Degradation of 4-chlorophenol mediated by Fe(III)-NTA in homogeneous and heterogeneous systems


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Abstract In this work, the comparison of 4-chlorophenol (4-CP) degradation by two different AOT processes has been performed: a) a homogeneous system with Fe(III)-NTA (1:1 complex), b) a TiO2/Fe(III)-NTA heterogeneous system. In both cases, NTA appears to play a positive role in the photochemical reaction. In the homogeneous system, the iron salt is the only absorbing species and is proved to be able to photoinduce 4-CP degradation ([4-CP] = 0.1–0.2 mM, [FeNTA] = 0.3–0.9 mM, pH 4, λ = 365 nm). The progress of the reaction was positively affected by the FeNTA concentration, and the reaction kept going even after the total disappearance of FeNTA. However, 4-CP complete degradation requires the presence of oxygen, otherwise the reaction stops. In the heterogeneous system ([4-CP] = 2.0 mM, [FeNTA] = 1.0–2.0 mM, [TiO2] = 0.1 and 1.0 g L−1, pH 3, λ = 300–400 nm), an important effect of the complex on the degradation extent and on the initial reaction rate can be seen, which overcomes the effect of non-complexed Fe(III). This behaviour is more important at the highest TiO2 concentration.

Keywords Advanced oxidation technologies; 4-chlorophenol; Fe-based AOTs; heterogeneous photocatalysis; NTA; TiO2

Introduction Photochemically active iron (III)-complexes of acids such as oxalic, NTA or EDTA promote degradation of organic matter through efficient homogeneous photochemical processes (Andrianirinaharivelo et al., 1993; Kari et al., 1995; Domènech et al., 2001). Under irradiation at the adequate wavelength and in the presence of oxygen, the cyclic process (1)–(2) takes place:

\[
\text{Fe(III)(RCO}_2\text{)}^{2+} + \text{hv} \rightarrow \text{Fe(II)} + \text{CO}_2 + \text{R}^* \quad (1)
\]

\[
\text{O}_2 \rightarrow \text{Fe(II)} \rightarrow \text{Fe(III)} \quad (2)
\]

In this way, besides being useful to explain photochemical processes occurring in natural waters, these systems can be employed for treatment of effluents, because they promote the oxidative transformation of pollutants, with the only requirement of Fe(III) salts and light radiation. As the addition of hydrogen peroxide is not necessary, they would be extremely inexpensive methods.

In this work, the iron (III)-photoinduced degradation of 4-chlorophenol (4-CP) in the presence of NTA was studied in: a) a homogeneous system, b) a TiO2 heterogeneous system. 4-CP has been chosen as a model pollutant often found in wastewaters due to its use at a large scale in industrial chemical synthesis (dyes, drugs, fungicides, etc.). On the other hand, NTA is a strong complexing agent frequently found in natural and contaminated waters, and FeNTA is a good model for natural organic matter.
Methods
All reagents were of the purest commercially available grade and used without further purification. All experiments and measurements were performed at 25°C.

Fe(III)-NTA was prepared by two methods: i) 10 mL of NTA solution (0.2 M), 3 mL of 0.67 M FeCl₃ and 7 mL of buffer (0.05 M potassium acetate adjusted to pH 4.0 with acetic acid) were mixed, vigorously stirred for 1 h and allowed to stand in the dark. The NTA ferric salt precipitated after 3 or 4 days. The precipitate was washed with water and dried overnight at 40°C; ii) by mixing appropriate volumes of freshly prepared aqueous solutions of Fe(NO₃)₃ and nitrilotriacetic acid. The total complexation of iron was controlled by UV-visible spectrophotometry. In both cases, the analysis gave evidence for a 1:1 stoichiometry.

Homogeneous photolytic runs for quantum yield determination were performed in a quartz cell (3 mL) at different irradiation wavelengths with a high-pressure mercury lamp (Osram HBO 200 W) equipped with a grating monochromator (Bausch and Lomb). The photon flow per unit volume, \( P_0 \), determined by potassium ferrioxalate actinometry (Hatchard and Parker, 1956), was 7.9 μEinstein L⁻¹ s⁻¹. The set-up for irradiation of larger volumes (V = 100 mL) at \( \lambda_{\text{exc}} = 365 \) nm was a cylindrical stainless steel container equipped with three high-pressure Hg lamps (Philips HPW 125 W). \( P_0 \) was 19.9 μEinstein L⁻¹ s⁻¹. The reactor, a water-jacketed Pyrex tube (d = 28 mm) was located in the centre. The solution was stirred during irradiation to ensure its homogeneity. Deoxygenation of the solution was obtained by bubbling nitrogen during 30 min before irradiation and all through the experiment.

The heterogeneous photocatalytic experiments were performed in an annular glass reactor, 415 mm-length, 35 mm-external diameter, 85-mL total volume, with a UV lamp (Philips TLDA/08, 15 W, maximum transmission at 366-nm). The incident photon flow per unit volume was 4.0 μEinstein s⁻¹ L⁻¹. A 200-mL suspension, containing 2.0 mM 4-CP, 1.0–2.0 mM FeNTA and TiO₂ Degussa P-25 (0.1 and 1.0 g L⁻¹), was recycled at a 1.0 L min⁻¹ flow rate from a reservoir by means of a peristaltic pump. Oxygen bubbling (0.2 L min⁻¹) was constantly kept in the reservoir, and pH was maintained at 3 with a pH-stat, using diluted nitric acid.

4-CP and Fe-NTA degradation in the homogeneous systems was followed with a Hewlett Packard liquid chromatographic system (HP 1050), equipped with a mono-channel UV-visible detector and an automatic injector. The determinations were performed by UV detection at 224 nm and by using a C₁₈ reverse phase column (Macherey-Nagel Nucleodur 5 μm, 250 mm × 4.6 mm). The flow rate was 1 mL min⁻¹ and the eluent was water:methanol (40/60 v/v).

In heterogeneous systems, 4-CP and NTA (as the FeNTA complex) concentrations were determined by HPLC (details of the instrument are reported in Babay et al., 2001) under 280 and 320 nm detection, respectively. C₁₈ reversed phase columns (Vydac, 150 mm × 4.6 mm and Alltech Adsorbosphere, 250 mm × 4.6 mm) were used; eluents: water 1% v/v AcOH:MeOH:acetonitrile (60:30:10) at 0.8 mL min⁻¹ was used for 4-CP (Theurich et al., 1996), and water/HNO₃ (pH 2.5) at 1.2 mL min⁻¹, for NTA. In this case, samples were previously treated with excess of Fe(NO₃)₃ for 2 h.

Results and discussion
Homogeneous system
The quantum yields of 4-CP (0.1 mM) disappearance and Fe(II) formation in the homogeneous system with FeNTA (0.3 mM) at pH = 4.0 follow a similar trend as those of Fe(III) aquo complexes (Brand et al., 1998), decreasing with the irradiation wavelength, as shown in Table 1. It was checked that there was no degradation of 4-CP by direct photolysis at 313 or 365 nm.
In the absence of NTA (Fe(III) = 0.3 mM with 75% of Fe(OH)²⁺, pH 3.0), the initial quantum yields of Fe(II) formation and 4-CP disappearance are lower by roughly one order of magnitude for Fe(II) and divided by four for 4-CP. In the absence of oxygen, the quantum yields of FeNTA disappearance and Fe(II) formation were lower (25%) and the quantum yield of 4-CP disappearance was divided by two.

The results presented in Figure 1 show that 4-CP disappearance (0.2 mM) is enhanced with increasing FeNTA concentration. This effect is particularly important for longer irradiation times and can be attributed to the absorbing iron complexes present in solution after the decomposition of FeNTA. This was confirmed by the curve depicted in Figure 2, where 4-CP disappearance continues even after the disappearance of FeNTA. The presence of complexing photoproducts such as iminodiacetic acid (Andrianirinaharivelo et al., 1993) or other dicarboxylic acids could favour the reoxidation of iron (II) into iron (III) in the presence of oxygen.

The influence of oxygen was established by the kinetics of Figure 3 ([4-CP] = 0.1 mM, [FeNTA] = 0.3 mM). The degradation of 4-CP is completely inhibited in the absence of oxygen.

<table>
<thead>
<tr>
<th>λ (nm)</th>
<th>Φ_{FeNTA disappearance}</th>
<th>Φ_{Fe(II) formation}</th>
<th>Φ_{4-CP disappearance}</th>
</tr>
</thead>
<tbody>
<tr>
<td>313</td>
<td>0.50</td>
<td>0.46</td>
<td>0.018</td>
</tr>
<tr>
<td>313 (without O₂)</td>
<td>0.36</td>
<td>0.36</td>
<td>0.009</td>
</tr>
<tr>
<td>365</td>
<td>0.27</td>
<td>0.28</td>
<td>0.011</td>
</tr>
<tr>
<td>365</td>
<td>Without NTA</td>
<td>0.03</td>
<td>0.003</td>
</tr>
</tbody>
</table>

Table 1 Quantum yields of 4-CP disappearance and Fe(II) formation in the homogeneous system with FeNTA (pH 4.0)

![Figure 1](https://iwaponline.com/wst/article-pdf/49/4/123/420824/123.pdf) Disappearance of 4-CP (0.2 mM) in the presence of different concentrations of FeNTA. λ = 365 nm; pH 4.0. (a) 0.3 mM FeNTA; (b) 0.6 mM FeNTA; (c) 0.9 mM FeNTA

![Figure 2](https://iwaponline.com/wst/article-pdf/49/4/123/420824/123.pdf) Disappearance of 4-CP (0.2 mM) in the presence of 0.3 mM FeNTA. Comparison with FeNTA disappearance. (a) 0.2 mM 4-CP; (b) 0.3 mM FeNTA
Heterogeneous system

4-CP (2.0 mM) degradation under UV irradiation in the presence of TiO₂ at two different concentrations (0.1 and 1.0 g L⁻¹) is shown in Figures 4 and 5, respectively. The results indicate an enhancement of the degradation by Fe(III) addition (2.0 mM), but a more important effect is operative in the presence of the FeNTA complex (2.0 mM), together with an increase of the initial rate. The effect is more remarkable at the highest TiO₂ concentration. 4-CP heterogeneous photocatalytic degradation over TiO₂ is produced through the action of photogenerated electrons and holes after TiO₂ excitation. Fe(III) improves degradation in this reaction by acting as an electron scavenger, decreasing the recombination rate of electrons and holes, a very detrimental reaction in all heterogeneous photocatalytic systems. On the other hand, Fe-based processes are promoted by two parallel mechanisms: a) by photolysis of FeNTA (Eq. (1)) and b) by heterogeneous photocatalytic degradation of the same complex over TiO₂. In this way, organic radicals and Fe(II) are produced, contributing to the whole degradation mechanism of 4-CP. In fact, a very low remaining FeNTA concentration was measured after 60 min ([TiO₂] = 1.0 g L⁻¹, not shown). NTA degradation products formed in the process also contribute to the overall 4-CP degradation by similar processes.

Figure 6 ([4-CP] = 2.0 mM) shows the influence of different amounts of FeNTA. It can be observed that the higher rate is obtained when equimolar concentrations of 4-CP and FeNTA were used.

Conclusions

In both homogeneous and heterogeneous systems, good evidence of the enhancement of 4-CP photodegradation by Fe(III)-NTA is given. The presence of NTA appears to play a positive role in iron (III)-based AOTs in the presence or in the absence of TiO₂. In the homogeneous system, two mechanisms are operative as a function of the irradiation wavelength. The one at 365 nm is oxygen dependent and has to be further investigated. The sec-
ond one (at 313 nm) involves radicals (HO• radicals detected by ESR spectroscopy) arising from the intramolecular charge transfer that takes place in FeNTA in the excited state. In the heterogeneous system, in addition to the common photocatalytic mechanism due to the presence of the semiconductor, an enhancement takes place by the contribution of processes promoted by photolysis and photocatalysis of FeNTA and its degradation products over TiO₂.

Although homogeneous and heterogeneous systems differ in experimental conditions, taking into account that P₀ is lower and 4-CP concentration is higher in the TiO₂ system, it can be concluded that this last system will be better for industrial applications, but that the homogeneous one is suitable to explain natural phenomena and to be used as a very cheap water treatment in cases where operation time is not a constraint.

References

Figure 5 Degradation of 4-CP (2 mM) over 1 g L⁻¹ TiO₂. (a) TiO₂; (b) TiO₂ in the presence of Fe(II) (2 mM); (c) TiO₂ in the presence of FeNTA (2 mM)

Figure 6 Degradation of 4-CP (2 mM) over 1 g L⁻¹ TiO₂ alone and in the presence of Fe(III)-NTA in different proportions with respect to 4-CP. (a) TiO₂; (b) TiO₂ + 1 mM FeNTA; (c) TiO₂ + 2 mM FeNTA
degradation of Fe(III)-EDTA: Implications for the environmental fate of EDTA in surface waters.
