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Photochemistry of the $[Fe^{III}(edta)(H_2O)]^-$ and $[Fe^{III}(edta)(OH)]^{2-}$ complexes in presence of environmentally relevant species

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Abstract

The study shows that the $^*[Fe^{II}(edta^\bullet)(H_2O]^-$ or $^*[Fe^{II}(edta^\bullet)(OH)]^{2-}$ LMCT excited state can undergo self-quenching generating the $[(H_2O)(edta^\bullet)Fe^{II}(\mu\text{-}OH_x)Fe^{III}(edta)]^{x-4}$ millisecond intermediate, the fate of which depends on the availability of molecular oxygen. In the presence of O_2 or another external electron acceptor the excited state undergoes oxidative quenching, whereas the presence of an external electron donor leads to its reductive quenching. In the former case, the EDTA undergoes oxidation by the external electron acceptor in reaction catalysed by the excited Fe(III) complex, which changes its coordination sphere to $[Fe^{III}(ed3a)]$. Thus, with reference to the Fe(III) complex the process can be classified as photosubstitution, whereas with reference to the oxidized electron donors it can be identified as oxidation photocatalysed by the Fe(III) complex.

The reductive quenching results in reduction of Fe(III) in the excited complex accompanied by oxidation of EDTA and/or external electron acceptor; thus the process can be identified as photoreduction of the Fe(III) complex.

Numerical analysis of the $[Fe(edta)(H_2O]^-$ and $[Fe(edta)(OH)]^{2-}$ absorption spectra leads to conclusion that there are two different LMCT excited states, which differ in location of the unpaired electron (on N or O atom). Reactive decay of these excited states leads, however, to generation of analogous products, although with different quantum yields.

The Fe(III) photocatalytic cycle can be driven by sunlight and in the aerated media plays a crucial role in abatement of the pollutants, which have either electron donor or electron acceptor character. Among others, the photocatalytic cycle contributes to abate one of the most noxious pollutants, i.e. chromate(VI).

Keywords: Fe(III)–EDTA complexes; LMCT photochemistry; Photoinduced electron transfer; Fe(III) photocatalytic cycle; EDTA photodegradation; Chromate(VI) abatement

1. Introduction

Iron is not only the most abundant transition element in the environment but also it is one of the most important promoters of circulation and speciation of other elements, such as carbon, oxygen, hydrogen and nitrogen. The role of iron coordination compounds in the environmental self-cleaning processes was discussed recently in detail [1]. Their contribution is especially important in abatement of pollution by the recalcitrant pollutants, like ethylenediaminetetraacetic acid (EDTA).

According to earlier reports [2–7], the $[Fe(edta)(H_2O)]^-$ or $[Fe(edta)(OH)]^{2-}$ undergoes photoinduced electron transfer (PET), initiated by excitation to the LMCT excited state, e.g.:

$$[Fe^{III}(edta)(H_2O)]^- \xrightarrow{h\nu(\text{LMCT})} {}^*[Fe^{II}(edta^\bullet)(H_2O)]^- \quad (1)$$

The LMCT excited state undergoes the back electron transfer or reacts with a substrate molecule yielding an intermediate of millisecond life-time, formulated as $[(H_2O)(edta^\bullet)Fe^{II}(\mu\text{-}OH_x)Fe^{III}(edta)]^{x-4}$, e.g.:

$$\begin{aligned}&{}^*[Fe^{II}(edta^\bullet)(H_2O)]^- + [Fe^{III}(edta)(H_2O)]^-\\&\quad\rightarrow\ [(H_2O)(edta^\bullet)Fe^{II}(\mu\text{-}OH_x)Fe^{III}(edta)]^{x-4}\end{aligned} \quad (2)$$

The intermediate decays by inner-sphere electron transfer reactions: (i) back electron transfer reproducing the parent $[Fe(edta)(H_2O)]^-$ complex, obviously via the Fe^{III}–O–Fe^{III} dimer (3):

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$$[(H_2O)(edta^\bullet)Fe^{II}(\mu\text{-}OH_x)Fe^{III}(edta)]^{x-4} + xH_2O \rightarrow [(edta)Fe^{III}(\mu\text{-}O)Fe^{III}(edta)]^{4-} + xH_3O^+ \quad (3)$$

$$[(edta)Fe^{III}(\mu\text{-}O)Fe^{III}(edta)]^{4-} + 2H^+ + H_2O \leftrightarrows 2[Fe^{III}(edta)(H_2O)]^- + \quad (4)$$

and (ii) next electron transfer, leading to reduction of the second Fe(III)-centre and oxidation of the edta$^\bullet$ radical to stable products [7]:

$$[(H_2O)(edta^\bullet)Fe^{II}(\mu\text{-}OH_x)Fe^{III}(edta)]^{x-4} \rightarrow [Fe^{II}(edta)(H_2O)]^{2-} + Fe^{II}{}_{aq} + ED3A + CO_2 + HCHO \quad (5)$$

where ED3A is the ethylenediaminetriacetic acid. The pathway proceeding in absence of molecular oxygen finally yields Fe(II) and CO_2 products in the 2:1 ratio [2,6].

In aerated or oxygenated media, however, an outer-sphere two-electron oxidation of the dangling $CH_2COO^\bullet$ group and the Fe(II) centre, yielding $[Fe^{III}(edta)]^-$, $[Fe^{III}(ed3a)]^-$ and EDTA oxidation products was reported [7].

$$[(H_2O)(edta^\bullet)Fe^{II}(\mu\text{-}OH_x)Fe^{III}(edta)]^{x-4} \xrightarrow{O_2} [Fe^{III}(ed3a)] + [Fe^{III}(edta)]^- + CO_2 + HCHO + H_2O \quad (6)$$

Thus, the presence of molecular oxygen converts the stoichiometric EDTA oxidation by Fe(III) (Eq. (5)) into the photocatalytic autoxidation (Eq. (6)), which can be continued as $[Fe^{III}(ed3a)]$ is also photochemically active and under prolonged irradiation is able to contribute to photocatalysed oxidation of the ED3A ligand [4,6–9].

The efficiency of photooxidation of EDTA coordinated to the Fe(III) centre was studied repeatedly and effect of oxygen and pH was analysed. The most essential influence on the quantum yield is, however, exerted by the irradiation wavelengths within the LMCT band of the Fe(III)–EDTA complex [1–6]. The latter effect never found its convincing explanation [2]. In the paper we try to solve this intriguing problem.

Moreover, considering the important role of the Fe(III) compounds in the environment, the present study is focused on outer-sphere interactions between the excited Fe(III)–EDTA complexes and external electron donors and electron acceptors. The reagents were chosen from among the environmentally relevant species, such as free EDTA, alcohols, nitrate(III), sulfate(IV), molecular oxygen and chromate(VI).

2. Experimental

2.1. Chemicals

All reagents of highest available purity were used as purchased. Solutions of all reagents were freshly prepared using water triply distilled or demineralised by Millipore Milli Q Plus filter. Aqueous solutions of 1×10^{-4} M $Na[Fe(edta)]\cdot 2H_2O$ in Britton–Robinson buffer (0.04 M H_3PO_4, 0.04 M H_3BO_3, 0.04 M CH_3COOH) adjusted with NaOH to pH 4 or pH 9 were used in all the experiments. Oxygen-free and oxygenated solutions were made by saturation over at least 30 min with argon or molecular oxygen, respectively. All measurements were performed at 293 ± 0.1 K.

2.2. Instrumentation and procedures

UV–vis spectra were recorded in thermostated 1 cm quartz cells using a Shimadzu UVPC 2100 or a Hewlett-Packard HP 8453 spectrophotometer. Electrochemical analyser CX-741 (Elmetron, Poland) equipped with a glass electrode was used for pH measurements. Other electrochemical measurements were performed on BAS CV 50W (Bioanalytical Systems, USA) electrochemical analyser. Classical three-electrode setup with glassy carbon working electrode, Pt-wire auxiliary electrode and Ag/AgCl reference electrode was used for all measurements. 0.1 M solution of KCl in Britton–Robinson buffer was used as supporting electrolyte.

Irradiations were carried out using a low-pressure mercury lamp as source of 254 nm radiation and a high-pressure mercury HBO-200 lamp equipped with 365 nm interference filter. The measurements were repeated at least three times and their average values are included in tables.

3. Results and discussion

The photochemical behaviour of two main Fe(III)–EDTA forms was studied, i.e. $[Fe^{III}(edta)(H_2O)]^-$ (investigated at pH 4, $\lambda_{max} = 258$ nm, $\varepsilon_{max} = 8530\ M^{-1}\ cm^{-1}$) and $[Fe^{III}(edta)(OH)]^{2-}$ (at pH 9, $\lambda_{max} = 248$ nm, $\varepsilon_{max} = 8170\ M^{-1}\ cm^{-1}$). The effect of external electron donors or electron acceptors was followed spectrally during continuous irradiation of the Fe(III)–EDTA complexes.

3.1. Electron donor effect

In all cases the nature of the final Fe-products depends only on the presence of O_2 or another electron acceptor. It means that the presence and nature of external electron donors do not affect the primary reaction pathways. Their contribution to the redox process is manifested by deceleration in the substrate decay observed in the presence of all studied donors (Table 1). The effect can be interpreted in terms of their competition with the substrate (reactions (2) and (5)) in the reductive quenching of the LMCT excited state, e.g.:

$$^*[Fe^{II}(edta^\bullet)(H_2O)]^- + D \rightarrow [Fe^{II}(edta)(H_2O)]^{2-} + D^+ \quad (7)$$

In reactions (2) and (5) one photon excitation can induce reduction of two substrate molecules, whereas in reaction (7) only one. Thus, the higher contribution of reaction (7) the lower Fe(III)-substrate consumption is recorded. Instead, the external donor is oxidized.

The most spectacular behaviour is observed during irradiation of the solutions containing an excess of free EDTA: the effect

Table 1
Initial rates of the $[Fe(edta)H_2O]^-$ (pH 4) or $[Fe(edta)OH]^{2-}$ (pH 9) photoconversion by 254 nm irradiation in the presence of some electron donors, $k_{obs} \times 10^3$ [s^{-1}], $c_0 = 1 \times 10^{-4}$ M, $T = 298$ K

Electron donor	Without O_2	In O_2
Without any	5.33 ± 0.31 (pH 4)	1.42 ± 0.05 (pH 4) 0.78 ± 0.02 (pH 9)
SO_3^{2-}, $c_0 = 1 \times 10^{-4}$ M	–	1.15 ± 0.29 (pH 4) 0.69 ± 0.02 (pH 9)
NO_2^-, $c_0 = 1 \times 10^{-4}$ M	–	0.90 ± 0.07 (pH 4) 0.45 ± 0.02 (pH 9)
Methanol, $c = 2 \times 10^{-2}$ M	2.57 ± 0.21 (pH 4)	0.63 ± 0.03 (pH 4)
Propan-2-ol, $c_0 = 2 \times 10^{-2}$ M	2.63 ± 0.22 (pH 4)	0.63 ± 0.03 (pH 4)
Butan-2-ol, $c_0 = 2 \times 10^{-2}$ M	2.71 ± 0.22 (pH 4)	0.63 ± 0.03 (pH 4)
EDTA		
$c_0 = 1 \times 10^{-4}$ M	5.03 ± 0.57 (pH 4)	≥ 0.01 (pH 4) 0.41 ± 0.08 (pH 9)
$c_0 = 2 \times 10^{-4}$ M	4.78 ± 0.66 (pH 4)	≥ 0.01 (pH 4) 0.17 ± 0.02 (pH 9)
$c_0 = 5 \times 10^{-4}$ M	4.62 ± 0.85 (pH 4)	≥ 0.01 (pH 4) 0.03 ± 0.01 (pH 9)

is quite different in the absence (Fig. 1) and in the presence (Fig. 2) of molecular oxygen. In deoxygenated solutions the rate dependence is similar to that affected by other electron donors (Eq. (7)). Furthermore, the reaction rate decreases adequately to increasing free EDTA concentration (Table 1).

The most impressive outcome is observed in the Fe(III)–EDTA system in the presence of free EDTA and molecular oxygen (Fig. 2): although the absorption increase at $\lambda < 240$ nm indicates EDTA oxidation, the Fe(III)-substrate concentration remains constant at the first stage of the continuous photolysis. The effect is more outstanding in the acidic medium. The efficient substrate decay starts only upon some induction time, which is the longer, the higher concentration of the external EDTA (Table 1, Fig. 3).

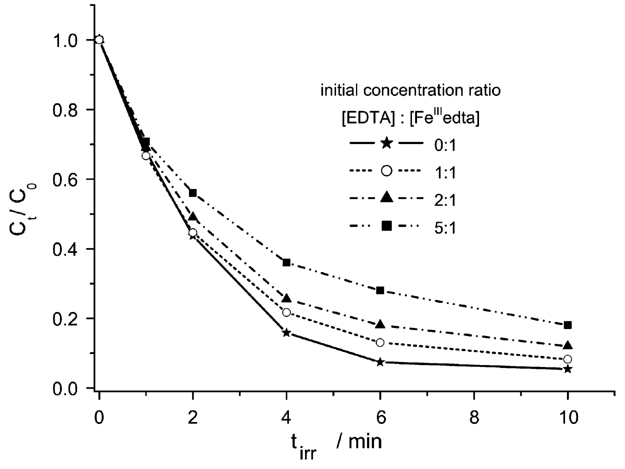


Fig. 1. Effect of the external EDTA on the initial rate of the $[Fe(edta)(OH)]^{2-}$ decay induced by irradiation ($\lambda_{irr} = 254$ nm) of deoxygenated solutions at pH 9 ($c_0 = 1 \times 10^{-4}$ M; measurements made not later than 1 min after stopping irradiation).

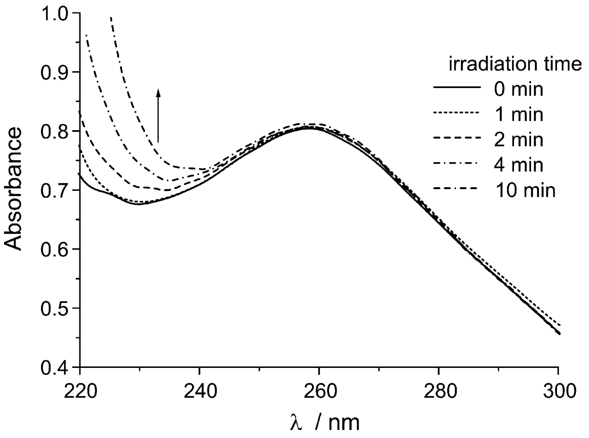


Fig. 2. Absorption changes induced by irradiation ($\lambda_{irr} = 254$ nm) of oxygenated $[Fe(edta)(H_2O)]^-$ solutions containing the external EDTA excess (4:1) at pH 4 ($c_0 = 1 \times 10^{-4}$ M).

The experimental results are consistent with the reaction (7) followed by fast oxidation of Fe(II) species with molecular oxygen (8):

$$[Fe^{II}(edta)(H_2O)]^{2-} + O_2 \rightarrow\rightarrow [Fe^{III}(edta)(H_2O]^- + H_2O \tag{8}$$

which was reported earlier [10,11] to proceed rapidly by the four-step mechanism involving oxidation of photogenerated $[Fe^{II}(edta)(H_2O)]^{2-}$ by molecular oxygen yielding $[Fe^{III}(edta)(H_2O)]^-$ and H_2O_2, followed by oxidation of $[Fe^{II}(edta)(H_2O)]^{2-}$ by H_2O_2. The latter pH dependent reaction was reported to produce H_2O not $OH^{\bullet}$, thus it cannot be treated as the Fenton reaction [12,13].

When free EDTA is consumed, the excited state quenching by the parent complex (Eq. (2)) becomes observable and its conversion to $[Fe^{III}(ed3a)]$ (Eq. (6)) is recorded.

3.2. Electron acceptor effect

Previous study [7] has shown that the presence of molecular oxygen changes the role of the Fe(III) centre from the

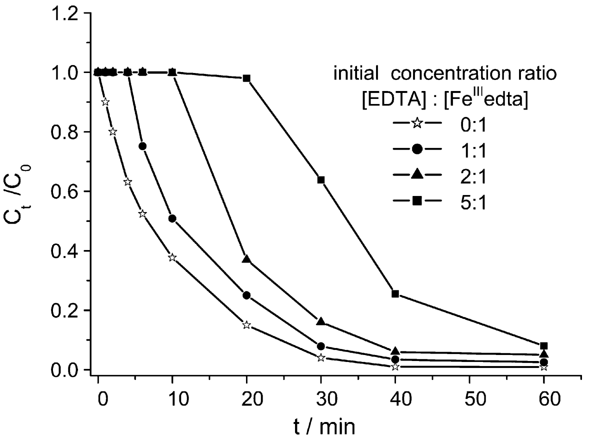


Fig. 3. Effect of the external EDTA excess on the initial rate of the $[Fe(edta)(H_2O)]^-$ decay induced by irradiation ($\lambda_{irr} = 254$ nm) of oxygenated solutions at pH 4 ($c_0 = 1 \times 10^{-4}$ M).

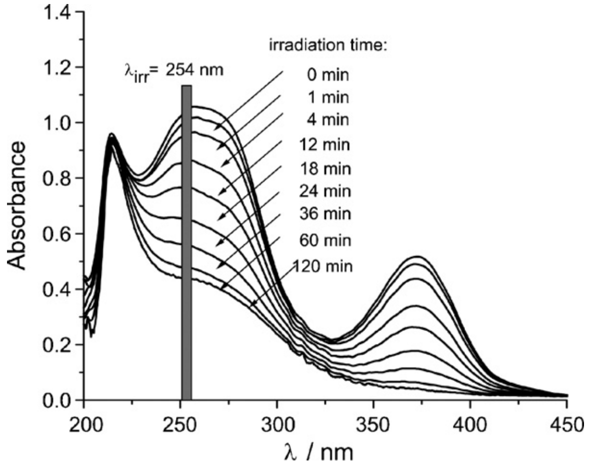


Fig. 4. Absorption changes recorded during irradiation with $\lambda_{irr} = 254$ nm of deoxygenated solution of $[Fe(edta)(OH)]^{2-}$ ($c_0 = 1 \times 10^{-4}$ M) and CrO_4^{2-} ($c_0 = 1 \times 10^{-4}$ M) at pH 9.

oxidant to the catalyst (cf. Eqs. (2) and (6)). Besides oxidizing the intermediate (Eq. (6)), also a direct oxidative quenching of the excited state, accompanied by the two-electron transfer, cannot be excluded, especially as the $[Fe^{III}(ed3a)]$ production is very fast ($k_{obs} \sim 1.4 \times 10^2\ s^{-1}$) [7] (Eq. (9)).

$$^{*}[Fe^{II}(edta^{\bullet})(OH)]^{2-} + O_2 \rightarrow [Fe^{III}(ed3a)] + CO_2 + HCHO + O_2^{2-} \quad (9)$$

Chromate(VI) was chosen to test the effect of another electron acceptor, which is of environmental relevance. Chromate(VI) is known, moreover, to undergo photoinduced electron transfer [14–16] and the cooperation of the two photochemical systems cannot be excluded.

At studied pH and concentration ranges two forms of the chromate(VI) anion should be taken into account: CrO_4^{2-} at pH 9 ($\lambda_{max} = 275$ nm, $\varepsilon_{max} = 3600\ M^{-1}\ cm^{-1}$ and $\lambda_{max} = 373$ nm, $\varepsilon_{max} = 4800\ M^{-1}\ cm^{-1}$) [17] and $HCrO_4^{-}$ at pH 4 ($\lambda_{max} = 260$ nm, $\varepsilon_{max} \sim 2600\ M^{-1}\ cm^{-1}$ and $\lambda_{max} = 350$ nm, $\varepsilon_{max} \sim 1600\ M^{-1}\ cm^{-1}$) [18]. Within wide spectral range the chromate(VI) absorption overlaps considerably that of the Fe(III)–EDTA complexes. The larger band separation is observed at pH 9 and this pH was selected for a more detailed study.

Irradiation with the 254 nm line, lying within the LMCT absorption bands of both components, induces relatively fast reduction of Cr(VI) and conversion of the $[Fe^{III}(edta)OH]^{2-}$ substrate into the $[Fe^{III}(ed3a)]$ product (Fig. 4). The same products are formed during irradiation using 365 nm line, i.e. light absorbed mainly by chromate(VI). The Fe-product analysis shows that irrespectively of the electron acceptor used (Cr(VI) or O_2) the same $[Fe^{III}(ed3a)]$ complex is formed. Moreover, the initial rates of the $[Fe^{III}(edta)OH]^{2-}$ conversion are also nearly independent of the electron acceptor nature (Table 2).

This suggests the similar oxidative quenching of the $[Fe^{III}(edta)OH]^{2-}$ excited state by O_2 (Eq. (9)) and chromate(VI) (Eq. (10)) accompanied by the two electron EDTA oxidation

Table 2
Effect of external electron acceptor on initial rates of the $[Fe^{III}(edta)OH]^{2-}$ photoconversion; ($c_0 = 1 \times 10^{-4}$ M, pH 9, $T = 298$ K)

λ_{irr} [nm]	$k_{obs} \times 10^3$ [s^{-1}]			
	No acceptor	O_2	CrO_4^{2-}	$O_2 + CrO_4^{2-}$
254	2.95 ± 0.67	0.61 ± 0.07	0.51 ± 0.07	1.12 ± 0.16
365	0.78 ± 0.06	0.16 ± 0.02	0.15 ± 0.02	0.35 ± 0.04

$$^{*}[Fe^{II}(edta^{\bullet})(OH)]^{2-} + CrO_4^{2-} \rightarrow [Fe^{III}(ed3a)] + CO_2 + HCHO + Cr^{IV}(aq) \quad (10)$$

Analysing chromate(VI) effect on the $[Fe^{III}(edta)OH]^{2-}$ photoconversion rate (Table 2), a not large but significant (by the factor of 1.15) increase of the 365 nm efficiency is observed, which is interpreted in contribution of the $^{*}\{CrO_4^{2-}\}$ reductive quenching by $[Fe^{III}(edta)OH]^{2-}$

$$^{*}\{CrO_4^{2-}\} + [Fe^{III}(edta)OH]^{2-} \rightarrow [Fe^{III}(ed3a)] + CO_2 + HCHO + Cr^{IV}(aq) \quad (11)$$

A possibility of two electron transfer and Cr(IV) formation in result of the $^{*}\{RCrO_4^{-}\}$ reductive quenching was demonstrated earlier [14]. Cr^{IV} (aq) is known to disproportionate

$$2Cr^{IV} = Cr^{III} + Cr^{V} \quad (12)$$

$$3Cr^{V} = Cr^{III} + 2Cr^{VI} \quad (13)$$

yielding a stable Cr(III) form and reproducing in part Cr(VI) [14,19–21].

In the systems containing both CrO_4^{2-} and O_2, the Fe(III)-substrate is consumed faster than in the presence of only one of the electron acceptors, whereas chromate is consumed much slower (Table 2, Fig. 5). The latter effect can be interpreted in terms of fast Cr(VI) regeneration from Cr(IV) and/or Cr(V) in their reactions with O_2.

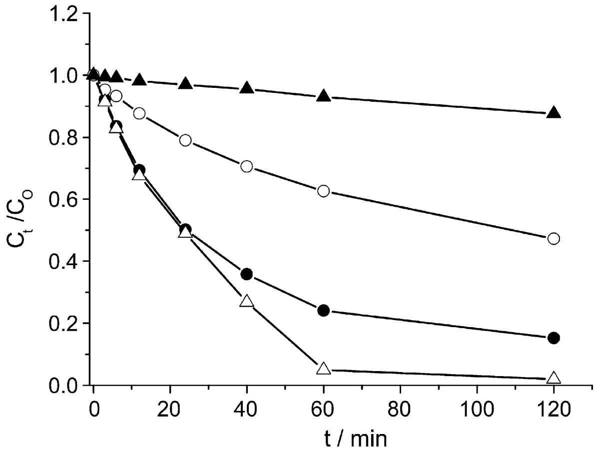


Fig. 5. Initial rates of the reactant decays under 365 nm irradiation: $[Fe(edta)OH]^{2-}$ (circles) and CrO_4^{2-} (triangles) in oxygenated (black labels) and in deoxygenated system (empty labels); initial concentrations of both reactants $c_0 = 1 \times 10^{-4}$ M, pH 9.

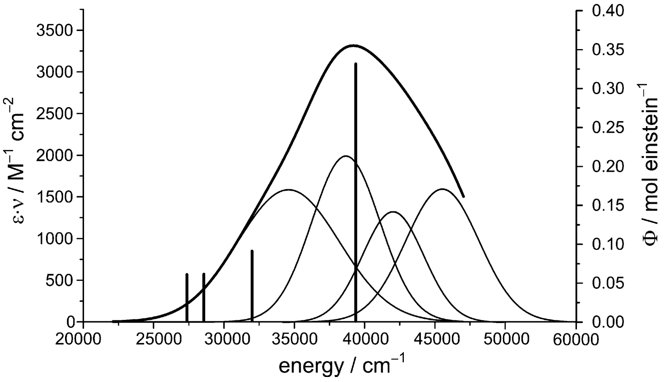


Fig. 6. Deconvolution of the $[Fe(edta)H_2O]^-$ spectrum into the Gaussian components. Vertical lines show the primary quantum yield values measured in deoxygenated medium [7].

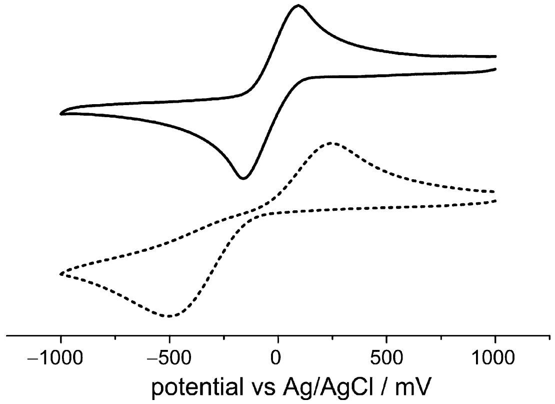


Fig. 7. Cyclic voltammograms of the $[Fe(edta)H_2O]^-$ (solid line) and $[Fe(edta)OH]^{2-}$ (dotted line) complexes.

3.3. Thermodynamic analysis

To provide an evidence for the suggested reductive quenching of the $*[Fe^{II}(edta^{\bullet})(H_2O)]^-$ or $*[Fe^{II}(edta^{\bullet})(OH)]^{2-}$ LMCT excited state (Eq. (7)) a detailed thermodynamic analysis was carried out. In order to determine the low energy limit a LMCT band was deconvoluted into the Gaussian curves. At pH 4 the experimental band is a convolution of four components with maxima at: 34,590, 38,672, 42,076 and 45,637 cm^{-1} (Fig. 6). All of these component bands are of comparable intensity. The lowest energy transition is characterised by a broad band of half-width of 8500 cm^{-1}; other peaks are much narrower (5200–6200 cm^{-1}). At pH 9 three bands were found at: 32,624, 38,230 and 42,222 cm^{-1}, the low energy transition is the weakest one and half-widths are 7615, 8105 and 5660 cm^{-1}, respectively.

Reduction potentials measured using differential pulse voltammetry amount +0.085 V versus NHE at pH 4 and −0.11 V versus NHE at pH 9 (Fig. 7); they are consistent with the previously reported values for somewhat different conditions [22,23]. One electron reduction of the $[Fe(edta)(H_2O)]^-$ complex is found to be quasi-reversible, while that of the $[Fe(edta)OH]^{2-}$ is irreversible. Irreversibility of electrochemical process indicates a consecutive reaction coupled with the interfacial electron transfer: it may be a mixed valence dimer formation or rearrangement of coordination sphere in the reduced $[Fe^{II}(edta)OH]^{3-}$ form.

The spectral and electrochemical data allow for estimation of reduction potentials of the lowest excited state as follows [24–26] (Eq. (14)):

$$E_{1/2}(^*A/A^-) = E_{1/2}(A/A^-) + E_{0,0} \qquad (14)$$

The free enthalpy of intermolecular electron transfer between excited iron complex and electron donor can be estimated according to Rehm–Weller equation [27–29] (Eq. (15)):

$$\Delta G = E_{1/2}(D/D^+) - E_{1/2}(^*A/A^-) + E_{\mathrm{coul}} \qquad (15)$$

The term E_{coul} represents the energetic effect due to Coulomb interactions between charged counterparts, but due to its low value in aqueous solutions can be neglected [30].

Calculated free enthalpies for ground and excited state redox reactions are collected in Table 3. These data substantiate the hypothesis of reductive quenching of the Fe^{III}–EDTA excited states by various electron donors, e.g.:

$$*[Fe^{II}(edta^{\bullet})H_2O]^- + CH_3OH \rightarrow [Fe^{II}(edta)H_2O]^{2-} + CH_3OH^{\bullet +} \qquad (16)$$

In the case of sulfate(IV) ions the contribution of $SO_3{}^{2-}$ oxidation by O_2, catalysed by the Fe–EDTA complex cannot be excluded [31,32], although due to low sulfite concentration it seems negligible.

3.4. Quantum yields

Quantum yield of the Fe-substrate decay was analysed repeatedly and its dependence on pH, substrate and oxygen concentrations was interpreted [2,6,7]. The most crucial effect of irradiation wavelengths included in one LMCT band was, however, never satisfactorily accounted for. Irradiation with low energy light (350–400 nm) results in the complex photoconversion with low primary quantum yield (0.06–0.01). Application of higher irradiation energy (313 nm) results in small increase

Table 3
Energy effects for thermal and photoinduced electron transfers between $[Fe(edta)H_2O]^-$ (pH 4) or $[Fe(edta)OH]^{2-}$ (pH 9) and selected electron donors; calculation were made for the lowest energy transitions (34,590 cm^{-1} at pH 4 and 32,624 cm^{-1} at pH 9)

Electron donor	$E_{1/2}$ [V]	pH 4		pH 9	
		ΔH, ground state	ΔH, excited state	ΔH, ground state	ΔH, excited state
$SO_3{}^{2-}$	0.65 [33]	0.55 eV, 53 kJ/mol	−3.75 eV, −362 kJ/mol	0.74 eV, 71 kJ/mol	−3.32 eV, −320 kJ/mol
$NO_2{}^-$	1.04 [33]	0.96 eV, 92 kJ/mol	−3.34 eV, −322 kJ/mol	1.15 eV, 111 kJ/mol	−2.91 eV, −280 kJ/mol
CH_3OH	1.8 [34]	1.72 eV, 166 kJ/mol	−2.58 eV, −249 kJ/mol	1.91 eV, 184 kJ/mol	−2.15 eV, −207 kJ/mol

of the quantum yield (0.09) while at 254 nm it reaches 0.33 [7]; further increase of irradiation energy causes again decrease of the quantum yield values [2].

The Gaussian analysis, presented in Fig. 6, shows that the LMCT spectrum of the Fe^{III}–EDTA complex is composed of several bands, which can differ in their character. Comparison of these results with the quantum yield values (Fig. 6) shows that irradiation within the low energy component (at 34,590 cm^{-1}) results in low quantum yield, while irradiation within the higher energy component (at 38,672 cm^{-1}) results in much higher quantum yields. Difference in bandwidths of these components implies the different nature of the first and the second excited states (Fig. 8). The explanation of these observations should take into account formation of two different edta-centred radicals: the low energy component should be associated with formation of nitrogen-centred radical intermediate, while the components of higher energy should involve the carboxylate moiety. The decrease in quantum yield, observed for still higher irradiation energies (at 42,076 and 45,637 cm^{-1}) can be consistent with the IL character of higher excited states, which are photochemically inactive [2].

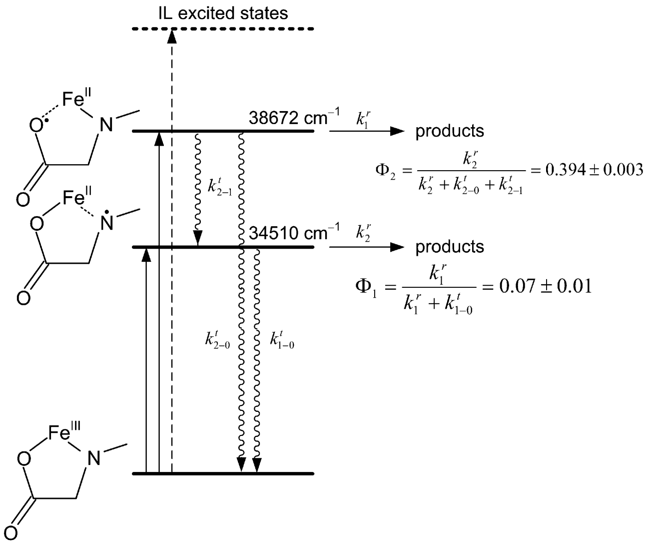
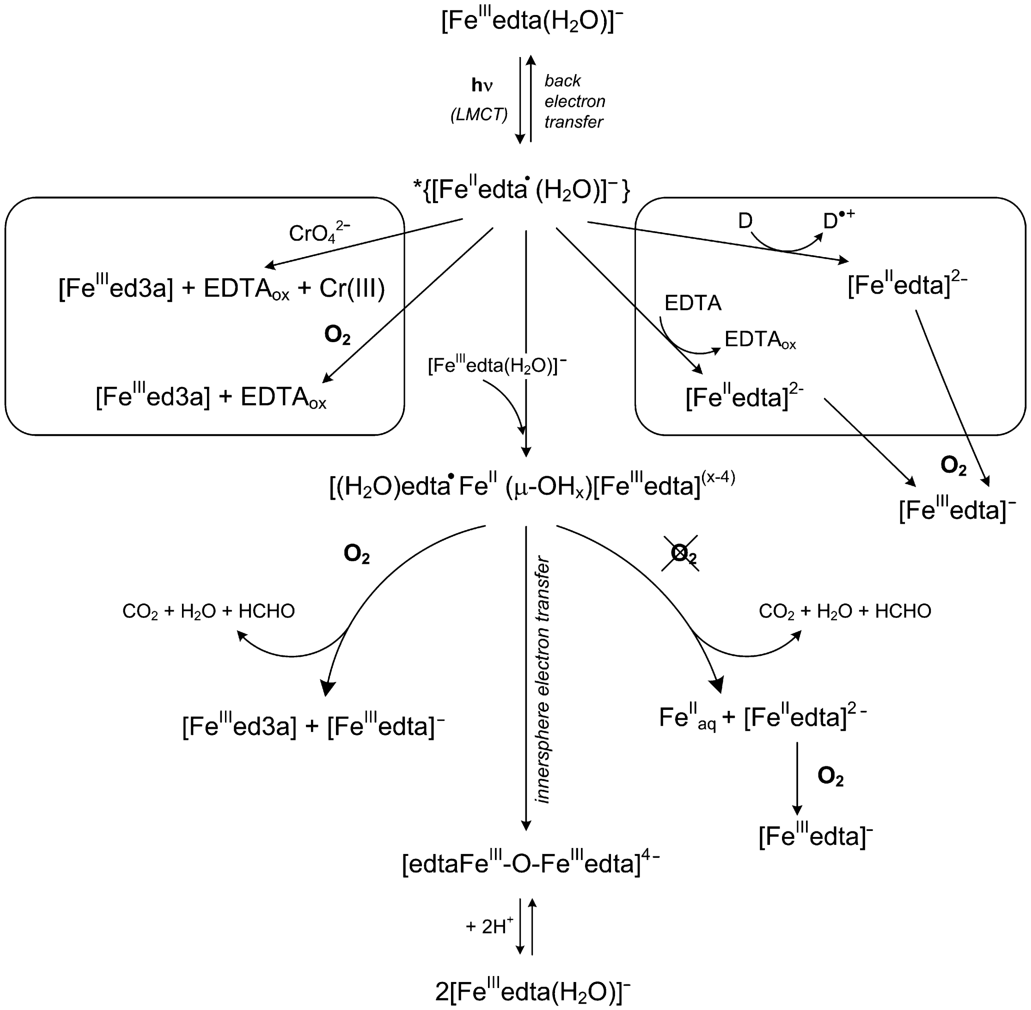


Fig. 8. Energy diagram of the $[Fe(edta)H_2O]^-$ complex with proposed structure of excited state radical-complexes.



Scheme 1. Mechanism of the photochemical behaviour of the $[Fe(edta)H_2O]^-$ complex in the presence of some environmentally relevant electron donors and acceptors; the reactivity scheme for $[Fe(edta)(OH)]^{2-}$ is analogous.

3.5. Reaction mechanism including outer-sphere interactions

The results obtained in this study lead to conclusion that the Fe^{III}–EDTA complexes are characterized by two LMCT excited states of different unpaired electron location and thereby the rate of the back electron transfer. Their chemical behaviour is, however, similar: both undergo self-quenching generating the dimeric intermediate of millisecond lifetime, the fate of which depends on the availability of molecular oxygen (Scheme 1). In the presence of an external electron donor or electron acceptor the excited state undergoes, respectively, either reductive or oxidative quenching. In the former pathway, the excited Fe(III) complex undergoes reduction accompanied by oxidation of EDTA or external electron acceptor; thus the process should be classified as the Fe(III) photoreduction. The latter case leads to the EDTA oxidation by the external electron acceptor in process catalysed by the excited Fe(III) complex, which changes moderately its coordination sphere. Thus, with reference to the Fe(III) complex the process is identified as photosubstitution, whereas with reference to the oxidized electron donors, it is classified as oxidation photocatalysed by the Fe(III) complex.

4. Conclusions

Considering the behaviour of the Fe^{III}–EDTA system in the environment we had to comment as following: (i) the actinic flux at the ground level covers the first band (with maximum at 34,590 or 32,624 cm^{-1}) and part of the second band ($\nu_{max} = 38{,}672$ or 38,230 cm^{-1}) enabling the photochemical transformation of the $[Fe^{III}(edta)H_2O]^-$ and $[Fe^{III}(edta)OH]^{2-}$ complexes in the nature with a moderate quantum yield. (ii) Environmental accessibility of molecular oxygen leads to assumption that the EDTA oxidation in the Fe^{III}–EDTA systems proceeds mostly as the photocatalytic process. (iii) The photocatalytic oxidation can apply not only to EDTA, but also to other electron acceptors available, such as alcohols, sulfate(IV), nitrate(III), etc. (iv) The photocatalytic cycle can be driven not only by molecular oxygen but also by other electron acceptors, first of all by chromate(VI). The Cr(VI) participation in the photocatalytic cycle not only increases the oxidation efficiency of the system, but also abates the toxic hazard due to reduction of Cr(VI) to Cr(III).

One could suppose that the mechanism of the processes, shown in Scheme 1, is similar to so-called photo-Fenton process. This would be, however, erroneous conclusion, as the essential part of the Fenton process is generation of $OH^\bullet$ radicals in reaction between Fe(II) and H_2O_2, whereas in the Fe–EDTA systems studied in this paper there is no chance of simultaneous presence of these reagents, except the aerated system consisted of the Fe(III)–EDTA complex and an excess of external EDTA. In other cases Fe(II) is generated only in deoxygenated solutions, where there are no possibility of the H_2O_2 production, whereas in aerated media, where production of H_2O_2 is probable, Fe(II) is not produced. Only in the aerated system containing external EDTA, H_2O_2 is produced and oxidizes $[Fe^{II}(edta)(H_2O)]^{2-}$, but the reaction is different from that called Fenton reaction [10,11].

Thus, it can be concluded, that the photoredox reactions described in this paper are complementary to the photo-Fenton processes, and activate other important pathways in the environmental self-cleaning.

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