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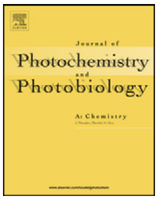

Photochemical efficiency of Fe(III)-EDDS complex: •OH radical production and 17β-estradiol degradation

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ABSTRACT

In this work, the photochemical impact of Fe(III)-EDDS complex on the quantum yield of •OH formation and on the degradation of 17β-estradiol (E2) was investigated. The quantum yield of •OH formation by photolysis of Fe(III)-EDDS increased with increasing pH in the range of 3.0–9.0. The effect of Fe(III)-EDDS concentration, irradiation wavelength and oxygen on the quantum yield of •OH formation was also investigated. The degradation of E2 was influenced by the concentration of Fe(III)-EDDS, the solution pH, oxygen and Fe(III) concentrations. This work demonstrates that Fe(III)-EDDS is a photoactive iron species especially at higher pHs and could play an important role in the transformation of organic compounds in the natural environment.

1. Introduction

Iron is the most abundant transition metal in the earth's crust. Iron is present under a variety of forms in water ranging from soluble to colloidal and particulate species. Most of the iron in natural water exists in the form of insoluble ferric oxides and (hydr)oxides [1]. The concentration of dissolved iron is very low and most of the dissolved iron is associated with strong organic ligands in natural water [2,3]. Polycarboxylates such as citrate, malonate, and oxalate are common constituents of precipitation, fog, surface water and soil solutions [4]. Polycarboxylates can form strong complexes with Fe^{3+} and enhance the dissolution of iron in natural water through photochemical processes. Moreover, such polycarboxylate complexes undergo rapid photochemical reactions under sunlight irradiation leading to the formation of oxidative species [5,6]. Therefore, research into the photochemistry of iron complexes is very important, since it substantially affects the speciation of iron in surface water and the biogeochemical cycle of iron and other elements.

Up to now, photolysis of Fe-polycarboxylates as one of the advanced oxidation processes (AOPs) has received much attention [7–10]. For instance, Zhou et al. [7] investigated the photooxidation of diethylstilbestrol (DES) by Fe-oxalate complex under a 250 W high-pressure mercury lamp. The photodegradation of DES in the Fe(III)-oxalate complex system is more efficient than in the Fe(III)-OH complex system (aquacomplexes). Ou et al. [9] also found that the presence of Fe(III)-citrate complex enhanced the photodegradation rate of atrazine as a result of •OH radical attack.

It was reported that light irradiation of Fe(III)-polycarboxylate complexes could produce both Fe(II) and ligand-free radical by the ligand-to-metal charge transfer (LMCT) reactions (reaction (1)). Then the reducing radical could react with Fe(III) species or O_2 to form Fe(II) species or superoxide radical $O_2^{\bullet-}$ (reaction (2)) respectively. The relative rates of the reactions of the reducing radical with O_2 or Fe(III) are very important for determining the steady state concentration of Fe(II) and $O_2^{\bullet-}$. The radical $O_2^{\bullet-}$ and its acid conjugated form $HO_2^{\bullet}$ ($pK_a = 4.8$ for the $HO_2^{\bullet}/O_2^{\bullet-}$) can participate in further reactions, including generation of H_2O_2 (reactions (3)–(6)) [11]. The yield of H_2O_2 depends critically on competition between H_2O_2-producing reactions (reactions (3)–(6)) and O_2-producing reactions (reactions (7) and (8)).

$$\text{Fe(III)-L} + h\nu \rightarrow [\text{Fe(III)-L}]* \rightarrow \text{Fe(II)} + \text{L}^{\bullet} \quad (1)$$

$$\text{L}^{\bullet} + O_2 \rightarrow O_2^{\bullet-} + \text{L}' \quad (2)$$

$$\text{Fe(II)} + O_2^{\bullet-} + 2H_2O \rightarrow \text{Fe(III)} + H_2O_2 + 2OH^-, \quad k = 1.0 \times 10^7\ M^{-1}\ s^{-1} \quad (3)$$

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$$Fe(II) + HO_2^{\bullet} + H_2O \rightarrow Fe(III) + H_2O_2 + OH^-, \quad k = 1.2 \times 10^6\,M^{-1}\,s^{-1} \tag{4}$$

$$HO_2^{\bullet} + O_2^{\bullet -} + H_2O \rightarrow H_2O_2 + O_2 + OH^-, \quad k = 9.7 \times 10^7\,M^{-1}\,s^{-1} \tag{5}$$

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2, \quad k = 8.3 \times 10^5\,M^{-1}\,s^{-1} \tag{6}$$

$$Fe(III) + HO_2^{\bullet} \rightarrow Fe(II) + O_2 + H^+, \quad k < 1 \times 10^3\,M^{-1}\,s^{-1} \tag{7}$$

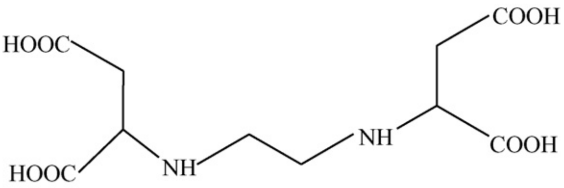
$$Fe(III) + O_2^{\bullet -} \rightarrow Fe(II) + O_2, \quad k = 5 \times 10^7\,M^{-1}\,s^{-1} \tag{8}$$

From these reactions it seems very likely that the concentrations of $HO_2^{\bullet}/O_2^{\bullet -}$ and Fe(III)/Fe(II) and as a consequence the formation of H_2O_2 in water are intertwined. In fact in such system it is well known that $^{\bullet}OH$ can be formed by oxidizing Fe(II) with H_2O_2 also called Fenton reaction (reaction (9)) [12].

$$H_2O_2 + Fe(II) \rightarrow Fe(III) + {}^{\bullet}OH + OH^-, \quad k = 63\,M^{-1}\,s^{-1} \tag{9}$$

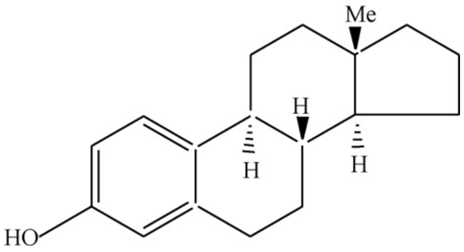
Aminopolycarboxylic acids (APCAs) may present behavior similar to that of polycarboxylic acid [13]. Aminopolycarboxylic acids have the ability to solubilize and inactivate metal ions by complex formation. For that reason, they are used in a wide variety of domestic products, industrial applications and soil remediation [14]. Among the APCAs, ethylenediaminetetraacetic acid (EDTA) has been the most widely used chelating agent for these processes. But due to its low biodegradability, EDTA is emerging as a contaminant of concern [15]. As reported, photochemical oxidation is the only effective way for removal of EDTA and its derivatives. The Fe(III)-EDTA complex is the only EDTA species that undergoes direct photolysis in the environment [16,17]. So the photochemistry reaction of Fe(III)-EDTA has been extensively studied. However the studies focus on the disappearance of EDTA through photodegradation of Fe(III)-EDTA, and not on the photoactivity of Fe(III)-EDTA [18–20].

Ethylenediamine-*N,N′*-disuccinic acid (EDDS) is a structural isomer of EDTA, and exists as three stereo isomers, namely [S,S]-EDDS, [R,R]-EDDS and [R,S/S,R]-EDDS. Among them, [S,S]-EDDS is readily biodegradable. It has been proposed as a safe and environmentally benign replacement for EDTA for environmental remediation products as it is also a strong complexing agent [21,22]. Our laboratory has studied the physicochemical properties of the Fe(III)-EDDS complex. Fe(III) is complexed by EDDS with a ratio 1:1. Under irradiation, Fe(III)-EDDS was easily photolyzed and $^{\bullet}OH$ was detected during photodegradation of Fe(III)-EDDS [23]. In our work, the quantum yields of $^{\bullet}OH$ formation from Fe(III)-EDDS complex solution under irradiation have been investigated for the first time.



EDDS

17β-Estradiol (E2) is one of the endocrine-disrupting chemicals (EDCs) and is well known to exhibit very potent estrogenic activity even at a very low concentration (~10^{-9} M, in vitro) [24,25].



E2

We used E2 as a model pollutant to investigate the photocatalytic activity of the Fe(III)-EDDS complex and the main influencing factors, such as pH, the concentrations of Fe(III)-EDDS/Fe(III) and O_2 were examined. This work leads us to a new proposal that Fe(III)-EDDS can act as a photoactive species in water.

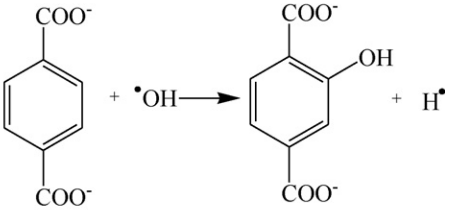
2. Experimental design

2.1. Chemicals

17β-Estradiol (E2) was purchased from Sigma. S,*S′*-Ethylenediamine-*N,N′*-disuccinic acid trisodium salt solution (30% in water) and ferric perchlorate ($Fe(ClO_4)_3 \cdot 9H_2O$), were from Fluka. Disodium terephthalate was from Alfa Aesar. 2-Hydroxyterephthalic acid (>98%) was from Atlantic. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used to adjust the pH values of the solutions with a JENWAY 3310 pH-meter to ±0.01 pH unit. All the other reagents were of analytical grade. A Milipore Ultra-Pure System purified water (18.2 MΩ cm resistivity) was used. Fe(III)-EDDS solutions were prepared by mixing appropriate volumes of freshly prepared aqueous solutions of $Fe(ClO_4)_3$ and S,*S′*-ethylenediamine-*N,N′*-disuccinic acid. The stoichiometry ratio of Fe(III)-EDDS complex is 1:1.

2.2. Photochemical experiment

For the determination of the $^{\bullet}OH$ quantum yields, terephthalate (TPA) was used as the scavenger for $^{\bullet}OH$. TPA, which is not fluorescent, gives a single fluorescent product, 2-hydroxyterephthalate (HTPA) in reaction with the hydroxyl radical as described by the following reaction [26]:



A high concentration of TPA (0.5 mM) was used. Under these conditions, the effective quantum yield of $^{\bullet}OH$ is equal to:

$$\Phi_{OH} = \frac{\Delta C \cdot 6.023 \cdot 10^{20} \cdot l}{I_a \cdot \Delta t \cdot f} \tag{10}$$

$$I_a = I_0(1 - 10^{-OD\lambda_{irr}}) \tag{11}$$

where $1 - 10^{-OD\lambda irr}$ represents the percentage of the light absorption by the solution at the irradiation wavelength when $t = 0$, I_0 is the number of the photons entering the reaction cell per second determined by actinometry and l is the length of the irradiation cell in cm. ΔC is the amount of HTPA produced during the irradiation period Δt. f is the yield of HTPA produced in the reaction of $^{\bullet}OH$ with TPA. In solutions containing oxygen and oxygen-free solutions, f is equal to 35% and 84% respectively [27,28]. For the quantum

Table 1
Photonic flux at 365, 313 and 296 nm.

λ_{irr} (nm)	365	313	296
I_0 (10^{15} photon s^{-1} cm^{-2})	4.25	1.40	0.83

yield the experimental error was estimated to 5%. The mixed solutions of TPA and Fe(III)-EDDS were irradiated in a parallel beam obtained from a Schöffel monochromator equipped with a xenon lamp (1600 W). The reactor was a quartz cell of 1 cm path length. The monochromatic irradiations were carried out at 365, 313 and 296 nm. The light intensity was measured by ferrioxalate actinometry [29]. The photonic flux of the monochromatic irradiation at different wavelengths is listed in Table 1.

Oxygen-free solutions were obtained by bubbling with argon for 30 min before irradiation.

For the degradation of E2, the irradiation experiments were performed in a home-made photoreactor placed in a cylindrical stainless steel container. Four fluorescent light bulb lamps (Philips TL D 15W/05) whose emission spectrum is from 300 to 500 nm with a maximum irradiation at 365 nm were separately placed in the four different axes, while the photoreactor, a water-jacketed Pyrex tube of 2.8 cm diameter, was placed in the centre of the setup. The solutions were magnetically stirred with a magnetic bar during irradiation. Control experiments showed that no degradation of E2 occurred in the presence of Fe(III)-EDDS complexes without irradiation in this photoreactor.

2.3. Analysis

The concentration of E2 was measured by high performance liquid chromatography (Alliance) equipped with a dual λ absorbance detector (Waters 2487), a multi λ fluorescence detector (Waters 2487) and Waters 2695 separations Module. The experiments were performed by UV detection at 280 nm and fluorescence detection at 280 nm for the excitation and 300 nm for the emission analysis. The flow rate was 1 mL min^{-1} and the eluent was a mixture of water containing 3‰ formic acid and acetonitrile (55/45, v/v). The column was a Nucleodur 100-5 C18 of 150 mm × 4.6 mm, particle size 5 μm.

Fluorescence measurements of HTPA were made with an LS 55 luminescence spectrometer (PerkinElmer). The excitation wavelength was set at 312 nm and the emission wavelength at 433 nm. The excitation and emission band-passes were both set at 5 nm. The concentration of HTPA was also detected by HPLC. Fluorescence detection was set at 320 nm for the excitation and 434 nm for the emission analysis. The flow rate was 1 mL min^{-1} and the eluent was a mixture of water containing 3‰ formic acid and acetonitrile (80/20, v/v). The column was the same column as used for the detection of E2.

Fe(II) concentration was determined by complexometry with ortho-phenanthroline, using $\varepsilon = 1.118 \times 10^4$ L mol^{-1} cm^{-1} for the Fe(II)-phenanthroline complex [27]. Fe^{3+} ions were reduced to Fe^{2+} with an excess of ascorbic acid to determine the total concentration of iron ions.

UV–vis spectra were recorded with a Cary 3 double beam spectrophotometer.

3. Results and discussion

3.1. Quantum yields of $^{\bullet}$OH formation

The stoichiometric ratio of the Fe(III)-EDDS complex is 1:1, which was established by the molar ratio method [23]. The UV–vis absorption spectra of Fe(III)-EDDS aqueous solutions is not pH dependent in the domain 3 < pH < 7. Between 7 and 9, a small decrease of absorbance was observed at wavelengths higher than 230 nm. Absorption started at 400 nm with a shoulder at 239 nm ($\varepsilon = 6530$ M^{-1} cm^{-1}), exhibiting an important overlap with solar emission (Fig. 1). The irradiation experiments were mainly performed at 365 nm. This wavelength is sufficiently energetic to cause the photochemical process of Fe(III)-EDDS. For TPA, no significant absorption was detected above 295 nm. The absorption of TPA did not interfere at the irradiation wavelengths used.

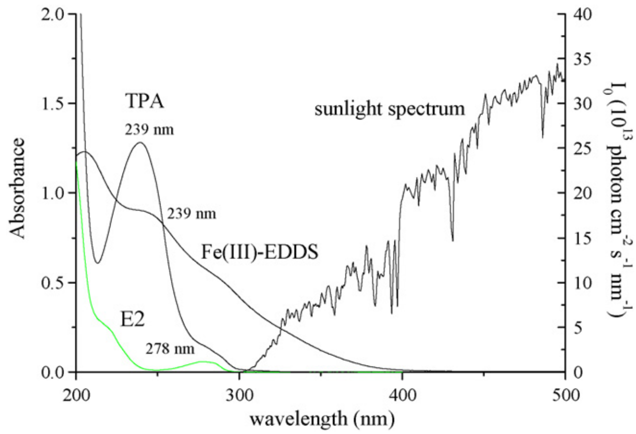


Fig. 1. UV–visible absorption spectrum of E2 (6 μM), Fe(III)-EDDS (100 μM), TPA (100 μM) and emission spectrum of sunlight.

The Fe(III)-EDDS complex was stable in the dark and at room temperature for at least 10 days. But under irradiation Fe(III)-EDDS was quickly photodecomposed. The UV–visible absorption spectra of Fe(III)-EDDS solution at pH 3.0 under monochromatic irradiation at λ = 365 nm is shown in Fig. 2. The Fe(III)-EDDS complex was almost completely decomposed after 10 min of irradiation.

The mixture of TPA and Fe(III)-EDDS was thermally stable. There was neither precipitation nor redox reaction in the dark at room temperature. No HTPA formation was observed in the dark in the TPA and Fe(III)-EDDS mixture solution. HTPA was detected in the Fe(III)-EDDS and TPA solution under irradiation, which proved the formation of $^{\bullet}$OH by the photochemical reaction of Fe(III)-EDDS.

3.1.1. Effects of Fe(III)-EDDS complex concentrations on the quantum yields of $^{\bullet}$OH formation

Quantum yields of $^{\bullet}$OH (Φ_{OH}) from photolysis of Fe(III)-EDDS complexes were measured with different Fe(III)-EDDS concentrations at pH 6 (λ_{irr} = 365 nm). As shown in Table 2, Φ_{OH} was

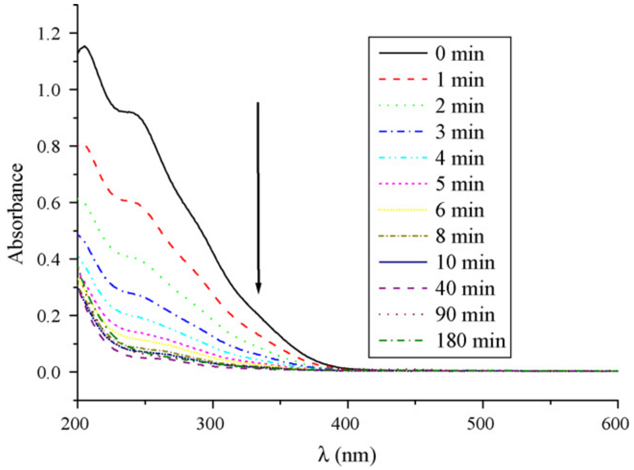


Fig. 2. UV–visible absorption spectra of Fe(III)-EDDS solution at pH = 3.0 during irradiation ([Fe(III)-EDDS] = 1×10^{-4} M, λ_{irr} = 365 nm).

Table 2
Quantum yields of $^\bullet$OH as a function of Fe(III)-EDDS concentration (pH = 6, λ_{irr} = 365 nm).

[Fe(III)-EDDS] (μM)	25	50	75	100
Φ_{OH}	0.021	0.024	0.026	0.025

independent of the Fe(III)-EDDS concentration. According to Eqs. (10) and (11), when the concentration of Fe(III)-EDDS complex is high, the flux of absorbed photons is larger, which generates more $^\bullet$OH radicals, so the generation rate of $^\bullet$OH radicals increases. The increase of $^\bullet$OH formation rate and the increase of I_a caused by the increase of the optical density $OD_{\lambda irr}$ of the solution are of about the same order, resulting in an invariant quantum yield.

3.1.2. Effects of pH on the quantum yields of $^\bullet$OH formation

The pH is a very important parameter that affects the species and stability of the Fe(III)-EDDS complex in solution, and consequently may have considerable influence on the photochemistry reaction of Fe(III)-EDDS. In contrast to earlier studies published, which were carried out only at low pHs, we investigated the Fe(III)-EDDS system over the entire environmentally relevant pH range: $3.0 \leq pH \leq 9.0$. As shown in Table 3, the quantum yield of $^\bullet$OH increased with the increase in pH. This result is unexpected and interesting. In previous studies, the quantum yield of $^\bullet$OH was much higher at acidic pH, and the optimum pH for the formation of $^\bullet$OH was limited to between pH 3.0 and 4.0, whatever the Fe(III) aquacomplexes or the Fe(III)-carboxylate complexes (Fe(III)-oxalate, Fe(III)-citrate) solutions [30]. At higher pHs, the quantum yield decreased and was negligible at pHs close to 7.0. On the contrary, in the presence of Fe-EDDS complexes, the quantum yield of $^\bullet$OH radical formation was higher at higher pHs more relevant to the natural environment. This interesting result could be explain by the formation of H_2O_2 (reactions (3)–(6)) which is mainly governed by the reactions (3) and (5). At higher pH (higher than 4.8, the pK_a of the couple $HO_2^\bullet/O_2^{\bullet-}$) where $O_2^{\bullet-}$ becomes the dominant reactive oxygen species, the formation of H_2O_2 is an order of magnitude faster than at lower pH. Moreover, the $^\bullet$OH radical formation depends also to the possible formation of Fe(II)-polycarboxylate complex, formed with the starting organic compounds or its oxidation compounds obtained after the first photochemical reaction. In the case of ferrioxalate complex the formation of $^\bullet$OH with H_2O_2 is 3–4 orders of magnitude higher than with Fe(II) aquacomplexes (comparison of rate constants of reactions (9) and (12)) [31]. The speciation of such Fe(II) complexes (not known for EDDS) could explain the difference observed between EDDS and other polycarboxylate complexes for the quantum yield of $^\bullet$OH radical as a function of pH.

$$\mathrm{Fe^{II}(C_2O_4)} + \mathrm{H_2O_2} \rightarrow \mathrm{Fe^{III}(C_2O_4)^+} + {}^\bullet\mathrm{OH} + \mathrm{OH^-}, \\ k = 3.1 \times 10^4\ \mathrm{M^{-1}\,s^{-1}} \tag{12}$$

3.1.3. Effect of wavelength on the quantum yields of $^\bullet$OH formation

The influence of irradiation wavelength on the quantum yields of $^\bullet$OH formation (Φ_{OH}) from Fe(III)-EDDS complex photolysis was examined at 296, 313 and 365 nm ([Fe-EDDS] = 1×10^{-4} M, pH = 6.0). As shown in Table 4, the quantum yields of $^\bullet$OH obviously increased with the decrease of wavelength. This result was attributed to the kinetic energy required for the ejection of $^\bullet$OH radicals from the solvent cage [32]. Decrease of the wavelength increased the level of excitation, thus raising the quantum yield of $^\bullet$OH.

Table 3
Quantum yields of $^\bullet$OH as a function of pH ([Fe(III)-EDDS] = 10^{-4} M, λ_{irr} = 365 nm).

pH	3.0	4.0	5.1	6.0	7.0	8.0	9.0
Φ_{OH}	0.0025	0.0091	0.019	0.025	0.034	0.051	0.069

Table 4
Quantum yields of $^\bullet$OH formation as a function of wavelength ([Fe(III)-EDDS] = 1×10^{-4} M, pH = 6.0).

λ (nm)	365	313	296
Φ_{OH}	0.025	0.037	0.040

3.1.4. Effect of oxygen on the quantum yields of $^\bullet$OH

Oxygen is an important parameter in the photochemical processes. Experiments were carried out to study the oxygen effects on the quantum yield of $^\bullet$OH formation ([Fe(III)-EDDS] = 1×10^{-4} M, pH = 6.0, λ_{irr} = 365 nm). As shown in Table 5, the quantum yields of $^\bullet$OH in deaerated solution is very low, almost twenty times lower than that in aerated solutions. Therefore oxygen is involved in the photocatalytic process of Fe(III)-EDDS when forming $^\bullet$OH. According to reaction (2), oxygen trapped the electron on the carbon centered radical formed after the Fe(III)-(amino)polycarboxylate complex photoredox process, then the $O_2^{\bullet-}$ formed rapidly reacted to finally result in the formation of hydroxyl radical (reactions (3)–(9) and (12)).

3.1.5. Comparison with the aquacomplex $Fe(OH)^{2+}$

The quantum yield of $^\bullet$OH formation was also detected by photolysis of $Fe(OH)^{2+}$ in our experimental conditions ([Fe(III)] = 1 mM, λ_{irr} = 365 nm). Among iron aquacomplexes, $Fe(OH)^{2+}$ is the most active species for photochemical production of hydroxyl radicals. Under our experimental conditions, we obtained the value of 0.044, which is approximately twenty times higher than the quantum yield of $^\bullet$OH formation for photolysis of Fe(III)-EDDS at pH 3 (Table 3). The quantum yields for Fe(III)-aquacomplex photochemical reactions have been reported in several studies. It was reported that the quantum yield for photolysis of $Fe(OH)^{2+}$ was 0.01–0.07 at the wavelength of 360–370 nm [32,33]; for Fe^{3+}, the quantum yield was 0.065 at 254 nm [32] and approximately 0.05 at wavelengths below 300 nm [32]; for $Fe_2(OH)_2^{4+}$, the quantum yield was 0.007 at 350 nm [34]. The quantum yield of $^\bullet$OH formation by photolysis of $Fe(OH)^{2+}$ obtained in this study is in good agreement with the literature values at the wavelength of 365 nm obtained in the previous studies. When comparing the value of 0.044 with the quantum yield of $^\bullet$OH formation by Fe(III)-EDDS at pHs higher than 5, the values are of the same magnitude. In addition, the quantum efficiency for the photolysis of Fe(III)-EDDS is higher at higher pHs, so the effect of Fe(III)-EDDS is more relevant to the natural environment. Moreover, it is important to note that the concentration of soluble iron aquacomplexes is negligible at pHs higher than 5.0 and consequently the quantum yield of $^\bullet$OH radical formation is negligible too.

3.2. Photodegradation of E2 in the Fe(III)-EDDS complex solutions

The UV–vis absorption spectrum of E2 in aqueous solution displayed one band at 278 nm (ε = 1900 $M^{-1}\,cm^{-1}$) (Fig. 1). No absorption was observed at λ > 300 nm. There was a pK_a at 10.4 [35] and the solubility in water is evaluated at 20 μM. Under our experimental conditions and in the dark, no degradation of E2 was observed in the absence or in the presence of Fe(III)-EDDS.

Table 5
Effect of oxygen on the quantum yields of $^\bullet$OH formation ([Fe(III)-EDDS] = 1×10^{-4} M, pH = 6.0, λ_{irr} = 365 nm).

	Aerated solution	Deaerated solution
Φ_{OH}	0.025	0.0011

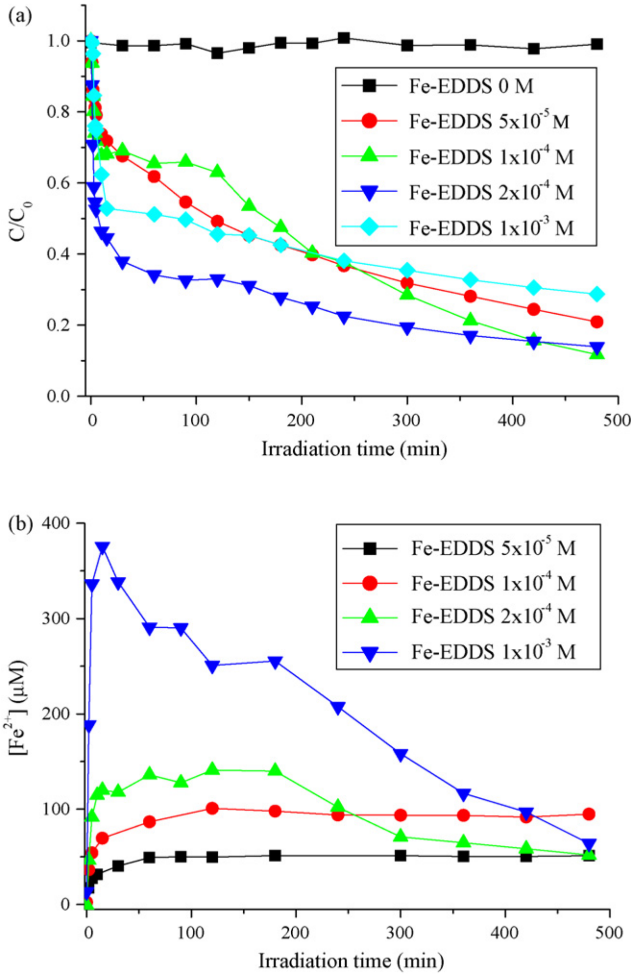


Fig. 3. (a) Effect of Fe(III)-EDDS concentration on the degradation of E2 ([E2] = 5 μM, pH = 3.0). (b) Photogeneration of Fe(II) as a function of Fe(III)-EDDS concentration ([E2] = 5 μM, pH = 3.0).

Similarly, there was no photodegradation of E2 under irradiation without Fe(III)-EDDS.

3.2.1. *Effect of Fe(III)-EDDS concentration on the degradation of E2*

Fig. 3a shows the kinetics of E2 disappearance at different initial concentrations of Fe(III)-EDDS of 0, 5×10^{-5}, 1×10^{-4}, 2×10^{-4} and 1×10^{-3} M at pH 3.0. The rate of E2 degradation increased with increased concentrations of Fe(III)-EDDS in the range of 0 to 2×10^{-4} M, but much higher concentration of Fe(III)-EDDS such as 1×10^{-3} M inhibited E2 degradation. These results gave clear evidence that photolysis of Fe(III)-EDDS could induce the degradation of E2. From Section 3.1, we know that •OH is formed during photolysis of Fe(III)-EDDS. •OH could react with both E2 and Fe(III)-EDDS. When the concentration of Fe(III)-EDDS is high, the role of Fe(III)-EDDS as a competitor for •OH reaction is much more important, and as a consequence inhibits E2 degradation. Therefore, the appropriate concentration of Fe(III)-EDDS should be chosen for E2 degradation. Fe(II) formation was also monitored during the irradiation time (Fig. 3b). The generation of Fe(II) by Fe-EDDS complex photochemical reactions was very fast. For Fe-EDDS 5×10^{-5} and 1×10^{-4} M, almost all of the Fe(III) was transformed to Fe(II) in the first hour, and the concentration of Fe(II) remained constant up to 8 h. But for Fe(III)-EDDS 2×10^{-4} and 1×10^{-3} M, it was observed that the concentration of Fe(II) decreased with irradiation after quick generation initially. This phenomenon can be due to the increase of pH during the irradiation time. A very fast increase in the pH of the solution was detected when irradiation had just started and then remained constant. The higher concentration of Fe(III)-EDDS resulted in the greater increase in the solution pH during irradiation, for example, initial pH 3–4 for [Fe(III)-EDDS] = 10^{-4} M and to 6.4 for [Fe(III)-EDDS] = 10^{-3} M after 3 h of irradiation.

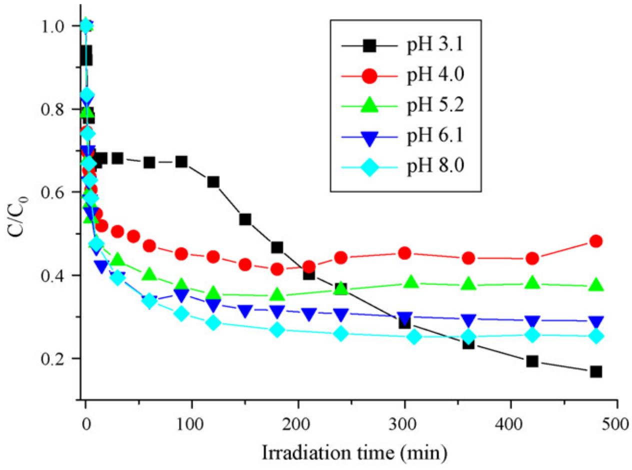


Fig. 4. Effect of pH on the degradation of E2 ([Fe(III)-EDDS] = 1×10^{-4} M, [E2] = 5 μM).

3.2.2. *Effect of pH on the degradation of E2*

Fig. 4 shows the kinetics of E2 degradation at different initial pHs with the same concentration of Fe(III)-EDDS (1×10^{-4} M) as a function of irradiation time. For pH 4.0, 5.2, 6.1 and 8.0, after very fast initial photodegradation of E2 in the first few minutes, the degradation of E2 then slowed down and stopped at about 90 min of irradiation, reaching a plateau value without further degradation. At an initial pH of 3.1, the degradation of E2 showed similar behavior during the first 90 min, but after the plateau, photodegradation of E2 started again and continued for the remaining irradiation time. The initial quick photodegradation of E2 was due to the photoredox process of Fe(III)-EDDS which induced the formation of •OH and also the decomposition of EDDS. With the decomposition of EDDS, the rate of photodegradation of E2 slowed down and finally stopped. After the first period of time and complete decomposition of Fe(III)-EDDS, the photodegradation of E2 depends on the species of Fe(III)/Fe(II) aquacomplexes in the solution. It is well known that the species $Fe(OH)^{2+}$, mainly present between pH 3.0 and 4.0, is the most photoactive iron aquacomplex. Except under the condition of initial pH = 3.1 where the pH of the solution increased to pH = 4.0, it was observed with other initial pHs that during irradiation the solution pH increased or decreased to neutral pH in the first few minutes. So we observed the continued degradation of E2 after a plateau only for the initial pH = 3.1. However, before 90 min of irradiation, the efficiency of photodegradation of E2 was pH 8.0 > pH 6.1 > pH 5.2 > pH 4.0 > pH 3.1, which is in agreement with the quantum yield of •OH formation as a function of pH. The concentration of Fe(II) and Fe(tot) during irradiation was also detected (data not shown). At pH 3.1 and 4.0, the major part of initial iron (Fe(III)) present in the solution was reduced to Fe(II) within a short period of irradiation. At pH = 5.2 and higher pHs, almost no Fe(II) was detected in the solution. This result could be explain by the fact that at higher pH Fe(II) aquacomplexes is easily oxidized by dissolved oxygen and by the hypothesis of the formation of Fe(II)-polycarboxylate complexes and a fast reaction with H_2O_2. Moreover, at these pHs the amount of Fe(tot) dissolved in the aqueous solution decreased very fast due to the degradation of EDDS which can maintain iron ions in solution. No new organic

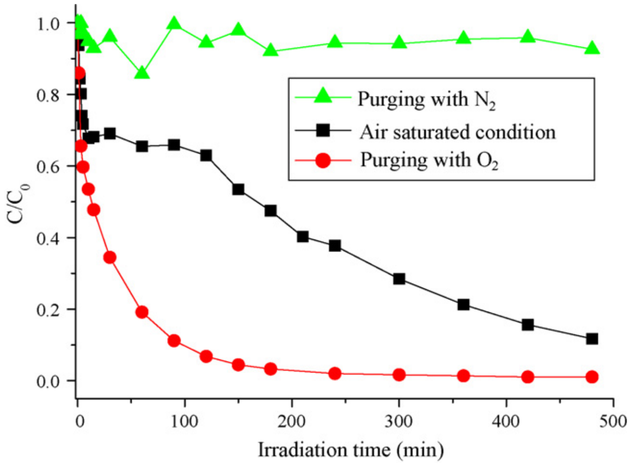


Fig. 5. Effect of oxygen on the degradation of E2 ([E2] = 5 μM, [Fe(III)-EDDS] = 1 × 10^{-4} M, pH = 3.0).

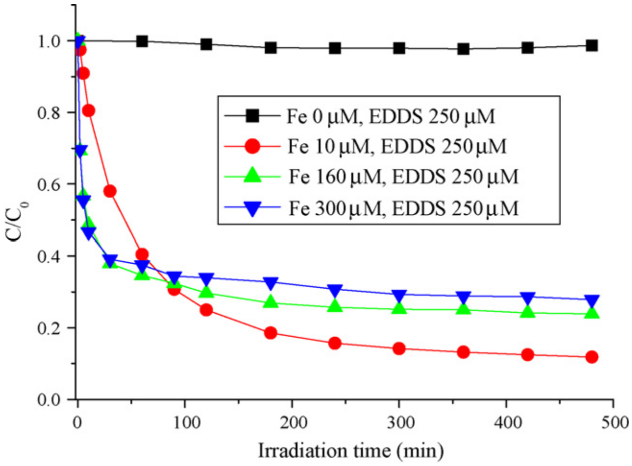


Fig. 6. Effect of iron concentration on the degradation of E2 ([E2] = 5 μM, pH = 6.0).

species formed from the degradation of EDDS are able to complex Fe(III) and avoid its precipitation. In the previous studies of iron carboxylate complex photochemistry, the formation of Fe(II) is positively related to the degradation of organic pollutants [9]. But no correlation was apparently observed between Fe(II) formation and E2 disappearance in our work. So it is supposed that the dominant factor that influences the photodegradation of E2 is not the amount of Fe(II) formation.

3.2.3. *Effect of oxygen on the degradation of E2*

As shown in Fig. 5, O_2 plays a crucial role in the degradation of E2. With solution purging with N_2, there was almost no degradation of E2 during irradiation. The photodegradation rate of E2 was much higher with solution purging with O_2 than in air saturated solution. This result is in agreement with the effect of O_2 on the quantum yield of •OH. On the contrary, in the conditions with oxygen, saturated oxygen, and without oxygen, most Fe(III) were quickly transformed to Fe(II) and Fe (tot) remaining constant during irradiation. So O_2 has no effect on the photoredox process of iron complexes. Combined with Section 3.2.2, this proves that the photoredox of iron complexes as the starting reaction (reaction (1)) is important, but not the key reaction controlling the amount of •OH formation.

3.2.4. *Effect of iron concentration on the degradation of E2*

According to the results for the pH and oxygen effect, the ratio between Fe(III) and EDDS concentrations seems to be very important for understanding the photochemical reaction of Fe(III)-EDDS. So the photodegradation of E2 with different concentrations of Fe(III) and the same concentration of EDDS was investigated. As shown in Fig. 6, there was no degradation of E2 without Fe(III) in the irradiation solution. The initial degradation rate was increased with a higher concentration of Fe(III), but the final photodegradation efficiency after 8 h of the irradiation had the opposite trend. With the higher concentration of Fe(III) in the solution, a higher concentration of Fe(III)-EDDS complex was formed, so faster photodegradation of E2 was observed at the beginning of irradiation. But along with the quick photodegradation of E2, EDDS was also quickly decomposed. After complete photodegradation of EDDS, Fe(III)-EDDS was no longer present in the solution. Thus, when the concentration of Fe(III) was lower, although the starting efficiency of Fe(III)-EDDS was lower due to the low concentration of Fe(III)-EDDS, the reaction of Fe(III)-EDDS could last a longer time. So even the much lower concentration of Fe(III) in the solution could achieve better photodegradation efficiency in the end.

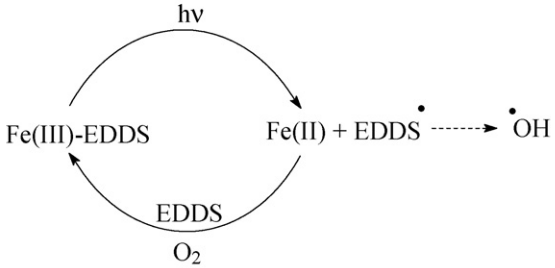


Diagram 1. The cycle of photochemical process of Fe(III)-EDDS in the presence of an excess of EDDS.

After the first photochemical reaction (reaction (1)), Fe(III) is reduced into Fe(II) and EDDS is oxidized. But if some EDDS is still present in solution, Fe(II) is easily reoxidized into Fe(III) through the formation of Fe(III)-EDDS complex. Therefore, the formation of •OH radicals and as a consequence the degradation of E2 photoinduced by Fe(III)-EDDS complex can continue (Diagram 1).

4. Conclusions

This study gives evidence of the potential role of Fe(III)-EDDS as a photoactive species in natural water. For the first time, the quantum yield of •OH was detected by photolysis of Fe(III)-EDDS. The quantum yield of •OH was independent of the concentration of Fe(III)-EDDS. The effect of O_2 and irradiation wavelength on the quantum yield of •OH are very well known and are the same as for any other iron species. On the contrary, the effect of pH is not obvious for this Fe(III)-EDDS complex. The quantum yield of •OH radical formation was higher at higher pHs between 3.0 and 9.0. This result is particularly interesting in terms of the natural environment. Correspondingly, E2 could be photodegraded by the photolysis of Fe(III)-EDDS, which is influenced by the concentration of Fe(III)-EDDS, pH, O_2 and the concentration of Fe(III). The Fe(III)-EDDS complex would be of importance for the transformation of organic compounds in the environment due to its higher photoactivity at pHs more relevant to the environment.

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