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Role of Iron and Chromium Complexes in Environmental Self-cleaning Processes

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Abstract: The present research includes solar-light-driven photocatalytic cycles based on the photoreductions of Fe(III), Cr(VI), and Cr(III) compounds with EDTA, oxalate and other ligands. Molecular oxygen is needed to close the photocatalytic cycles in which the metal species plays a role of photocatalyst; it affects the reaction mechanism and rate. The photoinduced electron transfer was also investigated in the presence of some external electron donors, such as EDTA, aliphatic alcohols, phenol, and its halogen derivatives, oxalate, nitrate(III), sulfate(IV). The results apply to the removal of such hazardous environmental pollutants as chromate(VI) or phenol derivatives and such recalcitrant pollutants as EDTA.

Keywords: Chromium(III) complexes, chromate(VI), EDTA, iron(III) complexes, phenol, photocatalysis, photoredox

INTRODUCTION

The role of transition metal complexes in the environment is as yet underestimated probably because of their low abundance in mobile forms. Due to their high spin states some metal centers in coordination compounds are, however, able to activate molecular oxygen leading in consequence to effective oxidation of organic compounds. The readiness of metal centers to increase or decrease their oxidation states, in reactions with the environmental electron acceptors and donors, respectively, is of crucial importance here. As

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the processes are reversible with reference to the metal ions, these play a role of catalysts and thus their effective concentrations can be really low.

The pollutant degradation in the redox reactions can be even more efficient when the complexes are in excited states of the ligand-to-metal-charge transfer (LMCT) character. Many transition metal chelates with such ligands as carboxylates, polyamines, aminopolycarboxylates, etc. absorb the sunlight which then is able to induce the photoredox processes. The condition is fulfilled only when the energy of the LMCT excited state is low enough to overlap the sunlight energy range.

The LMCT state may undergo reductive or oxidative quenching, accompanied by the photoinduced electron transfer. In consequence of the reductive quenching the central atom becomes reduced, and the ligand or external donor is oxidized via an inner-sphere or an outer-sphere mechanism, respectively. Oxidative quenching leads to ligand oxidation at the expense of molecular oxygen or other external acceptor, whereas the metal centre keeps in its original oxidation state, unchanged, modifying only its coordination sphere. Both processes lead to oxidation and thereby degradation of the organic pollutants, but in the former case it is driven by the photoreduction of the metal center, whereas the latter process consists of the electron donor oxidation by O_2 or other environmental acceptors, accompanied usually by some change in the coordination sphere of the complex. In an aerated medium the reduced central atom is re-oxygenated, resulting in nearly the same final effects of both mechanistic pathways; they differ only in the rate of the catalyst regeneration in the photocatalytic cycle.

There are several transition metal centers, such as Fe, Cu, Mn, Co, and Cr, which can drive the presented mechanisms; moreover their photocatalytic cycles can cooperate with each other (1). Iron is undoubtedly the most important of them, whereas chromium is unique, and its study is not only fascinating but also fruitful. These reasons induced us to investigate in detail the iron and chromium systems in aspect of interactions between the metal photocatalyst and possible environmental donors or acceptors. Moreover, we intended to get new information on the interplay between the systems differing the metal center: Fe(III) and Cr(VI) or Cr(III) and Cr(VI). Another goal was showing the pathway of efficient elimination of EDTA, whose practical application has recently got a chance to develop in remediation of soils contaminated by lead and other heavy metals (2).

EXPERIMENTAL

Materials

Na[Cr(edta)(H_2O)] was prepared from chromium(III) nitrate and disodium salt of ethylenediaminetetraacetic acid according to the method previously reported (3). All other reagents of highest available purity were used as purchased. Solutions of all reagents were freshly prepared using water triply distilled or demineralized by Millipore Milli Q Plus filter and stored in the dark to avoid out-of-control light-induced reactions. The following aqueous solutions were used for the most the experiments: 1×10^{-4} M $Na[Fe(edta)]\cdot 2H_2O$; 2 mM $K_3[Cr(ox)_3]$, 0.2–1.4 mM $KCrO_4$, 2–100 mM $Na_2C_2O_4$. If necessary pH was stabilized with Britton-Robinson buffer containing 0.04 M H_3PO_4, 0.04 M H_3BO_3, 0.04 M CH_3COOH, and KOH. In unbuffered solutions the pH was adjusted with H_2SO_4 and KOH. Oxygen-free and oxygenated solutions were made by at least 30 min saturation with argon or molecular oxygen, respectively. All measurements were performed at 293 ± 0.1 K.

Instrumentation and Procedures

Continuous irradiations were carried out using a low-pressure mercury lamp as a source of 254-nm radiation and a high-pressure mercury HBO-200 lamp equipped with interference or cut-off filter transmitting 365-nm or $\lambda \geq 300$ nm, respectively. UV-Vis spectra were recorded in thermostated 1 cm quartz cells using a Shimadzu UVPC 2100 or a Hewlett-Packard HP 8453 spectrophotometer. Changes in $[Fe^{III}(edta)H_2O]^-$ and $[Fe^{III}(edta)OH]^{2-}$ concentration complexes were monitored spectrally at 258 nm and 248 nm in alkaline and acidic solutions, respectively; concentration changes of CrO_4^{2-} and $[Cr^{III}(C_2O_4)_3]^{3-}$ were followed at 373 nm and at 570 nm, respectively. The measurements were repeated at least three times and their average values are included in tables. Rate constants (k_{obs}) were calculated using the first-order kinetic approximation.

PH values were measured using a CX-741 Elmetron pH-meter with a glass electrode. Pulse photolysis in the millisecond time scale was performed using a LKS 60 Spectrometer (Applied Photophysics) equipped with Nd-YAG laser pump source Surelite I-10 (Continuum), operating in fourth harmonic (266 nm, max. 75 mJ pulses, 6 ns FWHM). Data were recorded on a digital storage oscilloscope HP 54522A with 0.5 ns time resolution and transferred to a computer for subsequent handling.

Factor analysis of the irradiated solution spectra was performed using Target 96M software (MATLAB version) (4). This method is based on the algorithm of decomposition of the experimental spectroscopic information recorded as matrix into the concentration and molar absorbance matrices, which correspond to the Beer-Lambert's law as follows:

$$A(p \times q) = C(p \times n) \times E(n \times q),$$

where A is the experimental matrix, C is the concentration matrix and E is the matrix of molar absorption coefficients. Their sizes are indicated in parentheses, where n, p, and q are numbers of absorbing species, samples and wavelengths, respectively. The input matrix *A* was built from 12 experimental spectra obtained in individual experiments.

RESULTS AND DISCUSSION

Photocatalysis by the Fe(III)-EDTA Complexes

To demonstrate the role of iron complexes in the environmental self-cleaning processes the $[Fe^{III}(edta)H_2O]^-$ and $[Fe^{III}(edta)OH]^{2-}$ complexes were chosen, because their photochemical reactions belong to the most efficient methods of the EDTA pollution abatement (5–8).

The most important features of the Fe^{III}-EDTA systems in the environment may be summarized as follows:

(i) at the environmental pH values two main forms are present, i.e. $[Fe^{III}(edta)(H_2O)]^-$ ($\lambda_{max} = 258$ nm, $\varepsilon_{max} = 8530\ M^{-1}cm^{-1}$) and $[Fe^{III}(edta)(OH)]^{2-}$ ($\lambda_{max} = 248$ nm, $\varepsilon_{max} = 8170\ M^{-1}cm^{-1}$);
(ii) their excited states have the ligand-to-metal-charge-transfer- (LMCT) characters, which can induce the photoredox behavior;
(iii) the actinic flux at the ground level overlaps both absorption bands sufficiently to drive the photochemical reaction of the complexes with a moderate quantum yield.

The photochemical reaction was studied repeatedly and the effects of pH, light energy, and the presence of molecular oxygen were analyzed (7, 9–13).

In this study the effects of different environmental electron donors, and electron acceptors were investigated. First we compared the absorption changes induced by the 266-nm laser pulse in an aerated and a deaerated atmosphere (Fig. 1). The behavior can be interpreted as follows:

(i) Immediate decrease of absorption in the region characteristic of the Fe(III) complexes recorded directly after the laser pulse (at nanosecond time scale) is not affected by the O_2 presence and is ascribed to the LMCT excitation:

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

(ii) In deoxygenated media at times up to ~ 100 ms upon flash small but detectable post-irradiation Fe-substrate decay is recorded which is ascribed to the self-quenching, yielding a dimeric intermediate:

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

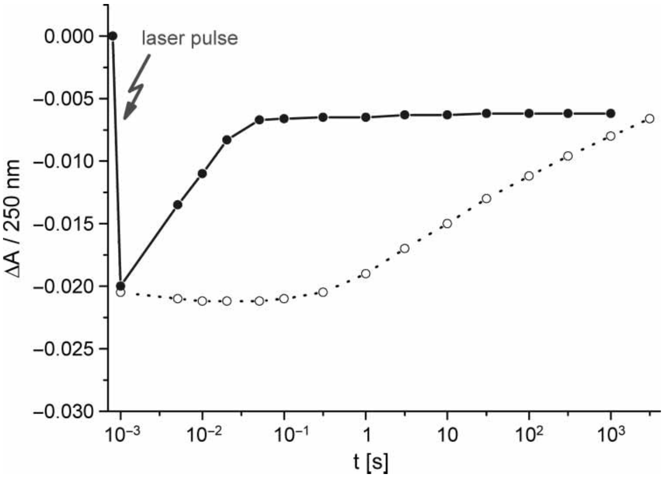

Figure 1. Post-irradiation absorption changes monitored at 250 nm in oxygenated (solid line) and deoxygenated (dotted line) solution of $[Fe^{III}(edta)(H_2O)]^-$ excited by a 266-nm laser pulse ($c_0 = 1.10^{-4}$ M, pH = 4).

The intermediate is characterized by a transient (millisecond life-time) absorption at ~ 430 nm (curve 2 in Fig. 2). At longer times (minutes) a slow substrate regeneration is observed. This proceeds probably via the back electron transfer within the dimeric intermediate, yielding the Fe^{III}-O-Fe^{III} dimer,

$$\begin{aligned}&[(H_2O)(edta^\bullet)Fe^{II}(\mu\text{-}OH_x)Fe^{III}(edta)]^{x-4} + xH_2O \longrightarrow \\ &\quad [(edta)Fe^{III}(\mu\text{-}O)Fe^{III}(edta)]^{4-} + xH_3O^+\end{aligned} \tag{3}$$

which in diluted and/or acidic medium reproduces the substrate (13–19):

$$\begin{aligned}&[(edta)Fe(\mu\text{-}O)Fe(edta)]^{4-} + 2H_3O^+ \longleftrightarrow \\ &\quad 2[Fe^{III}(edta)(H_2O)]^- + H_2O\end{aligned} \tag{4}$$

The substrate regeneration competes with the electron transfer from the $edta^\bullet$ radical to the Fe^{III} center, leading to Fe^{III} reduction and EDTA oxidation (curve 3 in Fig. 2):

$$\begin{aligned}&[(H_2O)(edta^\bullet)Fe^{II}(\mu\text{-}OH_x)Fe^{III}(edta)]^{x-4} \longrightarrow \\ &[Fe^{II}(edta)(H_2O)]^{2-} + Fe^{II}_{aq} + ED3A + CO_2 + HCHO\end{aligned} \tag{5}$$

where ED3A = ethylenediaminetriacetic acid.

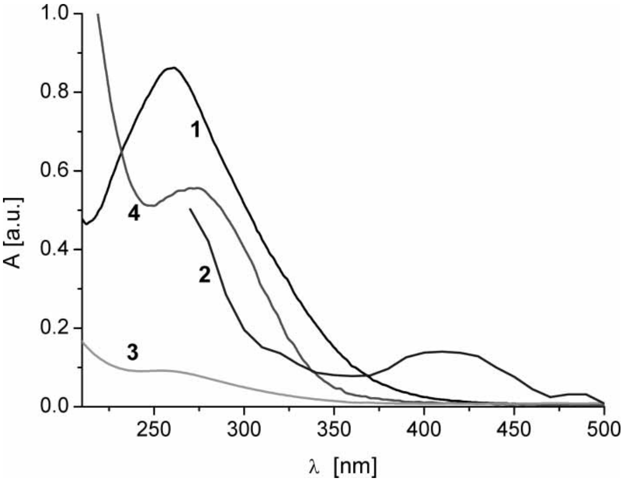

Figure 2. Absorption spectra of the $[Fe^{III}(edta)(H_2O)]^-$ complex (curve 1) and its photoproducts: the millisecond $[(H_2O)(edta^{\bullet})Fe^{II}(\mu\text{-}OH_x)Fe^{III}(edta)]^{x-4}$ intermediate (curve 2) and stable Fe^{II}_{aq} products (curve 3) and $[Fe^{III}(ed3a)]$ (curve 4). The intermediate spectrum (curve 2) is differential spectrum measured within 100 ms upon 266-nm pulse; stable products spectra (curves 3 and 4) were calculated by factor analysis of the spectra of continuously irradiated solutions.

(iii) In oxygenated solutions a fast (within 100 ms) increase in absorption implies the quick recovery of the Fe^{III} complex. The detailed analysis of its spectrum shows, however, that the Fe^{III} product is distinct from the Fe^{III} substrate (curve 4 in Fig. 2). The stable product was formulated as the Fe^{III} complex with ED3A, $[Fe^{III}(ed3a)]$.

(iv) The mechanism shown here for the $[Fe^{III}(edta)(H_2O)]^-$ complex is valid as well for its deprotonated form, $[Fe^{III}(edta)OH]^{2-}$, only the reaction rates are somewhat different.

The external electron donors and electron acceptors have moderate, but specified effect: the electron donors decrease the Fe^{III} substrate consumption, whereas electron acceptors generate $[Fe^{III}(ed3a)]$, instead of the Fe^{II} product (Table 1). The former effect is interpreted in terms of competition between substrate (Eq. 2) and external electron donor in quenching of the excited state:

$$^*[Fe^{II}(edta^{\bullet})(H_2O)]^- + D \longrightarrow [Fe^{II}(edta)(H_2O)]^{2-} + D^+ \qquad (6)$$

It means, moreover, that photoreduction of the Fe^{III}-EDTA complexes can lead to oxidation not only of EDTA, but also of other electron donors available, such as alcohols, sulfate(IV), nitrate(III) etc.

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

	Electron acceptor			
Electron donor	Without any	O_2 (Saturated solution)	CrO_4^{2-} 1×10^{-4} M	$O_2 + CrO_4^{2-}$
Without any	5.33 ± 0.31 (pH 4) 2.95 ± 0.67 (pH 9)	1.42 ± 0.05 (pH 4) 0.69 ± 0.07 (pH 9)	0.51 ± 0.07 (pH 9)	1.12 ± 0.16 (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)		
Alcohol[a], $c = 2 \times 10^{-2}$ M	2.63 ± 0.22 (pH 4)	0.63 ± 0.03 (pH 4)		
EDTA, pH 4		≥ 0.01		
$c_0 = 1 \times 10^{-4}$ M	5.03 ± 0.57	≥ 0.01		
$c_0 = 2 \times 10^{-4}$ M	4.78 ± 0.66	≥ 0.01		
$c_0 = 5 \times 10^{-4}$ M	4.62 ± 0.85	≥ 0.01		

[a] alcohol = methanol, propan-2-ol, butan-2-ol.

The $^*[Fe^{II}edta^\bullet(H_2O)]^-$ excited state can undergo as well the oxidative quenching by the electron acceptor such as molecular oxygen:

$$^*[Fe^{II}(edta^\bullet)(H_2O)]^- + O_2 \longrightarrow [Fe^{III}(ed3a)] + O_2^{2-} + CO_2 + HCHO \tag{7}$$

The oxidative quenching results in some change of coordination sphere of Fe^{III} complex, which plays a role of the photocatalyst of the EDTA oxidation by molecular oxygen. O_2 is really the most frequent environmental oxidant, but a recent study (20) has shown that also another two-electron acceptor, like chromate(VI) is able to drive oxidative quenching of the $^*[Fe^{II}edta^\bullet(H_2O)]^-$:

$$^*[Fe^{II}(edta^\bullet)(H_2O)]^- + CrO_4^{2-} \longrightarrow [Fe^{III}(ed3a)] + Cr_{aq}^{IV} + CO_2 + HCHO \tag{8}$$

The Fe-photocatalytic cycle can thus be driven not only by molecular oxygen but also by other electron acceptors, such as chromate(VI). The participation of

Cr(VI) in the photocatalytic cycle not only increases the efficiency of EDTA oxidation but also abates the toxic hazard due to reduction of Cr(VI) to Cr(III).

Photocatalysis by the Cr(VI) and Cr(III) Compounds

Chromium is much less abundant than iron, and the transition between their two main oxidation states involves three electron transfer and the species are completely different: cationic Cr^{III} is mostly immobile and benign, whereas anionic CrO_4^{2-} and $HCrO_4^-$ are mobile and highly toxic. Under environmental conditions both Cr(VI) forms undergo photochemical reactions and induce oxidation of accessible electron donors (21, 22). Also recently some Cr^{III} complexes able to contribute to the environmental photoredox processes were reported (9, 23).

Photoreduction of Chromate(VI)

Under environmental conditions (low Cr^{VI} concentration at pH 4 – 9) two forms of the chromate(VI) anion should be taken into account: CrO_4^{2-} ($\lambda_{max} = 275$ nm, $\varepsilon_{max} = 3600$ $M^{-1}cm^{-1}$ and $\lambda_{max} = 373$ nm, $\varepsilon_{max} = 4800$ $M^{-1}cm^{-1}$) (24) and $HCrO_4^-$ ($\lambda_{max} = 260$ nm ε_{max} ~2600 $M^{-1}cm^{-1}$ and $\lambda_{max} = 350$ nm ε_{max} ~1600 $M^{-1}cm^{-1}$) (25). Both forms absorb the sunlight but their excited states completely reproduce the ground states without any photochemical reaction unless an electron donor (D) is in contact with chromate(VI). Then the photoinduced electron transfer is observed, which yields oxidized D and reduced chromate, e.g.:

$$^*\{HCrO_4^-\} + D \longrightarrow HCr^VO_4^{2-} + D^+ \qquad (9)$$

If the contact between chromate(VI) and an electron donor is tight enough to form a chemical bond, as in esters, the inner-sphere two-electron transfer can be observed; when the interaction is weaker, the outer-sphere one-electron transfer is recorded. For the secondary alcohols the photoinduced electron transfers were reported (21):

$$^*\{R_1R_2CHOCrO_3^-\} + 5H^+ + 3H_2O \longrightarrow R_1R_2CO + [Cr(H_2O)_6]^{4+} \qquad (10)$$

$$^*\{(HCrO_4^-)_{alc}\} + R_1R_2CHOH \longrightarrow H_2Cr^VO_4^- + R_1R_2CHO^\bullet \qquad (11)$$

The reactions are followed by conversions of the Cr^{IV}.aq and Cr^V species into more stable Cr^{III} and Cr^{VI} products via disproportionation reactions, e.g.

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

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

yielding Cr(III) and reproducing some amount of chromate(VI) (21, 26–28).

As a result of the photoinduced electron transfer the environmental chromium(VI) undergoes reduction to Cr(III), whereas the available electron donors are oxidized. As yet, a number or electron donors were reported to be oxidized during the Cr(VI) photoreduction, such as: aliphatic alcohols, oxalate, citrate, salicylate, dissolved organic matter (DOM), benzene derivatives (aniline, benzaldehyde, benzoic acid, benzonitrile, nitrobenzene, phenol and its halogen derivatives) etc.; some of these processes are assisted by semiconductors, such as TiO_2, ZnO, CdS, WO_3 (8, 29). In the environment the Cr(VI) photoreduction follows the day and night sequences, which are illustrated in Fig. 3.

Redox Photochemistry of Cr(III)

The sparingly soluble hydroxo-compounds are expected to be dominant Cr^{III} species in the environment. Cr^{III} has however a strong tendency to bind oxygen-containing functional groups and form complexes with organic ligands, such as oxalate, citrate, malonate, EDTA, and DTPA, which are soluble and stable within the environmental pH range. The Cr^{III} coordination compounds are well known from their photochemical reactivity, which was studied repeatedly. The main mode of the Cr^{III} photochemistry consists in photosubstitution or related reactions. Photoredox behavior was found only in a few cases as following the LMCT excitation of the complexes containing ligands relatively susceptible to oxidation (9, 30–34).

The recent studies (9, 23) showed that LMCT excited states in the Cr^{III} complexes decay not only via back electron transfer, but also through redox pathways: in deoxygenated systems photoinduced electron transfer yields Cr^{II} species and oxidized ligand, whereas molecular oxygen quenches the excited state, oxidizing both the chromium centre and the ligand (Fig. 4).

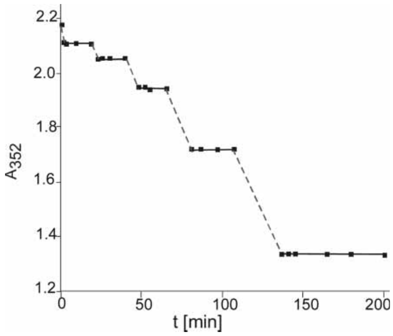

Figure 3. Irradiation (dashed lines) and post-irradiation (squares) changes in absorption characteristic of the $HCrO_4^-$ ion (352 nm) in the solution containing initially: 7.10^{-4} M K_2CrO_4 and 0.07 M butan-2-ol (pH = 4.0, $\lambda_{irr} \geq 300$ nm, T = 293 K).

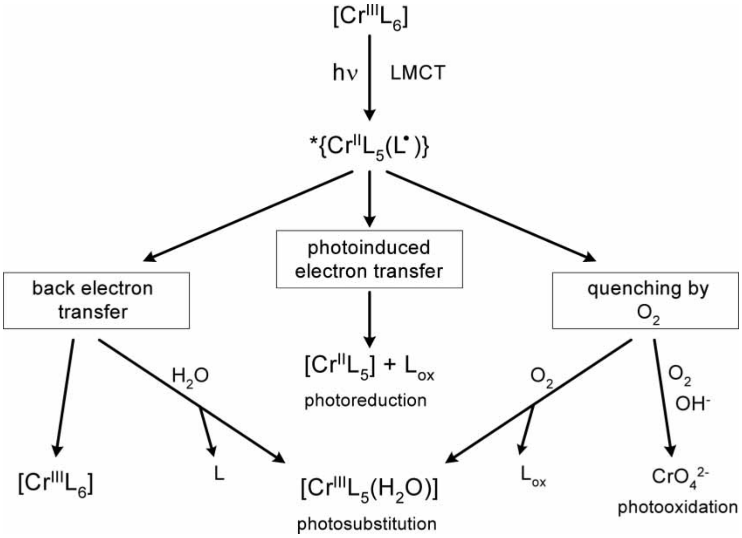

Figure 4. Reactive decay of the LMCT excited states of Cr^{III} complexes.

The major oxidation product is then substituted Cr^{III} complex, but in an alkaline medium and at a large excess of O_2 over the Cr(II) concentration, the oxidation proceeds up to CrO_4^{2-} (35).

The net photoconversion of Cr^{III} to Cr^{VI} is essential for the environmental processes. Its efficiency depends strongly on the presence, nature and concentration of electron donors, concentration of oxygen and hydroxide ions (8, 23). The former condition is connected with production of the Cr^{II} species, whereas the latter-with oxidation of Cr^{II} by O_2 to Cr^{VI}. The effect of the electron donor is illustrated in Fig. 5, which shows that the absorption characteristic of solvated electrons (~500 nm), generated in photochemical reaction of phenolate:

$$C_6H_5OH + H_2O \xrightarrow{hv} C_6H_5O^{\bullet} + H_3O^+ + e^-_{solv}. \qquad (14)$$

decays due to e^-_{solv} are scavenging by $[Cr(edta)(OH)]^{2-}$, which yields a Cr^{II} species. In consequence of enlarged Cr^{II} concentration, the chromate(VI) production in subsequent reactions with O_2 is crucially intensified (Table 2).

A number of electron donors were investigated; such as triethanolamine, alcohols (methanol, ethanol, propan-2-ol, butan-2-ol), diols (ethane-1,2-diol, propane-1,3-diol, butane-2,3-diol), propane-1,2,3-triol, aldehydes (methanal), ketones (acetone), phenol, and its derivatives. The typical behavior of these additives is the acceleration of the Cr(VI) production at least during the initial irradiation time and a moderate concentration of the additive; phenol, triethanolamine, and butane-2,3-diol belong to the most efficient (Table 2).

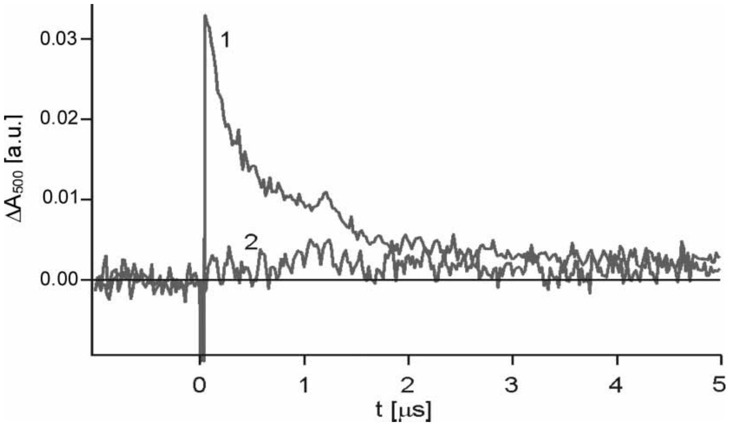

Figure 5. Kinetic traces recorded at 500 nm for 8.5 mM phenol (curve 1) and for the phenol solution containing additionally 8.5 mM $[Cr(edta)(OH)]^{2-}$ (curve 2) upon a 266-nm laser pulse; pH = 10, $\Delta A = A_t - A_0$.

Enlarged concentrations of the electron donors do not increase, however, the Cr^{VI} production and even in some cases the decreased Cr^{VI} yield is observed (e.g. for triethanolamine). Moreover, upon longer irradiations, i.e. when Cr^{VI} concentration becomes high enough to compete with Cr^{III} in the light absorption, photoinduced electron transfer between $^*\{Cr^{VI}\}$ and electron donor (Eq. 8) switches the reaction towards formation of the Cr^{III} (Fig. 6 a).

Photocatalytic Chromium Cycle

The possible switches between production and consumption of Cr^{VI} are illustrated in Fig. 6 b, which mimics the changes of the Cr-speciation occurring in

Table 2. Effect of electron donors on initial rates of the Cr(III) → Cr(VI) photoconversion calculated using the first-order kinetic approximation ($k_{obs} \times 10^6$ [s^{-1}]); experimental conditions: continuous irradiation of oxygenated 5×10^{-3} M $[Cr^{III}(edta)(OH)]^{2-}$ solutions using full light of mercury lamp, pH = 10, T = 293 K

	Electron donor		
	$k_{obs} \times 10^6$ [s^{-1}])		
Without any	Phenol	Butane-2,3-diol	Triethanolamine
2.52 ± 0.02	95.20 ± 0.06 (5 mM) 92.52 ± 0.05 (0.05 M) 97.34 ± 0.07 (0.125 M) 109.96 ± 0.07 (0.25 M)	7.16 ± 0.07 (0.125 M) 12.16 ± 0.04 (0.25 M) 12.77 ± 0.03 (0.50 M)	9.56 ± 0,07 (0.05 M) 11.92 ± 0.06 (0.125 M) 10.11 ± 0.07 (0.25 M) 8.87 ± 0.07 (0.50 M) 4.61 ± 0.05 (1 M)

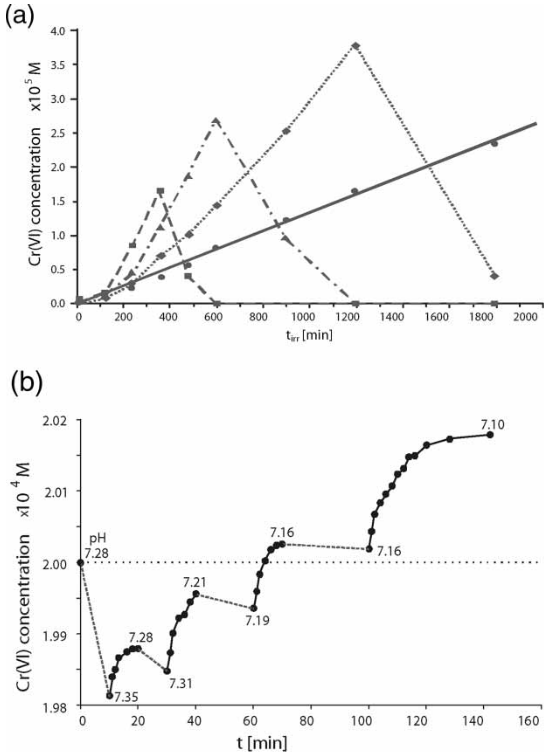

Figure 6. Cr(VI) production during (a) continuous irradiation of 5 mM $[Cr(edta)(OH)]^{2-}$ at pH = 10, containing butane-2,3-diol: 0 (circles), 0.125 M (diamonds), 0.25 M (triangles), 0.50 M (squares); (b) irradiation (dashed lines) and dark periods (circles) recorded for 2.10^{-3} M $K_3[Cr^{III}(C_2O_4)_3]$ and 2.10^{-4} M K_2CrO_4 in unbuffered solution (actual pH values are shown in the figure); oxygenated solutions were irradiated by full light from high-pressure mercury lamp, T = 293 K.

nature within the day and night periods. When the Cr^{VI} and Cr^{III} compounds are irradiated in a nearly neutral medium, both forms are excited and both excited states undergo reductive quenching by the available electron donors (Eq. 9 and Fig. 4) oxidizing them and yielding Cr^{V} or Cr^{IV} and Cr^{II}, respectively. The post-irradiation processes (Eqs. 12, 13 and Fig. 4) convert Cr^{VI} to Cr^{III} and vice versa. Although the two reactions need somewhat different conditions to proceed efficiently (such as pH and O_2 concentration), the results of this work demonstrate that they are able to co-operate and form a cycle functioning in aerated media at nearly neutral pH, i.e. under conditions common for natural waters (Fig. 7).

As each chromium photoconversion results in oxidation of the electron donor available in the vicinity, whereas each Cr form can be regenerated

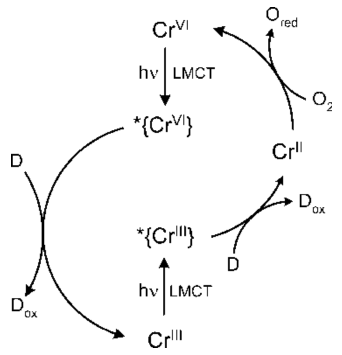

Figure 7. Model of chromium photocatalytic cycle of the environmental relevance.

under environmental conditions the photocatalytic Cr-cycle is important part of the environmental self-cleaning.

CONCLUSIONS

Results of this paper lead to the conclusion that in the nearly neutral sunlit media, which are quite ordinary for natural waters, various sophisticated photochemical processes can be observed, in which dissolved organic matter plays a role of sacrificial electron donor, whereas the atmospheric molecular oxygen is the main, although not unique, sacrificial electron acceptor. The DOM degradation proceeds in the photocatalytic cycles, in which transition metal complexes play a role of photocatalysts. The study is focused on iron and chromium compounds, but the phenomenon applies also to other transition metals provided that they are naturally occurring on at least two oxidation states, which undergo interconversion by the sunlight-driven photoreduction and oxidation by the atmospheric O_2.

A variety of chemical compositions make possible interactions between different environmental systems, which can result in enhancement of the pollution removal, or in the consequences that may be surprisingly different. In this paper two possible environmental interactions studied in detail showed the diverse effects:

(i) Cooperation of the Fe^{III}-EDTA with chromate(VI) leads both to increased EDTA photodegradation and chromate(VI) removal.

(ii) Photooxidation of phenol in the presence of Cr^{III}/Cr^{VI} is more effective, than photooxidation of neat phenol, because hydrated electrons photogenerated in reaction (14) are scavenged and back electron transfer is hindered; however, the photoconversion of Cr^{III} to Cr^{VI} becomes more efficient in the presence of phenol, than in the neat Cr^{III}/Cr^{VI} mixtures, because hydrated electrons enhance the Cr^{II} generation. The former interaction results thus in more friendly environmental conditions, whereas the latter accelerates the self-cleaning from organic pollutants but, unfortunately, at the same time increases the Cr(VI)-hazard.

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