of this species, $E_{\text{H}_7\text{C}_6\text{O}_7/\text{H}_7\text{C}_6\text{O}_7^-}^0$, is not known but it should be certainly lower than 2 V versus NHE, the known value for oxalic acid [37], because the tertiary carbon makes the molecule somewhat more oxidizable. Thus, h_{vb}^+ -TiO₂ (V_{fb} = +3.1 V at pH 3.7 for Degussa P-25 [41]) and HO[•] ($E_{\text{OH}/\text{H}_2\text{O}}^0 = 2.8 \text{ V}$ at pH 3.7 [42]) can easily oxidize citric acid. Attack of HO[•] to citric acid in homogeneous solution is fast ($k = 5.0 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ at pH 1 [43]), and at the interface semiconductor–water and pH 3.7, this value should not be very different. Therefore, HO[•] radicals are also able to degrade citric acid at an appreciable rate. In the case of oligocarboxylic acids like citric acid, which adsorb strongly over TiO₂, the proposed main route is hole attack [44–46]; however, HO[•] would produce the same radical as the primary product:

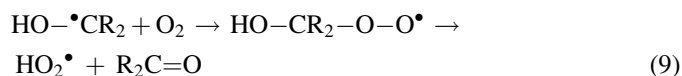


where Cit = HO–CR₂–COO, and R = –CH₂COOH. In an earlier paper, radicals formed in the photolysis of aqueous solutions of citric acid and sodium citrate were identified by EPR as (HO₂CCH₂)₂•COH (I), HO₂CCH₂C(OH)(CO₂H)•CHCO₂H (II) and HO₂CCH₂C(OH)(CO₂H)•CH₂ (III). Radical I is supposed to be formed by the loss of the central carboxyl group of the excited citric acid molecule. Radical III would result from the loss of one terminal carboxyl group. Radical II could be

generated by proton abstraction from a methylenic hydrogen [16]. As so far we only identified 3-OGA, we propose that the main radical formed in our systems is (I) because the formation of (II) and (III) has to be sustained by still not detected intermediates. In this way, Cit[•] can be easily decarboxylated to the C-centered radical I [8]. Thus, we can write:

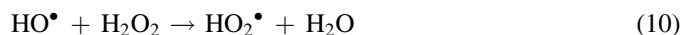


In the presence of oxygen, 3-OGA is formed:



3-OGA can be very fast decomposed to acetone and CO₂, but as already said, these compounds were not detected in the system. HO₂[•] (or O₂^{•-}) ends in H₂O₂, which forms more HO[•] with e_{cb}⁻, according to the set of Eqs. (4)–(6).

On the other hand, it is known that H₂O₂ addition enhances TiO₂ photocatalytic reactions by reacting with electrons (Eq. (6)), inhibiting recombination and forming additional amounts of HO[•]. However, an excess is detrimental because of its hole scavenging power, giving rise to hydroperoxyl radicals of less oxidizing power than HO[•] [47]:

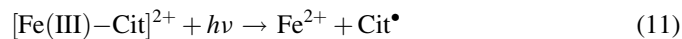


This explains why the degradation rate increases only until a limiting H₂O₂ concentration, here in the 1:1 H₂O₂/Cit molar ratio (Fig. 1).

4.2. Systems in the presence of Fe or Fe plus H₂O₂

Fe(III) could play a similar role as that of H₂O₂, because it has a very convenient redox potential to be reduced by e_{cb}⁻ ($E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 = 0.77 \text{ V}$ versus NHE), taking into account a value of –0.5 V for the e_{cb}⁻ redox potential at pH 3.7 [41]. This inhibits recombination and, in fact, this role has been recognized several times [47,48]. However, in the presence of excess of Cit, the main species will be the Fe(III)–Cit complexes, whose redox potential is rather more negative than that of the Fe(III)/Fe(II) uncomplexed couple. In fact, in the literature, a value for $E_{\text{Fe}^{\text{III}}-\text{citrate}/\text{Fe}^{\text{II}}-\text{citrate}}^0 \cong -0.25 \text{ V}$ versus NHE is reported [49]; this means a lower driving force for iron reduction by e_{cb}⁻.

In contrast, the photoactive 1:1 Fe–Cit complex undergoes an easy homogeneous photolytic process whose primary step is a rapid LMCT reaction with creation of a radical and Fe²⁺, according to



where Cit[•] means the same as before [9,10,50]. The highest values at 365 nm for the quantum yield of Fe(II) formation were found at pH 3 (0.28) and 4 (0.29), decreasing at higher pH [12,50]. This was interpreted in terms of a more photoactive FeCit complex formed between pH 2 and 3 and a less active Fe(OH)Cit complex formed at pH > 4 [9,12]; both forms are present under our conditions, and the quantum yields are quite high to favor the photolysis.

Following this initial LMCT reaction, H_2O_2 and HO^\bullet can be formed through a similar pathway as that of the Fe(III)–oxalate complex [19,51]. The fate of the Cit^\bullet is determined by several competing processes from which decarboxylation to form CO_2 and a C-centered radical (Eq. (8)) seems to be the most important, one reacting fast with Fe(III) and degrading rapidly [8,27,51]. Literature reports [11] indicate that the C-centered radical formed in the homogeneous photolysis of Fe(III)–Cit complexes is the same $\text{HO}^\bullet\text{-CR}_2$ mentioned in the previous section, and that the first degradation product is also 3-OGA, likely formed by an oxidative termination of the radical by iron(III):



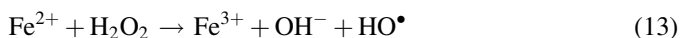
The formation of 3-OGA in our systems (either in the presence or in the absence of iron) was supported by HPLC measurements.

Recomplexation of Fe(III) with citric acid or its photodegradation products leads to new LMCT photolytic reactions. By all these reasons, the reaction in the presence of iron (or Fe plus H_2O_2) is greatly promoted, even at longer times.

As said before, reduction of Fe(III)–Cit complexes by e_{cb}^- does not seem to be important in our case. In agreement, we found that citrate can be excellently degraded by UV irradiation in the presence of only iron(III), and that the presence of TiO_2 was irrelevant (see Fig. 4, cf. 0:1:1 homog. versus 0:1:1 HP).

The amount of Fe(III) added to the system is very important, as found in other systems like the ferric citrate-induced photodegradation of dyes [11]. Addition of Fe(III) until an 1:1 molar ratio to Cit improves degradation because the photochemical reduction of the Fe(III)-complex is coupled to the Fenton reaction (see below) and to the heterogeneous photocatalytic process when TiO_2 is present. The detrimental effect of a higher iron concentration can be due to the preferential reoxidation of Fe(II) over that of the organic compound by holes or HO^\bullet . At long irradiation times, another effect due to a filter effect of Fe(III) species of low photochemical activity can be operative.

In the presence of oxygen, H_2O_2 , $\text{O}_2^{\bullet-}$ or HO_2^\bullet is formed, which induces a rapid reoxidation of Fe^{2+} . There is also the possibility of the contribution of the Fenton reaction:



This reaction, which can occur also in the presence of TiO_2 from H_2O_2 generated through Eq. (4), is an additional source of hydroxyl radicals [2,52–56]. Recreated Fe(III) can be reduced again to Fe^{2+} by superoxide or hydroperoxyl radicals, initiating a continuous Fe(III)/Fe(II) cycle, which enhances substrate degradation [19,51 and references therein].

Fe^{3+} (added or generated from Fe^{2+}) gives rise to the radical chain mechanism described above, and the Fenton reaction (13) is improved by the participation of photogenerated Fe^{2+} . In addition to the already mentioned species (HO^\bullet , $\text{O}_2^{\bullet-}$, etc.), other oxidants like Fe(IV) or Fe(V) species have been proposed to contribute to Fenton reactions [2 and references therein], but their presence has been not demonstrated yet.

In addition, Fe(II)–polycarboxylate complexes enhance even more reaction (13) because they react 10–1000 times faster with H_2O_2 than bare Fe^{2+} [50 and references therein].

When H_2O_2 is added in combination with Fe(III) and TiO_2 , HP-PF constitutes a very complex system in which several processes occur at the same time, contributing to the overall rate. However, in the ternary system, and with the optimal amount of H_2O_2 , results with 1/5 of the amount of Fe are similar. In addition, as soon as there is iron in the system in the presence or in the absence of H_2O_2 , TiO_2 effect becomes negligible if not detrimental.

4.3. Comparison with previous studied oligocarboxylic acids

Compared with the oxalic acid and EDTA systems, some differences arise. In all cases, heterogeneous photocatalysis is a rather efficient system to degrade the uncomplexed carboxylic acids. However, mineralization is difficult in the case of EDTA, due to a long pathway through the formation of resistant intermediates. Degradation is greatly improved by the addition of Fe(III) or H_2O_2 (until a limiting level) [29,30].

Oxalic acid, a much simpler compound, does not give rise to intermediates alongside its degradation, TOC reduction paralleling the decrease on concentration. Cit is in-between: it is not as recalcitrant as EDTA, due to the tertiary carbon, a weak point for oxidation, but it also mineralizes by steps. The ability to be degraded is noticed by the relative amounts of H_2O_2 needed to provoke changes in each system: the effect of minor amounts causes a profound impact on the oxidation of Cit and oxalate but not on EDTA [30,37].

On the other hand, the three acids form very stable Fe(III) complexes, which suffer LMCT photolysis under UV radiation but with different quantum yields of Fe(II) formation (at 366 nm, $\Phi_{\text{FeOx}} = 1.26$ [39], $\Phi_{\text{FeEDTA}} = 0.04$ [57], $\Phi_{\text{FeCit}} = 0.3\text{--}0.4$ [9,12]). This would explain the different influence of the homogeneous photolysis on the degradation and how may be the photocatalytic reaction affected. Fe-oxalate photolysis is very important and TiO_2 acts as a screen, reducing the efficiency of the homogeneous reaction; HP plays there a minor role. This behavior contrasts to that found for EDTA where photo-Fenton and photocatalysis yielded similar results and the absence or presence of TiO_2 is irrelevant [35,36]. The same occurs for citric acid. The detrimental effect of a high iron concentration is common to the three systems.

5. Conclusions

Heterogeneous photocatalysis with TiO_2 under UV irradiation of citric acid (0.024 M and pH 3.7), in the absence of oxidants other than O_2 , requires prolonged irradiation to reach significant degradation (45% in 6 h). In the presence of H_2O_2 , the percentage of degradation as well as the mineralization increase considerably, even with a H_2O_2 concentration two orders of magnitude lower than that of Cit. The addition of low amounts of Fe^{3+} does not introduce a considerable improvement in the degradation efficiency, but the effect is more

important with higher concentrations until a limiting value. Addition of both H₂O₂ and Fe(III) increases dramatically the rate; an optimal ratio of reagents can be found.

The next work will be focused on the photo-Fenton reaction, trying to optimize the system, and on the elucidation of the mechanism through the identification of more intermediate products.

The conclusions of the present work may have implications on the interpretation of processes occurring in natural systems (water, atmosphere), in which citric acid operates as a promoter for photochemical transformations. It is also part of a more extended study involving mixtures of liquid wastes of nuclear power plants.

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