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Photoredox behaviour of the Cr–EDTA complex and its environmental aspects

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Abstract

Polychromatic radiation from a mercury lamp or light mimicking the sunlight ($\lambda \geq 300$ nm) is able to initiate an innersphere electron transfer in the $[Cr^{III}EDTA(OH)]^{2-}$ complex, leading to formation of a Cr(II) centre and the EDTA radical. Under defined conditions (pH ≥ 7, O_2 in excess over the Cr(II) concentration) the photoreduction is followed by thermal multi-step electron transfer resulting in the Cr(II) $\rightarrow$ Cr(VI) oxidation by molecular oxygen, although EDTA is known to enhance the Cr(VI) reduction. Electron donors, present in the system, enlarge the efficiency of Cr(VI) production. These are also able to take part in the photoinduced electron transfer to $CrO_4^{2-}/HCrO_4^-$ in excited states, when pH reaches corresponding level. As Cr(VI) production is accompanied by decrease in pH, and its reduction with an opposite effect, the processes proceed according to an electron shuttle mechanism. Their progress under natural conditions seems attainable, because all conditions needed to the photocatalytic oxidation of organic pollutants by O_2, with oscillatory recovery of the Cr(III) and Cr(VI) species can be provided.

Keywords: Photoreduction; Organic pollutants; Electron shuttle mechanism; Cr^{III}-EDTA, photodegradation

1. Introduction

Chromium compounds play an important role in environmental and biochemical systems. The most essential feature of the compounds is an enormous difference between properties of Cr(III) and Cr(VI), the main Cr-forms existing in the environment. These are drastically different in charge, physicochemical properties as well as in chemical and biochemical activity. Cr(VI) exerts toxic effects on biological systems, whereas Cr(III) is considered as a trace element essential for proper functioning of living organisms. Not only toxicity, but also the mobility and bioavailability of chromium, depend fundamentally on its chemical form. Cr(VI) compounds are usually highly soluble, mobile and bioavailable compared to sparingly soluble trivalent chromium species [1].

As Cr(VI) is a strong oxidant, its presence in the environment has to be a consequence of the Cr(III) oxidation competing successfully with the Cr(VI) reduction. The oxidation process needs, however, interaction with a strong oxidant, and under environmental conditions is unlikely to proceed with a high efficiency. Moreover, the thermodynamically stable chromate(VI) can be transformed into a Cr(III) species via electron transfer induced by solar light [2]. Thus, the environmental conversion of Cr(III) to Cr(VI) needs an additional enhancement in photoredox processes induced by solar light [3–5].

Chromium(III) coordination compounds are well known from their photochemical reactivity, which was studied repeatedly. The main, and often the only one, mode of the Cr(III) photochemistry consists in photosubstitution or related reactions [6–11]. Photoredox behaviour was found only in few cases as following the LMCT excitation in complexes containing reducer ligands [3,4,6,9,11–19]. Then, innersphere electron transfer is effective in chromium reduction and ligand oxidation (Eq. (1)).

$$[Cr^{III}L_6] \xrightarrow[\text{LMCT}]{h\nu} [Cr^{II}L^{(+)}L_5] \xrightarrow{O_2} Cr^{III}_{aq} + 5L + L_{ox} \quad (1)$$

Generated photochemically Cr(II), releases readily its ligands, and in the presence of molecular oxygen is oxidised back to a Cr(III) species. In alkaline medium, however, and at large excess of O_2 over the Cr(II) concentration, the oxidation proceeds up to CrO_4^{2-} [16–18].

$$Cr^{II}\,(aq) \xrightarrow[OH^-]{O_2} CrO_4^{2-} \quad (2)$$

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The photoreduction Cr(III) → Cr(II), followed by the secondary thermal oxidation Cr(II) → Cr(VI), can be observed in the environment provided that energy of the solar light is enough to induce the LMCT excitation of the Cr(III) complex, and that the complex is situated in aerated and even weakly alkaline medium. The former condition is met easily, as a majority of environmental pollutants are of reducing character. Their oxidation in the Cr-complex photoreaction (Eq. (1)) is effective in removal of the ligand, which was previously coordinated to Cr(III).

The effect motivated us to choose the Cr–EDTA complex for the photochemical study: EDTA belongs to the organic pollutants which is released to natural waters in large amounts from industrial and domestic sources and cannot be removed easily either by conventional biological or by chemical wastewater treatment [19–23]. As yet, the Fe(III)–EDTA complex is the only environmentally relevant species that undergoes the direct photolysis leading to oxidation of EDTA [23]. Its photodegradation products such as: iminodiacetic acid (IMDA), *N*-aminoethyleneglycine (EDMA), *N*,*N*′-ethylenediglycine (EDDA-*N*,*N*′), *N*-carboxymethyl-*N*-aminoethyleneglycine (EDDA-*N*,*N*), *N*-carboxymethyl-*N*,*N*′-ethylenediglycine (ED3A) and glycine are identified as biodegradable [24].

The assumption of similar role of the Cr(III)–EDTA complex in the EDTA photodegradation spurred us to investigate the system. Moreover, similarly to Fe(III)–EDTA, the Cr complex can be easily modified due to lability of its sixth ligand. This is illustrated by the pH dependent equilibria existing in aqueous solutions:

$$[Cr^{III}EDTA(H_2O)]^- \underset{H^+}{\overset{OH^-}{\rightleftarrows}} [Cr^{III}EDTA]^- \underset{H^+}{\overset{OH^-}{\rightleftarrows}} [Cr^{III}EDTA(OH)]^{2-} \quad (3)$$

In the pH range characteristic for environmental systems (4–9) the $[CrEDTA]^-$ and $[CrEDTA(OH)]^{2-}$ forms are mostly present, as $pK_1 = 1.80$ and $pK_2 = 7.39$ [25–27]. These forms are expected to substitute one of the COO^- bonds of the $EDTA^{4-}$ or the OH^- ligand by another one. The feature creates a possibility of modifying the photochemical behaviour of the Cr-system not only in laboratory but also in the environment.

2. Results and discussion

Exposure of the Cr(III)–EDTA complex to full light of a mercury lamp or to radiation mimicking the solar light ($\lambda \geq 300$ nm) induces a photoredox process, which is perceptible provided that molecular oxygen is present in the system and the solution pH is equal or more than 7. Then, an increase in absorption at 274 and 373 nm is observed (Fig. 1), which is characteristic of the CrO_4^{2-} ion [28]. The reaction rate shows some induction period and depends on many various parameters, such as irradiation conditions, temperature, pH, concentration of molecular oxygen, as well as on the presence and concentration of different electron donors. This behaviour is consistent with the expected quite complex sequence of secondary thermal processes transforming the excited Cr(III)–EDTA complex into the chromate(VI) species. Rate of the Cr(VI) production increases to some, not very large, extent with increase in temperature (Table 1), demonstrating a noticeable contribution of thermal processes.

The pH dependence, illustrated in Fig. 2, can be a consequence of the Cr(III)/Cr(VI) redox potential dependence on pH [1], and/or may result from the Cr–EDTA transformation into a more photochemically active form. The latter hypothesis is supported by nearly linear dependence between rate of the Cr(VI) appearance and the initial concentration of $[CrEDTA(OH)]^{2-}$ in the equilibrium (Eq. (3)), recorded under conditions of the first-order kinetics (insert to Fig. 2, cf. also Table 1).

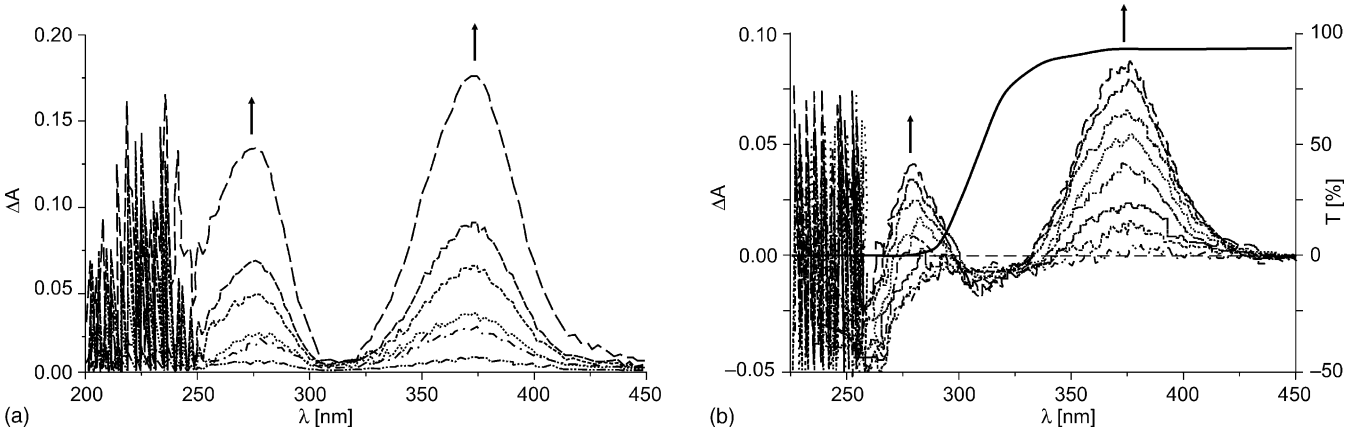

Fig. 1. Increase in absorbance recorded during continuous irradiation of $[CrEDTA(OH)]^{2-}$ oxygenated solutions at pH =10 (a) 5 mM Cr–EDTA exposed to full light of mercury lamp through 5, 10, 15, 20, 30 and 60 min, and (b) 10 mM Cr–EDTA irradiated with a cut-off filter $\lambda \geq 300$ nm (solid line, right scale), irradiation times 10, and 30 min, 1, 2, 3, 4, 5, and 6 h; all curves are differences between absorbance recorded upon irradiation and the initial one ($A_t - A_0$).

Table 1
Initial rates of Cr(VI) photoproduction in oxygenated 5 mM Cr–EDTA solutions irradiated by full light of mercury lamp at pH = 10, 293 K (if not otherwise stated)

Conditions/additive	Concentration of additive (mM)	k_{obs} ($\times 10^6$, s^{-1})
Effect of radiation range		
Full light of mercury lamp		2.52
With cut-off filter, $\lambda \geq 300$ nm[a]		0.09
Effect of oxygen		
Oxygenated		2.52
Deoxygenated		0
Effect of temperature (K)		
283		2.11
293		2.52
303		3.26
323		4.99
323, in the dark		0
Effect of pH		
6		0.04
7		0.72
8		1.51
9		2.29
10		2.52
11		2.58
Effect of phenol		
	5	95.20
	50	92.52
	125	97.34
	250	109.96
Effect of triethanolamine		
	50	9.56
	125	11.92
	250	10.11
	500	8.87
	1000	4.61
Effect of alcohols		
Methanol	50	3.03
	250	3.04
	500	2.64
Ethanol	50	2.63
	250	2.12
	500	2.36
2-propanol	50	2.59
	250	2.68
	500	2.48
2-Butanol	50	2.56
	250	2.81
	500	2.96
Effect of diols		
1,2-Ethanediol	125	1.08
	250	1.85
	500	2.28
1,3-Propanediol	125	2.87
	250	2.87
	500	3.40
2,3-Butanediol	125	7.16
	250	12.16
	500	12.77
Effect of 1,2,3-propanetriol		
	500	0.85
Effect of photosensitive additives		
Methanal	125	4.60
	250	4.61
	500	4.26
Acetone	125	5.99
	250	5.67
	500	5.44

[a] Concentration of Cr–EDTA 10 mM.

More enigmatic appears the role of electron donors which influence the rate of Cr(III) to Cr(VI) oxidation. A number of such species were investigated; these are, e.g. triethanolamine, alcohols (methanol, ethanol, propan-2-ol, butan-2-ol), diols (1,2-ethanediol; 1,3-propanediol; 2,3-butanediol), 1,2,3-propanetriol, aldehydes (methanal), ketones (acetone), phenol and its derivatives. The typical behaviour of these additives is an enhancement of the Cr(VI) production rate at least at initial irradiation times and moderate concentrations of the additives (Table 1).

Acceleration of the CrO_4^{2-} appearance by the electron donors has to have its origin in photoreduction of the Cr(III)–EDTA complex, which initiates the series of thermal redox reactions yielding a Cr(VI) species as the final product. Without interaction of any electron donor, a photoinduced innersphere electron transfer can generate a Cr(II) centre and the $EDTA^{\bullet}$ radicals (Eq. (4)):

$$[Cr^{III}EDTA(OH)]^{2-} \xrightarrow[LMCT]{h\nu} [Cr^{II}EDTA^{\bullet}(OH)]^{2-} \quad (4)$$

Preference of the $[Cr^{III}EDTA(OH)]^{2-}$ form to undergo the electron transfer demonstrates that the dangling COO^- group is more susceptible to oxidation, than the group coordinated to Cr(III). The $RCOO^{\bullet}$ radical group formed in this way, similar to other $RCOO^{\bullet}$ radicals, should decompose yielding CO_2 and $R^{\bullet}$ radical [19].

In the absence of molecular oxygen, or another Cr(II) scavenger, the reverse reaction competes effectively with the photoreduction (Eq. (4)); in the presence of O_2 substituted Cr(III) complexes can be formed; whereas at the sufficient O_2 excess over the Cr(II) concentration, its oxidation in even weakly alkaline medium can proceed up to CrO_4^{2-} (cf. Eq. (2)).

The thesis of the Cr(III) → Cr(II) photoreduction preceding the oxidation processes is supported by absorption changes accompanying irradiation of the solutions containing both $[Cr^{III}EDTA(OH)]^{2-}$ and phenol (Fig. 3). The results show that also in this case chromate(VI) is produced and, moreover, its yield is about two orders higher than without any additive and in practice is not sensitive to phenol concentration, when its photoreaction proceeds under conditions of the zero-order kinetics. The main phenol photoreaction in terms of quantum yield is electron ejection to form

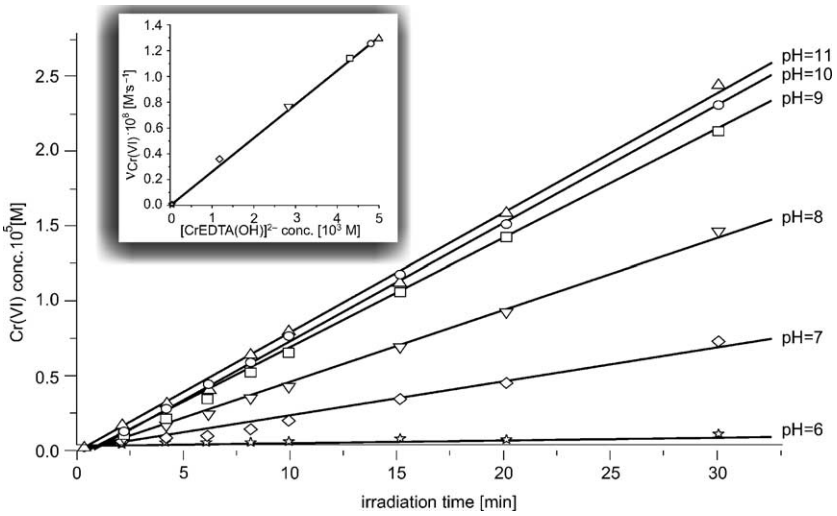

Fig. 2. Dependence of Cr(VI) photoproduction on pH of the oxygenated Cr–EDTA solutions; total Cr concentration 5 mM, full light of mercury lamp, $T = 293$ K; insert displays a correlation between the Cr(VI) production rate ($\nu_{Cr(VI)}$) and the $[CrEDTA(OH)]^{2-}$ concentration, calculated from equilibrium Eq. (3).

a hydrated electron and phenolic radical (Eq. (5)) [29–34].

$$C_6H_5OH + H_2O \xrightarrow{h\nu} C_6H_5O^{\bullet} + H_3O^{+} + e^{-}_{solv} \quad (5)$$

The $[Cr^{III}EDTA(OH)]^{2-}$ is expected to be a good electron scavenger and the reaction

$$[Cr^{III}EDTA(OH)]^{2-} + e^{-}_{solv} \rightarrow [Cr^{II}EDTA(OH)]^{3-} \quad (6)$$

enlarges significantly concentration of the Cr(II) precursor.

The crucial evidence of the reaction sequence (Eqs. (5) and (6)) is provided by the flash experiments illustrated in Fig. 4. Comparison of the transient absorption recorded upon a 266-nm laser pulse in neat phenol solution and in phenol with Cr–EDTA shows that (i) under applied experimental conditions generation of e^{-}_{solv} (broad absorption with λ_{max} ~700 nm) in phenol photooxidation (Eq. (5)) is observed at 100 ns ($\tau_{1/2} \approx 300$ ns); (ii) in the presence of the Cr(III) complex the photogenerated e^{-}_{solv} is completely scavenged within $\tau \leq 100$ ns upon pulse (Eq. (6)).

Other experiments were carried out to demonstrate formation of a Cr(II) species by direct spectral analysis (Fig. 5). As the Cr(II)–EDTA complex is thermodynamically stable [35], its spectrum was measured 10 min after flashing of deoxygenated Cr(III)–EDTA solution (curve 1) and the result was compared with the spectral changes observed during chemical reduction of the complex by zinc amalgam (curve 4). Both difference spectra are similar to each other and show that the Cr(II) species is characterized by absorption higher than that of the $[CrEDTA(OH)]^{2-}$ complex in whole range except ~500–700 nm. At $\lambda > 700$ nm a minute maximum at ~750 nm, within the 250–500 nm range an increase in absorption with a band at ~480 nm ($\varepsilon \sim 10^2$) and a shoulder at ~300–320 ($\varepsilon \sim 10^3$) are observed. When the $[CrEDTA(OH)]^{2-}$complex is irradiated in the presence of KCN a new, relatively short lived absorption is recorded (λ_{max} ~310 nm, $\tau_{1/2} \approx 100$ ns), which can be assigned to the spectrum of $[Cr^{II}(CN)_6]^{4-}$ reported earlier [17,36].

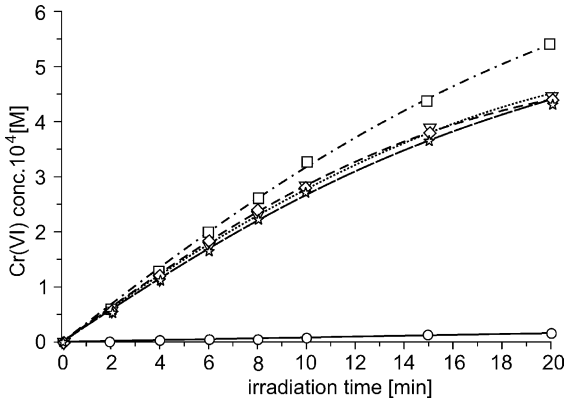

Fig. 3. Photoproduction of CrO_4^{2-} in the $[CrEDTA(OH)]^{2-}$–phenol–oxygen system; concentration of Cr–EDTA 5 mM, phenol concentrations: 0 (circles), 5 (triangles), 50 (stars), 125 (diamonds) and 250 (squares) mM; pH = 10, full light of mercury lamp, $T = 293$ K.

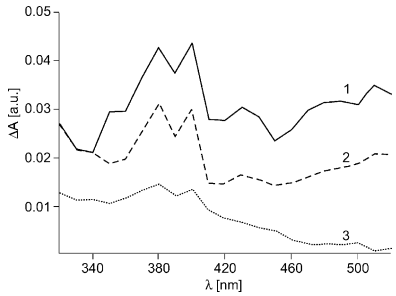

Fig. 4. Transient spectra recorded in 8.5 mM deoxygenated phenol aqueous solution (1) at 100 ns upon a 266-nm laser pulse and (2) after 300 ns delay; (3) transient spectrum of the same solution containing additionally 8.5 mM $[CrEDTA(OH)]^{2-}$, recorded 100 ns upon pulse; all curves are differences between the absorption recorded upon flashing and the initial spectrum ($A_t - A_0$); pH =10, $T = 293$ K.

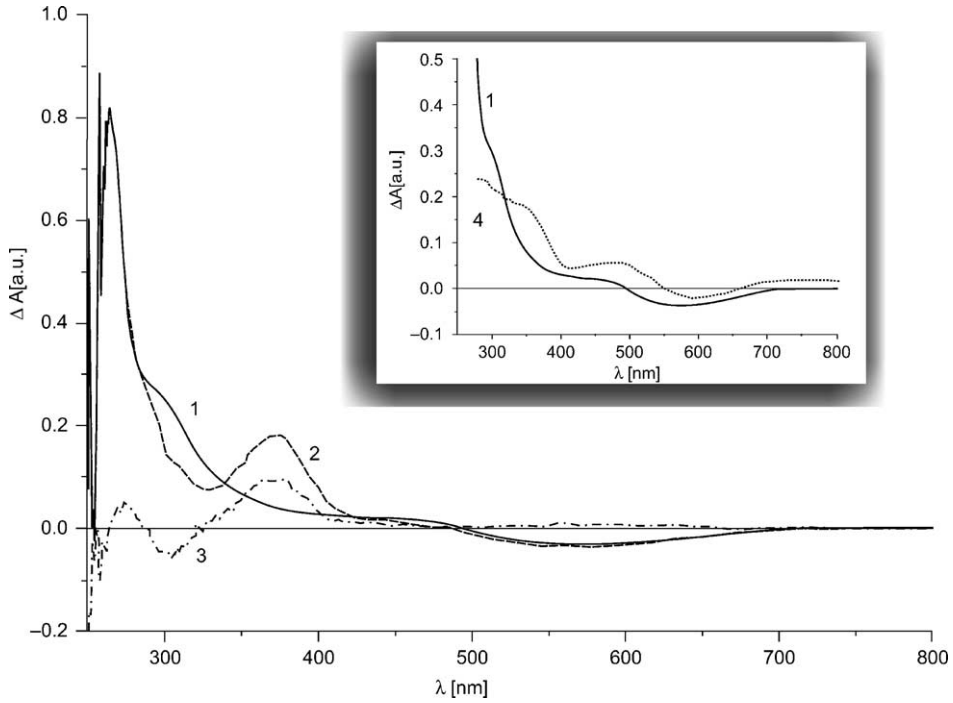

Fig. 5. Spectra of Cr(II)–EDTA intermediates (curves 1 and 4) obtained from 8.5 mM $[CrEDTA(OH)]^{2-}$ at pH = 10, and result of their oxygenation (curves 2 and 3); curves 1 and 2 are differential curves $(A_t - A_0)$, recorded at long time (10 min) after flashing with a 266 nm pulse of the deoxygenated (1) and oxygenated solution (2); curve 3 displays a difference between 2 and 1; insert: curve 4 is a differential spectrum $(A_t - A_0)$ recorded after 6 h of chemical reduction of $[CrEDTA(OH)]^{2-}$ at pH = 10 by zinc amalgam in deoxygenated system.

The Cr(II)EDTA product is thermally stable only in the absence of oxygen, in the other case its transformation into Cr(III) and Cr(VI) proceeds readily. Fig. 5 illustrates this conversion by comparison between spectra recorded after flashing of deoxygenated solution (curve 1), oxygenated one (curve 2) and difference between them (curve 3). The absorption characteristic for CrO_4^{2-} ion about 370 and 270 nm is then easily perceptible.

The photochemically not active electron donors, such as aliphatic alcohols, stimulate the Cr(VI) production, but much less effectively, than phenol, and the rate is somewhat dependent on the alcohol concentration. Typically, at larger alcohol concentrations the Cr(VI) production rate is enhanced, as is the case of butan-2-ol (Fig. 6) or enhanced only at moderate alcohol concentrations, whereas higher concentrations exert an opposite effect (Table 1). The latter behaviour can be a result the inner-filter effect competing effectively with the photoreduction rate.

Assistance from the electron donors, such as aliphatic alcohols, can be a consequence of different scenarios: (i) it may consist in inhibition of the reaction reverse to Eq. (4) by scavenging its free radical products; or (ii) the photoinduced electron transfer may be realized not only in the innersphere (Eq. (4)) but also in an outersphere pathway leading to oxidation of the electron donor (L):

$$[Cr^{III}EDTA(OH)]^{2-} + L \xrightarrow[LMCT]{h\nu} [Cr^{II}EDTA(OH)]^{3-} + L^{\bullet+} \quad (7)$$

or (iii) the donor oxidation can proceed via innersphere PET preceded by the OH^- ligand substitution:

$$[Cr^{III}EDTA(L)]^{-} \xrightarrow[LMCT]{h\nu} [Cr^{II}EDTA]^{2-} + L^{\bullet+} \quad (8)$$

The latter mechanism seems less probable due to lack of the spectral changes in the $[CrEDTA(OH)]^{2-}$ solutions after addition of any of the studied electron donors. The results obtained in this work does not allow, however, to make any decisive choice between these scenarios, but they seem to

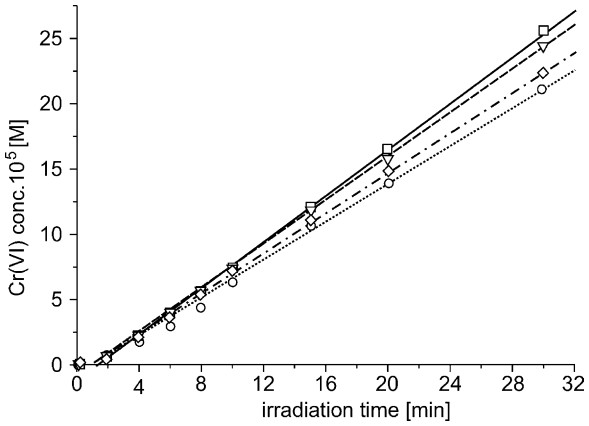

Fig. 6. Photoproduction of Cr(VI) in the $[CrEDTA(OH)]^{2-}$–butan-4-ol system at pH = 10; Cr–EDTA concentration 5 mM, butan-2-ol concentrations: 0 (circles), 50 (diamonds), 250 (triangles) and 500 mM (squares); full light of the mercury lamp, $T = 293$ K.

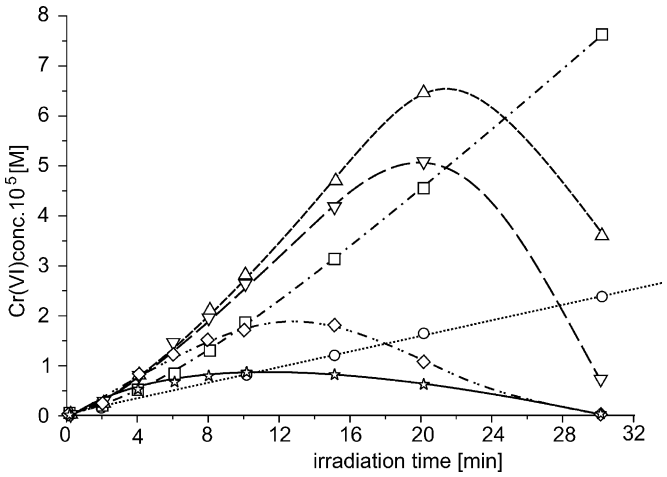

Fig. 7. Photoproduction of Cr(VI) in the $[CrEDTA(OH)]^{2-}$–triethanolamine system; concentration of Cr–EDTA 5 mM, TEA concentrations: 0 (circles), 5 (squares), 125 (triangles), 250 (reversed triangles), 500 (diamonds), 1000 mM (stars); full light of mercury lamp, $T = 293$ K.

demonstrate that choice of the reaction pathway depends strongly on the L nature.

Much higher effect and more complex behaviour is shown by triethanolamine (Fig. 7) for which the enhancement in Cr(VI) production is observed only at initial irradiation times and moderate TEA concentrations (Table 1), in the other case, not only increase in Cr(VI) concentration is less steep (e.g. for TEA concentrations higher than 0.1 M), but also the photoreduction of Cr(VI) is observed at prolonged irradiation times, which are the shorter the higher TEA concentration (Fig. 7). As the inner filter effect cannot be responsible for the Cr(VI) consumption, the concurrent photochemical process has to be taken into account, i.e. the photoinduced reduction of chromate(VI) mediated by TEA. Really, 0.1 mM CrO_4^{2-} irradiated exactly under the same conditions is reduced completely within half an hour. Thus, in the moderately alkaline medium containing $[Cr^{III}EDTA(OH)]^{2-}$, CrO_4^{2-} and TEA photoreduction of both chromium species can be induced by sunlight.

Similar effect is observed during irradiation the system containing Cr–EDTA and diols (Table 1). However, the photoinduced electron transfer between Cr(VI) and alcohols needs usually an acidic medium to proceed. On the other hand, increased number of OH groups in alcohols increases their susceptibility to mediate the electron transfer to the excited CrO_4^{2-} ion [2]. Moreover, conversion of Cr(II) to Cr(VI) in aqueous solution is known [37,38] to proceed via formation of the Cr(III) peroxide intermediate:

$$Cr^{2+}(aq) + O_2 \rightarrow CrO_2^{2+} \quad (9)$$

which transformation to chromate(VI) consumes significant amount of the OH^- ions.

$$CrO_2^{2+} + 4OH^- \rightarrow CrO_4^{2-} + 2H_2O \quad (10)$$

Similar OH^- consumption is expected in the case of the $[Cr^{III}EDTA(OH)]^{2-}$ complex. Thus, at longer irradiation times and especially at higher concentrations of the additives, the decrease in pH can initiate the chromate(VI) reduction mediated by the same electron donor. Moreover, the Cr(VI) reduction is known to be enhanced by the presence of EDTA [19]. The increased Cr(VI) concentration can cause that reduction rate surpasses the rate of its formation. The Cr(VI) reduction, in turn, shifts the pH in opposite site due

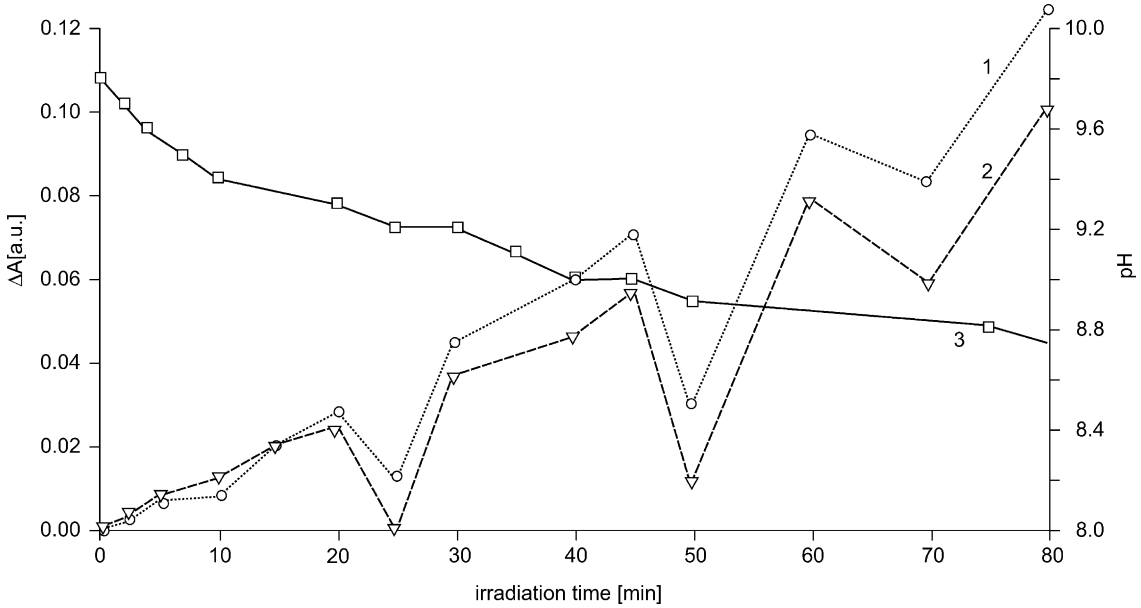

Fig. 8. The oscillatory photo-recovery of Cr(VI) and Cr(III) species during irradiation of not buffered solution containing 5 mM $[CrEDTA(OH)]^{2-}$ and 50 mM 2,3-butanediol; absorption changes $(A_t - A_0)$ characteristic of CrO_4^{2-} (1) at 373 and (2) at 274 nm; curve 3: concurrent changes in solution pH; starting pH = 9.8, full light of mercury lamp, $T = 293$ K.

to overall reaction.

$$CrO_4^{2-} + 10H_2O + 3e \xrightarrow{h\nu} [Cr^{III}(H_2O)_6]^{3+} + 8OH^- \quad (11)$$

When pH and Cr(III) concentration reach appropriate levels, the photoreduction of Cr(III)–EDTA can again prevail and Cr(VI) formation rate surpasses that of its disappearance. The electron shuttle mechanism, is displayed in not buffered or only weakly buffered solutions containing Cr(III)–EDTA and 2,3-butanediol (Fig. 8); the effect could be easily observed because photoreduction of CrO_4^{2-} mediated by 2,3-butanediol can proceed even at pH ≈ 9.

The oscillatory photo-recovery of Cr(VI) and Cr(III) species entails continuous oxidation of 2,3-butanediol by both photoreductions (Eqs. (4) and (11)), thus the process illustrated in Fig. 8 consists in photocatalytic oxidation of the diol or other electron donor in the Cr(III)/Cr(VI) cycle. As oxidation of Cr(II) to Cr(VI) proceeds readily in the presence of O_2, the photocatalytic Cr(III)/Cr(VI) cycle leads consequently to oxidation of the organic substances, such as EDTA, by molecular oxygen.

When photoreduction of Cr(VI) (Eq. (11)) is preferred over that of Cr–EDTA (Eq. (4)), as in the case of 1,2-ethanediol and 1,2,3-propanetriol [39], the mechanism of photodegradation proceeds without any apparent oscillations, but the resultant conversion rate of $[Cr^{III}EDTA(OH)]^{2-}$ into CrO_4^{2-} is suppressed by presence of the electron donor (Table 1).

The photocatalytic oxidation of organic pollutants by O_2 with oscillatory recovery of the Cr(III) and Cr(VI) species can be additionally enhanced by photoreactivity of the organic pollutants. Beside the photogeneration of solvated electron, as, e.g. in the case of phenol, also other radical generation can assist the transformation. This is illustrated by increase in the Cr(VI) formation rate when $[Cr^{III}EDTA(OH)]^{2-}$ is irradiated together with methanal or acetone (Table 1). It means, that generation of the $H^\bullet + HCO^\bullet$ and $CH_3^\bullet + CH_3CO^\bullet$ radicals in photodissociation of methanal and acetone, respectively, enhances the Cr(III) photoreduction, followed by the thermal oxidation to Cr(VI).

3. Conclusions

The MLCT excitation of the Cr–EDTA complex leads to photoreduction to the Cr(II) species, which in the presence of molecular oxygen can be oxidized to Cr(VI). The process can be also induced by sunlight under environmental conditions, although with minor efficiency. Due to its high sensitivity to the medium components the actual efficiency could be, however, much higher. The Cr(III) → Cr(VI) conversion entails decrease in pH, what can switch on the opposite photoreduction Cr(VI) → Cr(III), which, in turn, is accompanied by the increase in pH and at its appropriate level the former process can be re-switched, etc. In this way the oscillatory photo-recovery of Cr(III) and Cr(VI) compounds results in continuous oxidation of the organic partner by molecular oxygen. The system can be taken as model for real wastewaters, where chromium compounds and reducing pollutants are frequently present together.

The detailed pathways may be different depending to the nature of the electron donors and especially their susceptibility to participate in the photoinduced electron transfer processes, sensitivity of their reactions into the pH changes and their photoreactivity under the sunlight.

These findings entail three important aspects:

(i) The photocatalytic oxidation of organic pollutants by O_2 with oscillatory recovery of the Cr(III) and Cr(VI) species can be useful to convert the environmental EDTA, and probably its analogues, to a more biodegradable form.

(ii) The cycle should be useful as well to the sunlight degradation of various environmental pollutants independently or in cooperation with other thermal or photochemical systems.

(iii) Due to possibility of photogeneration of toxic and/or mutagene Cr-forms, the use of Cr(III)–EDTA in medicine should be realized with great caution and with warning against the drug or patient insolation. This aspect needs urgently more investigations.

4. Experimental

4.1. Chemicals

$Na[CrEDTA(H_2O)]$ was prepared from chromium(III) nitrate and disodium salt of ethylenediaminetetraacetic acid according to the method previously reported [40]. Its purity was checked by UV-Vis spectroscopy. Other reagents of highest available purity were used as purchased. Solutions of all reagents were prepared using demineralized and triply distilled water. The Cr–EDTA concentrations used in experiments were 5–10 mM, in buffered solutions (pH 6–11), containing 0.04 M H_3PO_4, 0.04 M H_3BO_3, 0.04 M CH_3COOH and NaOH. All chromium solutions were stored in the dark to avoid out-of-control light-induced reactions. The additives, such as triethanolamine, methanol, ethanol, propan-2-ol, butan-2-ol, 1,2-ethanediol; 1,3-propanediol; 2,3-butanediol; 1,2,3-propanetriol, methanal, acetone or phenol, were added in concentrations between 5 mM and 1 M. Oxygenated and oxygen-free solutions were made by 30-min saturation of samples with oxygen and argon, respectively. Effect of temperature was measured within 283–323 K; most measurements were performed at 293 ± 0.1 K.

Cr(II)–EDTA species was obtained by the chemical reduction of $[CrEDTA(OH)]^{2-}$ at pH = 10 by zinc amalgam in deoxygenated system, following the procedure reported [41].

4.2. Instrumentation

UV-Vis spectra were recorded in thermostated (1 cm) or tandem (0.874 cm) quartz cells using a Shimadzu UVPC 2100 or a Hewlett-Packard HP 8453 spectrophotometer. Continuous irradiations were carried out using full light of a high-pressure mercury HBO-200 lamp or with a cut-off glass filter ($\lambda \geq 300$ nm). Solution pH was measured using a CX-741 (Elmetron) pH-meter with a glass electrode. Pulse photolysis within nano- to micro-seconds was performed using a LKS 60 Spectrometer (Applied Photophysics) equipped with Nd:YAG laser pump source Surlite I-10 (Continuum), operating in fourth harmonic (266 nm, max. 75 mJ pulses, 6 ns FWHM). Absorbance changes were monitored using a 150 W Xenon arc lamp supplied with a pulse unit, and a photomultiplier tube 1P28 or R928. Data were recorded on a digital storage oscilloscope HP 54522A with 0.5 ns time resolution and transferred to a computer for subsequent handling.

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