



## Review

# Homogeneous photocatalysis by transition metal complexes in the environment

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**Abstract**

The role of transition metal complexes is overviewed for the iron, copper and chromium compounds, for which photoreactivity is of crucial environmental importance. Attention is paid to these complex systems, in which metal centres are photoreduced by organic matter under solar irradiation and re-oxidized by molecular oxygen, i.e. to the systems, that play a part in the environmental photocatalysis. The photoreduction is accompanied by simultaneous oxidation of organic matter, which plays a role of ligand and/or sacrificial electron donor. Under favourable conditions a complete photodegradation of the organic pollutants can be achieved. The general mechanisms are analysed and examples of different photocatalytic behaviours are presented in some details. The systems are more sophisticated due to concurrent generation of active oxygen species, such as the  $O_2^{\bullet-}$ ,  $HO_2^{\bullet}$ ,  $OH^{\bullet}$ ,  $H_2O_2$ , and  $HO_2^-$ , which are involved in the redox reactions of the photocatalytic cycling and influence the pollutant degradation.

Beside the monometallic cycles, the mixed metal systems can function in nature. The cooperation between the photocatalytic cycles of two metals can abate diverse environmental pollutants, but their efficiency can be either higher or lower in comparison with that of the sum of single cycles.

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**Keywords:** Environmental homogeneous photocatalysis; Photoreduction of metal complexes; Photodegradation of organic pollutants; Photocatalytic cycles of iron, copper and chromium

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## 1. Introduction

The growing interest in the development of new methodologies for the degradation of toxic water pollutants has led to conclusion that the most effective oxidation of organic pollutants can be achieved when a powerful oxidizing agent, especially  $\text{OH}^\bullet$  or another radical, is generated. The advanced oxidation processes (AOP) have been developed, such as photochemical degradation reactions using photodecomposition of hydrogen peroxide ( $\text{H}_2\text{O}_2/\text{UV}$ ), ozone photolysis ( $\text{O}_3/\text{UV}$ ), photocatalysis by semiconductors ( $\text{TiO}_2/\text{UV}$ ) [1,2] and photoredox reactions of transition metal complexes. The latter scope is also of crucial relevance to the environmental metal cycling and self-cleaning processes. Furthermore, the presence of such complexes and their environmentally benign catalytic activity is more desirable than applying other, “non-green” AOP processes.

Transition metal complexes play a special role in the environmental processes. Their easiness in change of the oxidation state makes the transition metal ions responsible for most redox processes occurring in nature directly or via a catalytic mechanism. Due to presence of unpaired electrons the metal ions react readily with molecular oxygen, mediating thereby oxygenation of other compounds, especially those constituting the natural organic matter.

Transition metal ions are able to coordinate most of the organic substances from natural or anthropogenic sources, producing complexes of diversified stability, solubility and volatility. The properties are substantial for transport of the transition metals between the environmental compartments, as well as for the chemical, biological, photochemical and photobiological degradation of the organic ligands.

The chemically inert complexes of metal ions in their higher oxidation state, as Fe(III) and Cu(II), undergo readily photoreduction to Fe(II) and Cu(I), respectively, which is accompanied by oxidation of the organic ligand, or other sacrificial donor. Thus, the environmental photochemistry of the

transition metal complexes with organic ligands is of crucial importance for the pollution abatement because it may cause the photodegradation of especially persistent pollutants, such as phenol and its derivatives or EDTA and related aminopolycarboxylic acids [3–8].

The photochemical reaction of the coordination compounds can lead efficiently to degradation of an organic pollutant in the environment only when their CT excited states are low enough to be included within the sunlight energy range (i.e. its energy should be lower than  $\sim 34,000\text{ cm}^{-1}$ ). The reactive decay of the LMCT state via the photoinduced electron transfer (PET) is realised either by inner- or outer-sphere mechanism (Fig. 1). In the first case, the ligand radical ( $\text{L}^{\bullet+}$ ) is produced, which is the precursor of the ligand oxidized form, whereas the coordinatively unsaturated  $[\text{M}^n\text{L}_{n-1}]$  complex regenerates the parent  $[\text{M}^{n+1}\text{L}_n]$  compound in reaction with another ligand molecule and molecular oxygen (Fig. 1a). In the outer-sphere mechanism (Fig. 1b) the  $[\text{M}^{n+1}\text{L}_n]$  to  $[\text{M}^n\text{L}_n]$  reduction is realised in reaction of  $^{\text{LMCT}}\{\text{M}^{n+1}\text{L}_n\}^*$  with an electron donor (D). In the reaction  $[\text{M}^n\text{L}_n]$  complex is produced, which has the same coordination sphere, as the parent  $[\text{M}^{n+1}\text{L}_n]$ , which is next easily regenerated mainly in reaction with  $\text{O}_2$ .

In consequence of the LMCT excitation, the central metal ion undergoes reduction, whereas ligand or a sacrificial donor is a subject of oxidation. Both inner- and outer-sphere photoinduced electron transfers lead thus to the metal ion reduction and oxidation of the organic compound present in the medium.

The energy of the sunlight spectrum is high enough to overlap the LMCT band only when the transition metal complex consists of both easy oxidizable ligand(s) and fairly reducible central ion. The former condition is easily met in the environment, whereas among the environmental metals the best predispositions to such behaviour are demonstrated by the Fe(III) species. It is not only prone to undergo photoreduction to Fe(II), but it is also the most abundant transition metal in the Earth's crust. The fairly good candidates to undergo the LMCT photochemistry in the environment are also

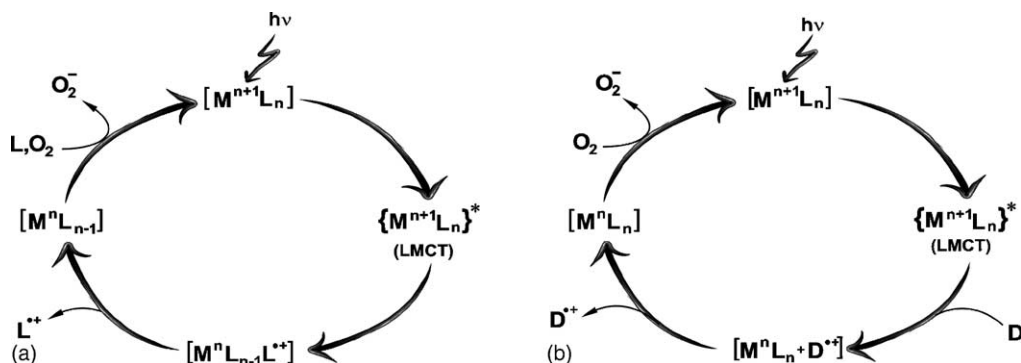


Fig. 1. Two alternative pathways of the photocatalytic cycles initiated by the reactive decay of transition metal complexes in their LMCT excited states: (a) inner-sphere electron transfer, (b) outer-sphere electron transfer;  $M^n$ ,  $M^{n+1}$  are the metal ions in their lower and higher oxidation state, respectively; D – electron donor, L – ligand.

complexes of copper, chromium and manganese with central atoms in their higher oxidation states. Their abundance in natural waters, wastewaters and soils is also relatively high.

The relevance of the metal ion to the pollution abatement consists also in the easy regeneration of its original higher oxidation state in reaction with the ambient molecular oxygen, enabling thus the existence of the closed photocatalytic cycles. In such a cycle the organic substance plays a role of a sacrificial electron donor and undergoes degradation, leading favourably to complete mineralization. The central metal ion is photoreduced and re-oxidized by molecular oxygen to its initial oxidation state, playing thus a role of photocatalyst. The radicals and oxygen active species co-produced in the cycles enhance the redox processes, which can be also co-catalysed by other metals or by semiconductors that create often quite complicated systems.

The photoredox and photocatalytic systems are responsible for oxidation of dissolved organic matter by means of the atmospheric oxygen and solar light and thus play a crucial role in photodegradation of pollutants, and thereby in the environmental self-cleaning mechanisms.

## 2. Photocatalysis by the Fe(III)/Fe(II) complexes

### 2.1. Environmental iron

Iron is the fourth most abundant element in the Earth's crust, and accordingly is the most abundant transition metal in soil. In the seawater, however, it is present only at nanomolar concentrations due to low solubility of most of the Fe(III) species, which are thermodynamically stable forms in the oxygenated waters. Their solubility, and thereby, their biological availability, is influenced by chelation with organic ligands, hydrolysis of dissolved iron species, biological or photochemical reduction of the Fe(III) chelates and re-oxidation of Fe(II). Consequently, only a small fraction of dissolved Fe(III) occurs in hydrated forms or is complexed by other inorganic ligands, whereas a vast

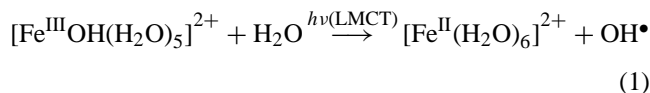
majority (80–99%) is bound by organic ligands [9,10]. Nevertheless, dissolved iron compounds are probably the most important of the transition metal species, because they are present in concentrations at least an order of magnitude higher than those of other metals and they react rapidly with many oxidants and reducers in atmospheric waters [11].

### 2.2. Mechanisms of Fe(III) photoreduction

The photoreduction that occurs with the Fe(III) compounds, giving rise to the Fe(II) species, plays an important role in the geochemical cycles and strongly affects the chemical and biological processes, which are sensitive to the iron speciation. This is illustrated in Fig. 2, where thermal and photochemical behaviours of the iron species in seawater in contact with different environmental compartments are outlined.

The nature of the Fe(III) species, which are able to undergo photochemical reaction in sunlit surface waters, is of special relevance. Generally, the environmental Fe(III) compounds are classified into two groups, the hydroxo species and chelate complexes, depending on the nature of their ligand oxidation products. These are  $\text{OH}^\bullet$  or  $\text{L}_{\text{ox}}^\bullet$  radicals, respectively [12].

The main interest is focused on the photochemical behaviour of the Fe(III) complexes, which are ligated solely by the aqua and/or hydroxo ligands. The  $[\text{Fe}^{\text{III}}(\text{H}_2\text{O})_6]^{3+}$  complex prevails only at  $\text{pH} < 2$ , whereas at higher pH values it is transformed into the aqua-hydroxo compounds. The  $[\text{Fe}^{\text{III}}\text{OH}(\text{H}_2\text{O})_5]^{2+}$  complex, the predominant species at  $\text{pH} \sim 3$ , is capable to undergo the LMCT excitation ( $\lambda_{\text{max}} \sim 300 \text{ nm}$ ,  $\epsilon_{\text{max}} \sim 2 \times 10^3$ ) by the sunlight irradiation [13]. The excitation (Fig. 3a) is followed by the inner-sphere photoinduced electron transfer producing Fe(II) aqua complex and the  $\text{OH}^\bullet$  radical [13,14].



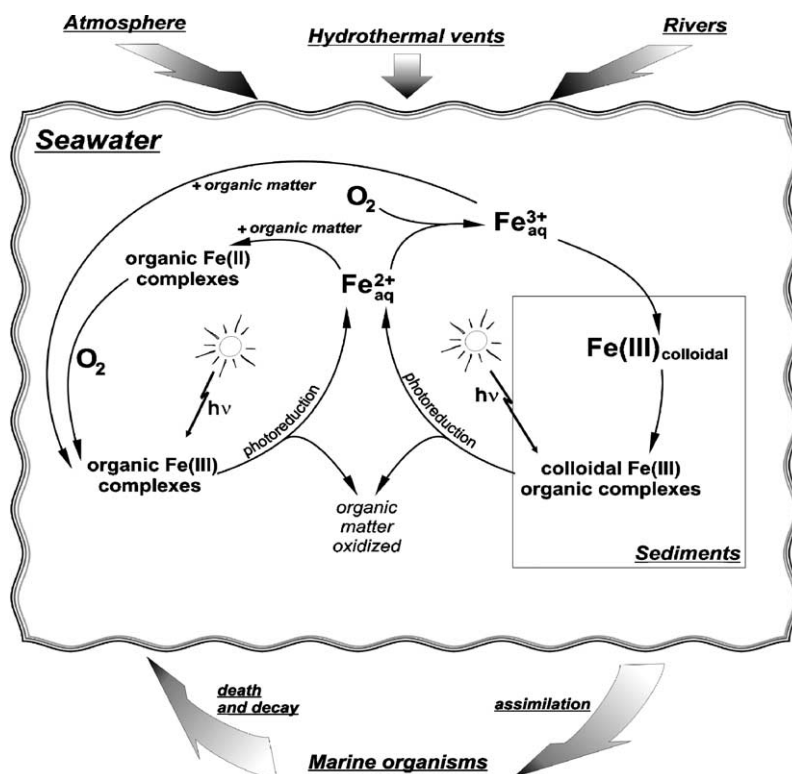


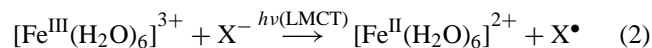
Fig. 2. Conceptual model of iron speciation and photo-cycling in seawaters. Adapted from [9].

Similar effect is demonstrated also by other Fe(III)-OH species, such as different hydroxo-complexes, oxides and hydroxides even in the colloidal or solid form [15,16].

The  $\text{OH}^\bullet$  radicals, belonging to the most powerful oxidizing agents, would be thus responsible for the fast oxidation of the diverse accessible organic matter, what is illustrated in Fig. 3a. The higher efficiency of the pollutant degradation is obtained when  $\text{H}_2\text{O}_2$  is added to the UV-irradiated Fe(II)/Fe(III) solution (photo Fenton reagent), which provides an increased production of  $\text{OH}^\bullet$  radicals and faster Fe(II)/Fe(III) interconversion [17].

The oxidizable ions or molecules present in the vicinity, were also reported to undergo oxidation, as a result of the

outer-sphere PET between the excited Fe(III) aqua-complex and the ions:



( $\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{NCS}^-$ ), which yields the relevant, other than  $\text{OH}^\bullet$ , radicals [18].

Still another behaviour is demonstrated by the Fe(III) centres ligated by chelating ligands, mostly those stemmed from carboxylic and aminopolycarboxylic acids (Fig. 3b). Photo-reduction of the Fe(III) chelate can be induced by sunlight only when the ligand is of an electron donor character. The excitation into the LMCT state can be then followed by the inner-sphere photoinduced electron transfer, leading to re-

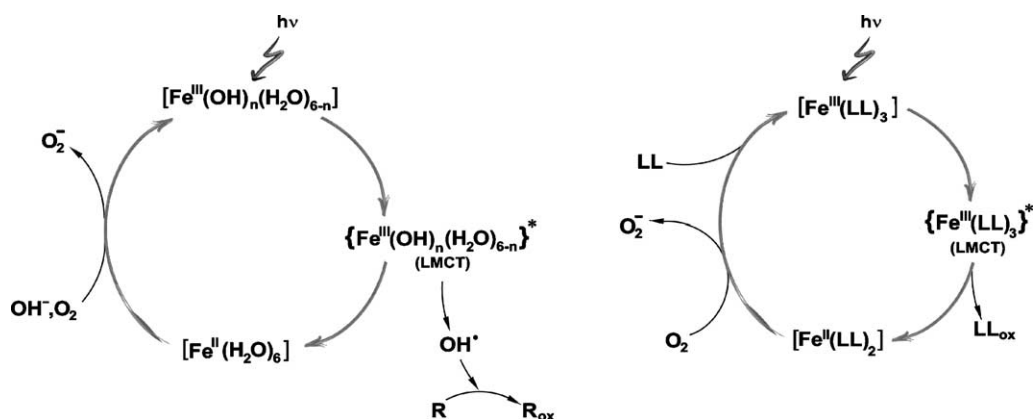
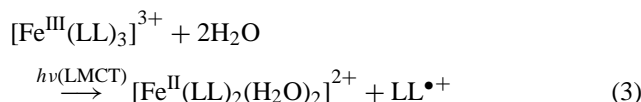
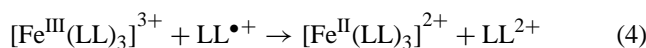


Fig. 3. Inner-sphere electron transfer in excited Fe(III) compounds: (a) aqua-hydroxo species, (b) complexes with chelating ligands; R – accessible organic matter,  $\text{R}_{\text{ox}}$  – oxidized organic matter, LL – bidentate ligand able to coordinate to Fe(III),  $\text{LL}_{\text{ox}}$  – LL oxidized.

duction of Fe(III) to Fe(II) and one-electron oxidation of the chelating ligand (LL), e.g.



The ligand radical generated in the photoredox process (3) needs, in general, the second electron transfer to reach its stable oxidation state. This can be realised in reaction with the parent Fe(III) complex:



with the ambient molecular oxygen:



or with another oxidant present in the medium, e.g. Cu(II) [18]. The reaction of the  $\text{LL}^{\bullet+}$  radicals with Fe(III) (4) increases the Fe(II) yield, decreasing at the same time the photodegradation efficiency. On the other hand, the reaction with oxygen produces  $\text{O}_2^{\bullet-}$  radicals, which readily take part in further redox processes enhancing the photodegradation [19]. The final result of the photochemical and secondary thermal processes (3)–(5) of the Fe(III) chelate compounds is reduction of Fe(III) to Fe(II) and oxidation of the chelating ligand. Both pathways of the Fe(III) photoredox processes (Fig. 3a and b) yield the Fe(II) species and lead to photodegradation of various organic pollutants. The Fe(III) photoreduction can be, however, decelerated by competitive thermal reductions with other electron donors, which in some cases, e.g. for the sulfur(IV) compounds, can proceed effectively [20–22].

The pollutant oxidation in the iron cycle proceeds thus either indirectly in thermal reaction of the photogenerated  $\text{OH}^{\bullet}$  (or other) radicals (Fig. 3a) or directly in photochemical reaction of the coordinated ligand molecule in the primary photochemical reaction (Fig. 3b).

### 2.3. Thermal oxidation of Fe(II) to Fe(III)

Under ambient conditions Fe(II) is readily re-oxidized to Fe(III). The re-oxidation, leading to the continuous supply of the environmental Fe(III), is achieved mostly by the atmospheric molecular oxygen, but also  $\text{HO}_2^{\bullet}/\text{O}_2^{\bullet-}$  radicals and  $\text{H}_2\text{O}_2$  have their significant contribution [23]. The inorganic Fe(II) is oxidized back to Fe(III) with half time of a few minutes. The Fe(II)  $\rightarrow$  Fe(III) oxidation rate depends strongly on pH, especially when the inorganic Fe(III) species are dominated by their hydrolysis products (e.g.  $\text{Fe}(\text{OH})_2^+$ ,  $\text{Fe}(\text{OH})_3$ ). It is also affected by formation of inorganic complexes in the natural waters, such as  $\text{FeCO}_3$ ,  $\text{FeOH}^+$ ,  $\text{FeHCO}_3^+$  [24–26] as well as by the natural organic compounds, e.g. alanine, glutamic acid, cysteine and aminocarboxylates [27]. The Fenton reaction produces  $\text{OH}^{\bullet}$ , which can rapidly oxidize organic substances, and also Fe(II). The presence of additional oxidants in the solution, such as  $\text{HO}_2^{\bullet}/\text{O}_2^{\bullet-}$  accelerates the Fe(II) oxidation. Hydrogen peroxide reacts much faster with

Fe(II)–polycarboxylate complexes than with inorganic Fe(II) [28].

### 2.4. Photoredox cycles mediated by $\text{OH}^{\bullet}$ radicals

The photocatalytic destruction of harmful or undesirable compounds in the presence of Fe(III) hydroxo-complexes takes an active part in many environmental decomposition reactions (also for polymers). The Fe(III) compounds are able to act as photocatalysts in oxidation of alcohols and diols to aldehydes, ketones and acids. The diols oxidation is very efficient with a 99% yield of product formation, turnover numbers up to  $10^2$  and regioselective oxidation cleavage of the 1,2 carbon-carbon bond in 1,2-diols [18,29].

Generation of the  $\text{OH}^{\bullet}$  radicals was recognized as responsible for the photodegradation of alcohol ethoxylates, diethyl phthalate, dibutyl phthalate, 4-dodecylbenzenesulphonate and selected dyes in the sunlight irradiated Fe(III)-hydroxo systems [30–36]. The photodegradation of dyes such as malachite green, acridine orange or alizarin violet in the presence of photo-Fenton was found enhanced by visible radiation due to increased generation of the  $\text{OH}^{\bullet}$  radicals [37,38].

The UV-photodegradation of phenol catalysed by Fe(III) complex was found to be highly effective [39], whereas 2-aminophenol, 3-chlorophenol and chlortoluron can be eliminated also by irradiation representative of atmospheric solar emission (365 nm) [40–42]. The oxidative destruction of phenol and other phenolic pollutants (vanillin, protocatechinic acid, syringic acid, *p*-coumaric acid, gallic acid, L-tyrosine and bisphenol) was reported to be more effective with the photo-Fenton reaction than without any  $\text{H}_2\text{O}_2$  [43–45]. Similar effect was observed also for nitrobenzene [39,46,47].

Photolysis of herbicides and pesticides catalysed by the Fe(III) ions was found to lead to their complete mineralization [18,48–50]. The reduction rate of the Fe(III) species by humic acids was reported to be significantly (about  $10^2$  times) accelerated by light mimicking the solar one [51,52]. Oxidation of  $\text{NO}_2^-$ , induced by light and Fe(III), was suggested as important pathway responsible for the rapid transformation of nitrates(III) in acidic surface waters [53]. The system was found useful as well for fast oxidation of As(III) to As(V) [54]. For especially biorecalcitrant wastewater, coming from textile industry, the photo-Fenton process was explored as photochemical pre-treatment to improve its biodegradability [55].

### 2.5. Cycles based on direct photoreactions

The photoredox behaviour has been found for some simple Fe(III)–carboxylate complexes in atmospheric and surface waters [10,19,28,56,57]. Study of the photochemical/chemical cycling of the Fe(III)/Fe(II) oxalato complexes in sunlight under the conditions typical for acidified atmospheric waters has shown the depletion of the oxalic acid and the generation of  $\text{H}_2\text{O}_2$  [56]. Peroxides were reported to quench the light-induced excited state of ferrioxalate and the



implications of these observations for the light-driven degradation of pollutants were analysed [58].

Photochemical redox reactions of Fe(III) complexes with polycarboxylates, such as citrate, malonate and oxalate, were found to occur on time scale of minutes in sunlight and to be a potentially important sources of  $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$  and  $\text{OH}^\bullet$  radicals,  $\text{H}_2\text{O}_2$  and Fe(II) species in atmospheric water drops and surface waters [57].

The Fe(III) photoreduction by hydroxycarboxylic acids (HCA), such as sugar acids in the seawater was reported to depend on the complexation ability of HCA with Fe(III) and the photoreactivity Fe(III)–HCA complex. The reaction yield decreases in the order: glucaric acid-1,4-lactone = glucaric > tartaric > gluconic  $\gg$  citric > glyceric = malic > glucuronic acid [59]. Photoreduction of tris(diethylthiocarbamato)iron(III) to a stable Fe(II) complex and  $\text{et}_2\text{dtc}^\bullet$  radical was reported to be induced by LMCT excitation [60].

For some recalcitrant organic pollutants, e.g. EDTA and related compounds, which can be removed neither by conventional biological nor by chemical wastewater treatment the photoinduced oxidation of their Fe(III) complexes is often the only way of their removal under environmental conditions. EDTA belongs to the organic pollutants which are 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 [3–7]. As yet, the Fe(III)–EDTA complex has been recognized as the only environmentally relevant species that undergoes the direct photolysis leading to oxidation of EDTA [7,61]. 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 were identified as biodegradable [62].

UV irradiation of  $[\text{Fe(III)EDTA}]^-$  or  $[\text{Fe(III)(H}_2\text{O)EDTA}]^-$  in aqueous solution yields Fe(II) and  $\text{CO}_2$  with relatively high quantum yields, which ratio,  $\Phi(\text{Fe})/\Phi(\text{CO}_2)$ , is about 2, apparently independent of the ambient conditions [12,61,63,64].

The high quantum yield of the  $[\text{Fe(III)EDTA}]^-$  photoreduction and fast EDTA depletion in sunlit water basins makes the method useful for wastewater treatment [65]. The EDTA removal is accelerated and results in the complete mineralization when the system contains additionally hydrogen peroxide and oxalate [66].

Similar photodegradation under natural conditions was observed for the Fe(III) complexes with ligands derived from other aminopolyacids, such as ethylenediamine disuccinic acid (EDDS) [4], nitriloacetic acid (NTA), ethylenediamine-tetra(methylenephosphonic) acid (EDTMP) [67], *N*-hydroxyethylenediaminetriacetic acid (HEDTA) and diethylenetriaminepentaacetic acid (DTPA) [68]. The recent study on the DTPA degradation confirmed its persistence toward biodegradation and effectiveness of the

photocatalytic Fe(III)-DTPA cycle for DTPA photodegradation [69].

Due to the complexity of the natural organic ligands, EDTA as a complexing agent can be used to model the behaviour of other organic complexes in seawater. The photocatalytic destruction of pollutants in the presence of Fe(III) complexes or iron-doped semiconductor particles appears to be a viable process for pollution control. The degradation of the organic compounds is observed also in aerated iron oxide suspension. The effect is interpreted in terms of LMCT excitation within the Fe(III) surface, followed by organic compound oxidation and Fe reduction and re-oxidation at the surface [11]. Moreover, in the presence of organic compounds, which can play a role of ligands and/or sacrificial donors (as oxalate) the light induced dissolution of insoluble Fe(III) species (as hematite or colloidal iron oxides) was reported to be promoted [16,70].

## 2.6. Effect of photocatalysis on the accessible iron forms

The photoreduction that occurs with the Fe(III) compounds giving rise to the Fe(II) species plays an important role not only in photodegradation of organic matter but also in the geochemical cycles and the chemical and biological processes, which are sensitive to the iron speciation. It controls thus the global and/or local distributions of the iron forms. The distribution is of special importance, due to iron participation in plant metabolism, where it is substantial for photosynthetic and respiratory electron transport, chlorophyll synthesis, nitrate reduction and detoxification of reactive oxygen species [71].

Iron is essential for marine organisms growth, as it is involved in the photosynthesis process and carbon fixation. Light limitation of the algae is another limiting factor in the rough seas and the evidence was found that phytoplankton needs more iron at low light levels [72]. It was reported, that an addition of iron in a very low concentration to high-nitrate and low-chlorophyll waters dramatically increases the productivity and growth of phytoplankton, both small and large, as well as zooplankton that grazes on both size classes [72–75].

On the other hand, the biotic factors also can contribute to generation of a specific iron form in natural environments, e.g. iron oxide formation depends on a wide array of microorganisms. Bacterial cell walls and viral capsids possess highly reactive surfaces with respect to iron binding and it has been revealed that Fe-oxides are formed on the cell wall. Bacteria and viruses have the potential to impact the cycling of iron in aquatic systems and directly affect the morphology and structural order of Fe-oxides [76].

The redox change between Fe(II) and Fe(III) is not only of vital influence on the plant life but also plays an important role in redox processes proceeding in anoxic soils and sediments. Fe(II) forms minerals such as siderite, vivianite or iron sulfide only in anoxic habitats under weakly acidic to neu-

tral conditions. Fe(III) forms minerals that are widespread in both aerated and anoxic habitats [77,78].

### 3. Photocatalysis by the Cu(II)/Cu(I) complexes

#### 3.1. Environmental copper

Copper is known to occur in high concentrations, as relatively unavailable particulate and complexed colloidal forms. Only a small portion of the total Cu burden of soil is bioavailable [79–82]. In soil most of the metal is insoluble or bound to various inorganic and organic ligands. In storm water, however, and subsequently urban rivers its concentrations frequently exceed freshwater quality criteria. Sources of this copper in urban runoff are corosions of building materials and engine vehicles.

Dissolved copper compounds are important to transformation reactions, because they react much faster with hydroperoxyl ( $\text{HO}_2^\bullet$ ) and superoxide ( $\text{O}_2^{\bullet-}$ ) radicals than the other species present in solution [11]. The dissolved copper levels in uncontaminated fresh waters usually range from 0.5 to 1.0  $\mu\text{g/L}$ , increasing to  $>2 \mu\text{g/L}$  in urban areas [83]. Generally, only a very small fraction of soluble Cu is actually present in inorganic form as the free  $\text{Cu}^{2+}$  aq. ion species in the solution [84] and the speciation is dependent on several factors including organic matter, pH, and Eh [85]. In water basins copper occurs commonly as aqua complexes of Cu(II). The main inorganic cupric species present in freshwater systems vary with pH.  $\text{Cu}^{2+}$ ,  $\text{Cu}(\text{OH})^+$ ,  $\text{Cu}(\text{OH})_2$ , and  $\text{Cu}(\text{CO}_3)_2^{2-}$  make up 98% of dissolved inorganic copper; the rest 2% of dissolved inorganic copper is coordinated mostly by chlorides and phosphates. In seawater, however, copper complexes with naturally occurring organic ligands are predominant [86]. Dissolved organic copper complexes include those with aminoacids, carboxylic acids and humic acids. Substantial organic-copper complexation may occur even in water with relatively low organic content [87]. In addition, copper complexation capacity increases with decreasing pH and increasing salinity [88].

Complexation of Cu(II) by EDTA or its analogues is responsible for its re-mobilization from sediments and aquifers [89]. The presence of organic chelating agents generally decreases the toxicity of copper to aquatic organisms [90].

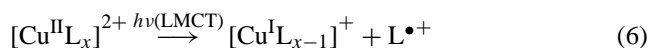
One of the significant constituents of the urban rivers at the variable level is copper(I). Cu(I) compounds are in general sparingly soluble [90], which in aerated medium are easily oxidized to Cu(II) species; they show also a tendency to disproportionate into Cu(0) and Cu(II). In seawater, Cu(II) reduction is enhanced by increased chloride concentration and is likely controlled by organic chelating agents [91]. The proportion of Cu(I) relative to Cu(II) increases with an increase in bicarbonate concentration and an increase in pH. Nevertheless, Cu(I) is still  $<0.5\%$  of Cu(II) [92].

Chloride can strongly bind to Cu(I) and this explains the presence of Cu(I) in seawater [91]. The reactive species un-

der urban river conditions with relatively high concentration of  $\text{Cl}^-$  would probably be  $\text{Cu}^+$  ions and  $\text{CuCl}$  [93]. The Cu(I) concentration can be also increased by the presence of dissolved mercury [94]. First of all, however, Cu(I) formation can be enhanced by the increased intensity of the UV-radiation. Under suitable conditions, a dynamic steady state due to photoreduction and re-oxidation is established [95].

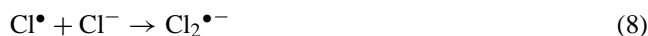
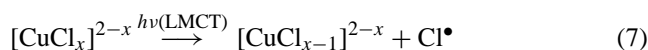
#### 3.2. Photoredox copper cycles

The photoredox behaviour of the Cu(II) complexes, similar to the Fe(III) ones, is derived mostly from the reactive decay of their LMCT states. Excitation to LMCT excited states can be attainable by direct sunlight, when the ionization energy of the ligands coordinated to Cu(II) is not very high. In consequence of the reactive decay of the LMCT excited state by inner-sphere electron transfer, the Cu(II) central atom is reduced to Cu(I), whereas ligand is oxidized to its radical and leaves the coordination sphere.



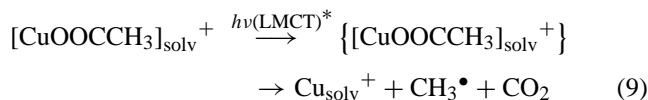
Formation of Cu(I) from Cu(II) during UV-irradiation has been known for a long time [91,96]. The photochemistry of copper complexes was reviewed more than once and its environmental aspects have been included recently [18,97,98].

The photoredox behaviour is demonstrated by the simple Cu(II) complexes with halogens, i.e.  $[\text{CuCl}_x]^{2-x}$ ,  $[\text{CuBr}_x]^{2-x}$ . After excitation of  $[\text{CuCl}_x]^{2-x}$  within its LMCT band the metal centre is reduced and  $\text{Cl}^\bullet$  and  $\text{Cl}_2^{\bullet-}$  radicals are formed [99]:



The  $\text{Cl}_2^{\bullet-}$  radicals are strong oxidation and chlorination agents. For instance they are able to oxidize phenol and its derivatives to para-benzochinone and/or  $\text{CO}_2$  [100,101]. Other co-ligands in the Cu(II) halogen compounds were found to have only small effect on the photoredox efficiency [102].

Carboxylate Cu(II) complexes, such as acetate, malonate, oxalate were reported to undergo photodecarboxylation during irradiation within their LMCT bands. For example, in Cu(II) acetate solution irradiated by UV-radiation the inner-sphere electron transfer was found to generate the  $\text{CuCH}_3^+$  intermediate, followed by the  $\text{CO}_2$  production with a fairly low quantum yield [103]:



Similar behaviour was demonstrated by the malonate and oxalate Cu(II) complexes, for which the low values of the

photodecarboxylation yields were interpreted in terms of efficient deactivation of their LMCT excited states and effective back electron transfer [103]. The electron donor ability of several carboxylic acids to the Cu(II) reduction photoassisted by TiO<sub>2</sub> has been compared recently and formate was found better electron donor than oxalate [104].

One of the interesting classes of copper complexes is that with aminocarboxylate ligands, such as glycine, glutamine, alanine, EDTA, NTA, IDA [100]. Unfortunately, the [Cu(EDTA)]<sup>2-</sup> was found insensitive to the sunlight, and even UV excitation to its LMCT state is ineffective, probably due to rapid non-radiative relaxation of the electronic state [103].

Other aminopolyacids appeared, fortunately, to be more effective. For example, Cu(II) nitrilotriacetate irradiated at 350 nm demonstrated a significant photodecomposition of the ligand to CH<sub>2</sub>O, iminodiacetic acid (IDA) and CO<sub>2</sub> [50,67,100,105,106]. The quantum yield decreases with increase in pH and depends on the Cu-NTA concentration. Complete photooxidation of these ligands yields among other products carbon dioxide and ammonia [100].

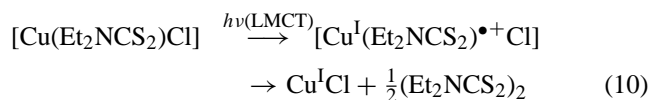
UV-irradiation of Cu(II) diketonate complexes generate Cu(0), which can originate from disproportionation of a Cu(I) species [97]. The yields of the β-diketonate photodegradation are relatively high at UV-irradiation (254 nm) and the threshold energy for the LMCT transitions is within the solar spectrum [107,108].

Polyamine Cu(II) complexes, excited to their LMCT, undergo photoreduction of Cu(II) and oxidation of the carbon fragments, producing NH<sub>3</sub> and CO<sub>2</sub> [96,109]. Not only simple polyamine ligands, as ethylenediamine, but also more complex macrocyclic ones, as teta (meso-5,7,7,12,14,14,-hexamethyl-1,4,8,11-tetraazacyclotetradecane) and tetb (racemic-5,7,7,12,14,14,-hexamethyl-1,4,8,11-tetraazacyclotetradecane) have shown a similar behaviour [110].

Phenanthroline and related compounds in mixed ligand Cu(II) complexes were reported to undergo excitation to their LMCT on UV-irradiation, followed by the copper photoreduction and generation of the different radicals originated from co-ligands, as OH•, CH<sub>3</sub>O•, CH<sub>3</sub>OH•<sup>+</sup> [97,111]. The radicals are able to oxidize many organic compounds, such as primary and secondary aliphatic alcohols or aromatic hydrocarbons (benzene, toluene) and phenol [100].

For some Cu(II) chelates the mechanism of the photoredox process was elucidated in more details. This may be illustrated for reactions of the copper(II) dithiocarbamate mixed-ligand complexes [Cu(R<sub>2</sub>NCS<sub>2</sub>)X], where X = Cl<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, although the studied processes could be followed only in non-aqueous medium [112]. The complexes are characterized by strongly allowed LMCT transition in visible range. The reaction from the lowest LMCT state is reduction of Cu(II) to Cu(I) proceeding via an intramolecular electron transfer from equatorially bound sulfur atom of the ligand to Cu(II). The primary intermediate [Cu<sup>I</sup>(Et<sub>2</sub>NCS<sub>2</sub>)•<sup>+</sup>X] was identified and its transformation to

the Cu<sup>I</sup>Cl and disulfide products was investigated.

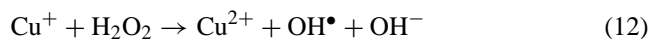


Cu(I) produced from Cu(II) by photoreduction undergoes relatively fast re-oxidation mostly in reaction with molecular oxygen:

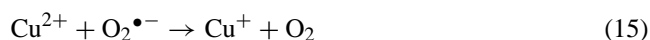
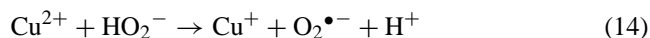


what makes the Cu(I) disappearance in oxic environments very fast (in milliseconds). In suboxic rivers, however, the Cu(I) concentration varies with solar UV-irradiation and can reach even 50% of the dissolved copper [113]. Chloride ions retard the Cu(I) oxidation through its stabilization in the CuCl form.

Oxygen dissolved in water, reduces thus the Cu(I) concentration, the O<sub>2</sub>•<sup>-</sup> and H<sub>2</sub>O<sub>2</sub> are produced instead. These play an important role in the Cu cycle as they can act either as an oxidant or a reducing agent with copper. The oxidation proceeds in two steps slow (Eq. (12)) and fast (Eq. (13)).



Similarly, reduction goes through the slow (Eq. (14)) and the fast steps (Eq. (15))



Peroxide and superoxide species are thus not only formed in the copper cycle, but they have also an influence on the Cu(I)/Cu(II) interconversion, which is of importance in natural waters [91].

It is now realised that copper as metal next to iron and chromium participates in photoredox cycles and its role cannot be ignored. The most important part of the cycle is photoreduction of Cu(II) to Cu(I) induced by solar light and oxidation of ligands to the environmentally benign forms. Then Cu(I) is oxidized with easiness to the Cu(II), which may coordinate next ligand molecule, and thereby the Cu photocatalytic cycle contributes to the environmental cleaning. Besides the oxidation/reduction other critical processes relevant to the copper cycle are adsorption/desorption and precipitation/dissolution that control the Cu environmental speciation and thus its bioavailability and toxicity [98,114].

Photooxidation of pollutants with participation of Cu(II) complexes may also occur in heterogeneous systems, on semiconductor surfaces. Since this system requires presence of other substances such as TiO<sub>2</sub> or WO<sub>3</sub>, it seems to be more useful rather for wastewater cleaning from hazardous species than for environmental self-cleaning [115–119].



## 4. Photocatalysis by Cr(VI) and Cr(III) compounds

### 4.1. Environmental chromium

Chromium is seventh amongst the most abundant elements in the Earth, but its majority is situated in the core and mantle of the Earth. In the Earth's crust it is located at the 21st place. The emission from natural sources (mainly volcanic eruption and soil erosion) is rather low, whereas that from anthropogenic sources can lead to the level creating a menace to the local community [120]. For instance, in the atmosphere over the contaminated urban and industrial areas about 70% of chromium is of the anthropogenic origin [121,122].

Chromium occurs generally in ionic forms, mostly as Cr(III) and Cr(VI), and accordingly its concentration in hydrosphere exceeds that in the atmosphere. In the natural water basins the Cr average concentration is of the nanomolar order (0.1–100 nM) [123,124]. Chromium speciation in groundwater depends on the redox potential and pH conditions in the aquifer. Under anoxic or suboxic conditions, trivalent chromium seems to be the only form. The redox potential Cr(VI)/Cr(III) depends, however, steeply on pH and thus in oxygenated aqueous solutions, Cr(III) is predicted by thermodynamic calculations as the stable species only at  $\text{pH} \leq 6$ , whereas at  $\text{pH} \geq 7$  the  $\text{CrO}_4^{2-}$  ions should predominate [125]. At intermediate pH values, the Cr(III)/Cr(VI) ratio is dependent on the  $\text{O}_2$  concentration. Oxidizing conditions are generally found in shallow aquifers, and reducing conditions generally exist in deeper ground waters. In sea water, chromium(VI) is generally stable [126].

In natural groundwater, the pH is typically within 6–8, and thus  $\text{HCrO}_4^-$  and  $\text{CrO}_4^{2-}$  are the predominant species of chromium in the hexavalent oxidation state, while  $[\text{Cr}(\text{OH})_2(\text{H}_2\text{O})_4]^+$  is the dominant species in the trivalent oxidation state. The  $[\text{Cr}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$  and  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  complexes prevail in more acidic pH; whereas in more alkaline waters the sparingly soluble  $\text{Cr}(\text{OH})_3$  dominates [127].

Cr(III) speciation in surface waters shows that aqua/hydroxo complexes are dominant, although Cr(III) exhibits a tendency to form many different complexes with  $\text{O}^-$ ,  $\text{N}^-$ , and S-containing ligands, especially from naturally occurring organic substances such as fulvic, humic [128], carboxylic [129] and aminocarboxylic acids and aminoacids [130]. Only some organic ligands are able to convert the immobile Cr(III) forms into the soluble and mobile chelates, whereas Cr(III) complexes with bulk organic ligands are not so mobile and easily oxidizable as their aqua/hydroxo analogues because of immobilisation by macromolecular complexes.

### 4.2. Thermal redox processes in the environment

The redox transformation of Cr(III) into Cr(VI) or vice versa can take place only in the presence of another redox couple, which accepts or donates the electrons. Some organic compounds that exist in aquatic environments are able to re-

duce Cr(VI). Those with carboxylate, alcoholate and phenolate functional groups are the most abundant in natural organic matter [131,132]. Direct Cr(VI) reduction by these compounds is usually slow near neutral pH with half-lives of years in some cases. Two essentially different mechanisms of Cr(III) generation in natural waters have been suggested. First of them consists in thermal reduction of dissolved Cr(VI) to Cr(III) mostly by reducing agents such as  $\text{S}^{2-}$ , Fe(II) or some organic compounds [133]. The second pathway includes photochemical reduction of Cr(VI) in the organic matter systems [134–137].

Simultaneously, it was confirmed that under the conditions prevalent in natural waters, dissolved oxygen by itself did not cause any measurable oxidation of chromium(III) to chromium(VI) even in long observation period [138]. Cr(III), however, can be readily oxidized to Cr(VI) by  $\text{O}_2$  in the presence of manganese oxides [138–142]. Although there are few oxidants capable of converting Cr(III) to Cr(VI), and the oxidation kinetics are normally very slow, it has been recently suggested that labile (including dissolved and colloidal) forms of Cr(III) can be converted to Cr(VI) relatively fast by oxidants such as  $\text{H}_2\text{O}_2$ , that are produced photochemically in aerobic surface waters [133,143,144].

The thermal reactions described above became the basis of the chromium cycle constructed for the first time some years ago [142,145,146]. A more detailed analysis of the cycle shows, however, that the redox processes in the cycle cannot be characterised by a high efficiency. The particular reactions proceed slowly and each of the redox pathways needs completely different conditions, such as pH, oxygen concentration, and presence of proper ligands, electron donors and/or electron acceptors.

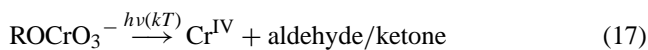
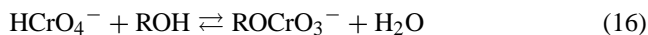
From the environmental point of view the knowledge of chromium(VI) (photo)reduction mechanisms is essential not only for tracing the Cr(VI) fate in the environment but also for understanding its role in remediation of the pollution by the organic compounds. Especially, significant quantities of Cr(III) determined in oxygenated sunlit surface waters suggest strongly that the Cr(VI) reduction in the environment proceeds not only via thermal but also via photochemical processes [139,147].

### 4.3. Photoreduction of chromate(VI)

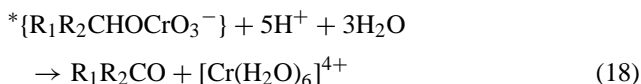
The neat chromate(VI) is photochemically inactive but its effective photoreduction is observed upon irradiation in the presence of a sacrificial electron donor, such as aliphatic alcohol, phenol and its derivatives, carboxylic acids, aminopolycarboxylic acids [135,136,148–154]. It means that in these systems the photoinduced electron transfer (PET) competes effectively with the physical deactivation of its excited LMCT state. The electron transfer may occur via inner- or outer-sphere mechanism, depending on the strength of interaction between chromate and electron donor.

The former was recognized in the Cr(VI)–alcohol–acid systems, for which the generally accepted mechanism com-

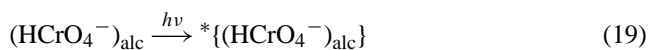
prises of the two-electron reduction of Cr(VI) giving rise to an aldehyde or ketone and a Cr(IV) species. The formation of the chromate(VI) ester is, however, assumed as condition *sine qua non* of initiation of the redox or photoredox reaction [135,149,150,153–156].



e.g.

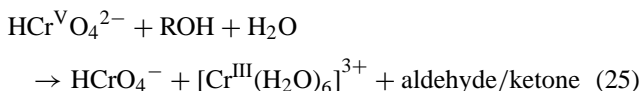
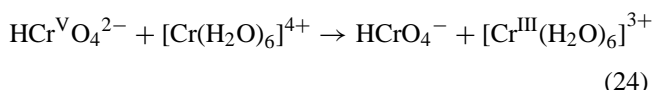
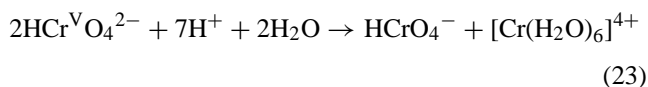
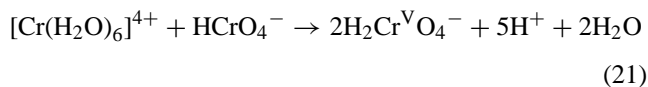


The two-electron mechanism works provided that the solution pH is low enough to enable the ester formation. At somewhat higher pH the thermal Cr(VI) reduction is never observed in these systems, but photoreduction can be still recorded due to weak interaction between Cr(VI) and the alcohol ( $\text{HCrO}_4^-$ )<sub>alc</sub>, followed by the outer-sphere one-electron transfer, e.g. [135,153,157–159]:



The choice of one of the two modes depends in this case on pH, as the higher  $\text{H}^+$  concentration favours esterification, and thus two-electron reduction to Cr(IV) (Eq. (18)), but the decisive stimulus in the mechanism choice is the strength of bond between chromate(VI) and the sacrificial electron donor. This is undoubtedly connected with the instability of both Cr(IV) and Cr(V) forms. In particular, the Cr(IV) formation is accompanied by reconstruction of the chromium coordination sphere [160].

The electron transfer processes are followed by a series of secondary thermal reactions heading towards stable chromium forms, i.e. Cr(III) and Cr(VI) [135,149,153–156].



The fate of the generated Cr(V) species depends strongly on its surrounding: in some solid or organic matrices [157,161] or at low temperatures [155] its formation could be easily observed. In other cases Cr(V) is reduced fast into a Cr(III) species and/or is re-oxidized to Cr(VI) (Eqs. (23)–(25)).

The mechanism of the photoinduced electron transfer substantiated for the Cr(VI)–alcohol system [135] has been recently documented also in other systems, containing Cr(VI) and electron donor, such as oxalate or phenol and its derivatives [136,137]. It is probably also responsible for the Cr(VI) photoreduction initiated by sunlight in natural waters that was earlier interpreted solely in terms of photochemical generation of such reducers as copper(I), superoxide ( $\text{O}_2^-$ ), or iron(II) [129,147,162–164]. More detailed studies showed, however, that the Cr(VI) reduction by  $\text{H}_2\text{O}_2$  proceeds inefficiently [165,166], whereas Cu(I) photochemical generation in nature is strongly reduced by the ligating species (e.g. EDTA analogues, increased concentration of  $\text{Cl}^-$ ) [162]. The mostly studied system consisted of Cr(VI) and Fe(II) added or generated photochemically, which appeared to be strongly dependent on pH and other parameters [139,147,163,167,168]. Moreover, under similar conditions, opposite reaction, i.e. oxidation of Cr(III) to Cr(VI) induced by light and Fe(III) was also reported [101,169,170].

Considering these results, one has to conclude that the environmental photoconversion of Cr(VI) to Cr(III) proceeds via photoinduced electron transfer between the excited Cr(VI) ion and a sacrificial electron donor. Depending on the mutual interaction between the two species, controlled by the medium acidity and its chemical constitution, the photoreaction may proceed by one or two-electron transfer pathway. This phenomenon enables to abate the Cr(VI) pollution within relatively wide environmental pH range. The results certify the environmental relevance of photoreduction of hexavalent chromium, which can be accomplished in sunlit surface waters containing adequate electron donors.

Moreover, photoreduction of the Cr(VI) species is accompanied by oxidation of the electron donor, what results in photodegradation of different organic pollutants. The idea, fascinating from the ecological point of view, of simultaneous abatement of the Cr(VI) pollutant and organic pollutants, carried out in one photoredox system, is thus apparently viable under environmental conditions.

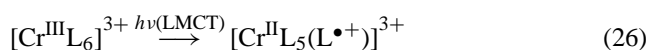
Pollutant photodegradation in the mixture can be more effective than for each component separately, when not only metal species, but also electron donor is able to undergo the photochemical reaction under sunlight, as in the case of the chromate(VI)–phenol system [136]. This system demonstrates an interesting example of synergism in the environmental self-cleaning.

The additional advantage comes from sensitivity of the Cr(VI) photoreduction to the surface catalytic effects [129,171–174] or to the presence of an additional electron donors and/or acceptors: then a synergistic effect is observed in two- or multi-component systems [172–177]. The role of the environmental photoactivators can be played as well by

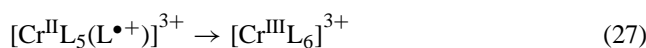
semiconductors such as TiO<sub>2</sub> (both rutile and anatase), WO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, SrTiO<sub>3</sub>, etc., which were found to drive the Cr(VI) to Cr(V) photoreduction, and finally to Cr(III) stable product [178–183].

#### 4.4. Redox photochemistry of Cr(III)

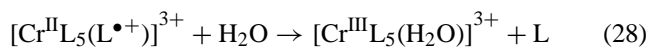
Photochemistry of Cr(III) complexes has been investigated for a long time but the studies were focused on photosubstitution processes which are of minor environmental relevance in comparison with the photoredox ones [123,184–191]. Subsequent research [137,192–194] has shown that in the Cr(III) complexes with reducible ligands (L) the LMCT transitions can induce the inner-sphere photoinduced electron transfer (PET), e.g.,



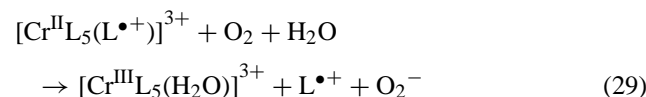
The fast back electron transfer regenerates the original Cr(III) complex



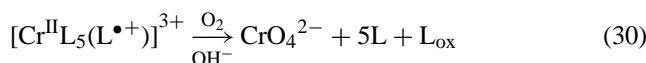
or the back electron transfer is accompanied with the L<sup>•+</sup> substitution.



At last, Cr(II) species can be oxidized by molecular oxygen to Cr(III)



or, under specific conditions, to chromate(VI). The latter oxidation (Eq. (30)) needs alkaline (or at least neutral) medium, and a large O<sub>2</sub> excess over the Cr(II) concentration [195].



The L<sup>•+</sup> radicals are scavenged either by the parent Cr(III) complex



or by molecular oxygen:



The reaction sequence (27)–(32) demonstrates that LMCT excitation of Cr(III) complex (26) can induce both photosubstitution and photoredox processes. The detailed substitution mechanisms can be different, but catalytic effect of Cr(II) on substitution in Cr(III) complexes is well known [96,196]. The photoredox reaction is characterized by an unusual pathway: the oxidation of Cr(III) to Cr(VI) is initiated by its photoreduction to Cr(II).

The Cr(III) → Cr(II) path was observed in a number of Cr(III) complexes, such as: [Cr(CN)<sub>6</sub>]<sup>3-</sup>,

[Cr(CN)<sub>5</sub>(H<sub>2</sub>O)]<sup>2-</sup>, [Cr(CN)<sub>5</sub>(OH)]<sup>3-</sup>, [Cr(CN)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>], [Cr(CN)<sub>3</sub>(OH)<sub>3</sub>]<sup>3-</sup> [192,193,197,198], [Cr(CN)<sub>5</sub>(OH)]<sup>3-</sup>, [Cr(CN)<sub>4</sub>(N<sub>3</sub>)(OH)]<sup>3-</sup> [199], [Cr(NH<sub>3</sub>)<sub>5</sub>(CN)]<sup>2+</sup>, [*trans*-Cr(NH<sub>3</sub>)<sub>4</sub>Cl(CN)]<sup>+</sup> [200–203], [*trans*-Cr(NH<sub>3</sub>)<sub>4</sub>(NCS(CN))]<sup>+</sup> [204].

The photoredox Cr(III) mode (Eqs. (26)–(32)) is of the environmental importance, but the condition *sine qua non* of its progress is relatively low energy of the LMCT transition, which has to be included within the sunlight energy range. It turned out, that there is quite a lot of environmental ligands, which complexes with Cr(III) meet this requirement. Cr(III) has a strong tendency to bind oxygen-containing functional groups [205], and form stable and soluble complexes with organic ligands, including oxalate, citrate, malonate, EDTA and DTPA, within environmental pH range. All these carboxylic acids are released by organisms and plants or produced by the breakdown of large polymers and have been found in surface soil layers at relatively high concentrations.

Their behaviour may be well represented by the oxalate ligand because its concentration is the highest among them [205]. The oxalate complex [Cr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>3-</sup> was found to undergo photoisomerization [206], photodissociation or photoreduction. The last behaviour was reported as induced by ultraviolet irradiation (254 nm) in vacuum [207], and by radiation mimicking the sunlight under environmental conditions [137].

Thermally stable chromium(III) complex with EDTA appeared to behave similarly to its iron analogue, which was assumed earlier as the only environmentally relevant species resulting in photodegradation of EDTA [65]. The LMCT excitation of the Cr–EDTA complex has been recently reported to yield the Cr(II) species, which in the presence of molecular oxygen can be oxidized to Cr(III) and Cr(VI). Sunlight under environmental conditions is able to activate the process, although with less efficiency than UV-radiation. Due to its high sensitivity to the medium components the actual efficiency could be, however, much enhanced [195].

#### 4.5. Photocatalytic chromium cycle

Photocatalytic chromium cycle has been newly recognized [134–137,195]. The cycle fundamentally differs from the previously known iron or copper cycles, which are based on photochemical reduction of the metal ion and its thermal oxidation by molecular oxygen. In the chromium cycle both its main forms, Cr(VI) and Cr(III), undergo the photochemical reduction, and the secondary thermal processes are responsible for the ultimate Cr(VI) to Cr(III) reduction or Cr(III) to Cr(VI) oxidation (Fig. 4). Each deactivation of the excited LMCT state, which is effective in chromium reduction, is accompanied by oxidation of the ligand or other sacrificial electron donor. Each re-oxidation of photoreduced chromium species takes place mostly by the atmospheric molecular oxygen. The results demonstrate that although the

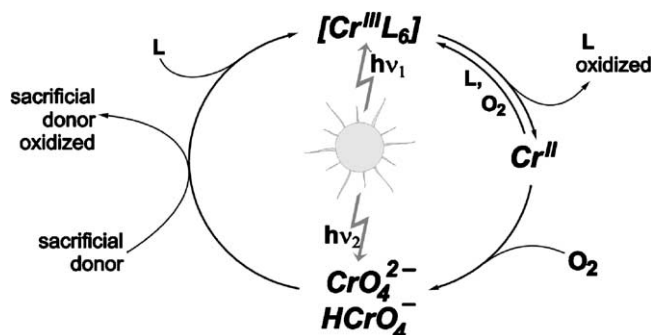


Fig. 4. Doubly photocatalytic chromium cycle consisted of two cooperating photoreduction pathways; L is ligand coordinating to Cr(III) and contributing to the inner-sphere electron transfer.

main chromium forms differ drastically between themselves they can be a part of one compact system, in which photoreduction of either of these forms initiates the multistep process. The chromium cycling proceeds in the natural waters and wastewaters, provided that they are sunlit, aerated, at nearly neutral pH range and the system consists of chromium species and organic substance(s), which can play a role both of ligand and sacrificial donor, such as oxalate.

To recapitulate, organic matter, molecular oxygen and sunlight are consumed in the chromium cycle (Fig. 4), whereas the Cr(III)/Cr(VI) compounds form the catalytic system, which enable atmospheric oxygen to oxidize and thus degrade some organic pollutant. Thus the chromium cycle contributes to consumption of organic pollutants and presents one of the pathways of the environmental self-cleaning processes. The sunlight photo-conversions of Cr(III) to Cr(VI) and *vice versa* may help to explain the time dependence of chromium distribution in the surface waters. Moreover, it suggests that the chromium system can be used for abatement of the dissolved and/or volatile organic pollutants even when only the Cr(VI) half of the cycle is effective; then the photodegradation of both organic matter and Cr(VI) (dechromification) is expected.

## 5. Mixed metal systems

Each of the described cycles consists of the metallic photo-oxidant and reducer and in many cases the electron

transfer takes place via outer-sphere mechanism. These prerequisites, enable the interpenetration of two (or even more) photocatalytic cycles and their cooperation in the pollutant photodegradation when the relevant components are in close vicinity. Moreover, the adaptation of the system is facilitated by the effect of medium components, which are able to modify the potentials of the redox systems involving transition metal ions. The effect can promote thermodynamically particular oxidation or reduction over other reactions [115].

The cooperation between the photocatalytic cycles of two metals is presented schematically in Fig. 5. The two-cycle system should be more useful than each of the single metal cycles independently, because it can induce the sunlight degradation of diverse environmental pollutants (e.g., D and D'). When, however, metal complexes, denoted here  $M^{(m+1)+}$  or  $M'^{(n+1)+}$ , are reduced thermally by  $M^{n+}$  or  $M'^{n+}$ , respectively, the efficiency of electron donor (D or D') oxidation pathway can be increased or decreased, depending on the photocatalytic ability and spectral properties of generated thus  $M'^{(n+1)+}$  or  $M^{(m+1)+}$  species. When the overall yield of the pollutant photodegradation in the bimetallic system is higher than for the sum of independent monometallic ones the synergistic effect is observed. Such synergistic effect was reported, e.g. for the system consisted of Fe(III) and Mn(II), in which the photodecomposition of bromoxynil herbicide in the solution containing both metal ions was faster than for the sum of separated solutions [208].

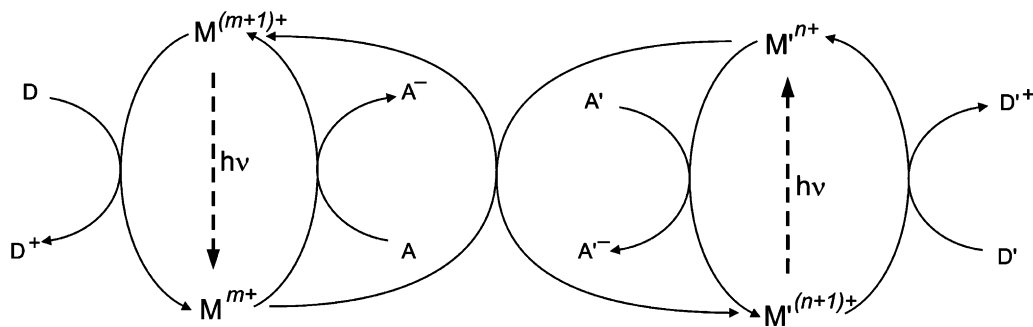
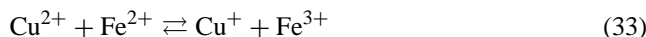


Fig. 5. Bimetallic photoredox cycle;  $M^{(m+1)+}$ ,  $M'^{(n+1)+}$  and  $M^{m+}$ ,  $M'^{n+}$  denote transition metal complexes in their higher and lower oxidation states, respectively, D and D' – sacrificial electron donors, ligated or not to the metal central ion, A and A' – extraneous electron acceptors.



### 5.1. Fe and Cu systems

Iron and copper co-exist in natural waters and in such systems most certainly there is a prevailing equilibrium between the redox states of Fe and Cu, which is closely dependent on UV-radiation, redox conditions and medium components [79]. The equilibrium constant of the redox reaction of Cu(II) with Fe(II)



calculated from the standard redox potentials of Cu(II)/Cu(I) and Fe(III)/Fe(II) amounts  $10^{-10.5}$  [209]. The direct reaction between Cu(II) and Fe(II) is thus impossible. However, the equilibrium (Eq. (33)) can be shifted to the right in the presence of a ligand forming more stable complex with Fe(III) than with Fe(II) and of another ligand forming of more stable complex with Cu(I) than with Cu(II) [209].

Addition of an aminopolycarboxylate to solution containing the iron and copper compounds stabilizes strongly their higher oxidation states. The Fe(III) complexes usually absorb in the visible and near UV-radiation, whereas absorption of the Cu(II) complexes is strongly hypsochromically shifted, what entails smaller, than for Fe(III), overlap with the solar emission spectrum. Complexes of both metals undergo excitation to their LMCT by solar light, but the yield of the ligand photodegradation is much higher in the case of the Fe(III) species. Thus, when Cu(II) is added to the Fe(III)–aminopolycarboxylate system the ligand photodegradation becomes less effective [67]. Presumably, addition of Fe(III) to the Cu(II)–aminopolycarboxylate solution would cause an opposite effect. The system is surely dependent on the reagent concentration, pH, presence of extraneous electron donors and other medium characteristics, and thus needs further studies.

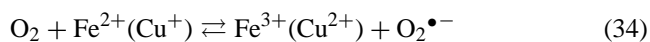
In the natural water systems Cu(I), formed from Cu(II) by reduction or photoreduction, contributes noticeably to the reduction of the Fe(III) compounds [11]. The cooperation between copper and iron is of environmental significance also because of strong absorption of copper on oxide surfaces in soils, including iron oxides [210].

### 5.2. Fe and Cr systems

The Cr(VI)/Cr(III) cycling occurring in natural waters with increase of Cr(III) concentrations over the course of sunlit day was as well interpreted by the Cr(VI) reduction induced by the Fe(II)/Fe(III) photocatalytic system [101,139].

Results of mathematical modelling under default conditions [211], indicate that the Fe(II) is the predominant environmental reducer of Cr(VI) at nearly neutral pH (6.5–7.5); at pH > 8, dissolved molecular oxygen rapidly oxidizes Fe(II), decreasing thus conversion of Cr(VI) to Cr(III) by this way. In acidic solutions (e.g. pH 4–5) the predominant environmental Cr(VI) reducer appears S(IV). Moreover, the reaction kinetics is controlled by concentration of dissolved molecular oxygen and radicals

generated by its reduction [212].



The  $\text{O}_2^{\bullet-}$  radicals are scavenged fast by Cu(I), whereas  $\text{H}_2\text{O}_2$  is an important sink for Fe(II) [211].

The importance of the problem made the system consisted of Cr(VI)/Cr(III) and Fe(III)/Fe(II) the most studied bimetallic environmental system [11,101,139–141,147,163,167,168,170,212,213]. The complexity of the system made, however, that the results of these papers lead sometimes to divergent conclusions, such as ‘the reaction of Fe(II) with Cr(VI) is extremely rapid’ or ‘the reaction is too slow to explain seasonal changes in the Cr(VI) to Cr(III) ratio’ (for a more detailed discussion see [129,164]). Moreover, under similar conditions, opposite reaction, i.e. oxidation of Cr(III) to Cr(VI) induced by light and Fe(III) was also reported [169,170].

The influence of aquatic dissolved organic matter (DOM) on the photochemical reduction of Cr(VI) in the presence of iron was investigated [101]. The Cr(VI) to Cr(III) reduction was observed at pH 5.5 for all target DOMs used in this study, but rates varied widely and faster reduction was observed for larger and more aromatic compounds [101].

The photochemical Cr(VI) reduction in the presence of Fe(III) hydroxo complexes was reported to be influenced by both Cr(VI) and  $\text{Fe}^{\text{III}}\text{-OH}$  concentrations and pH; the optimal pH was found within 2.5–3 range [213].

The hydroxo species of Cr(VI)/Cr(III) and Fe(III)/Fe(II) were found to form the dimeric complex,  $[(\text{H}_2\text{O})_4\text{Fe}(\text{OH})_2\text{Cr}(\text{H}_2\text{O})_4]^{4+}$ , which catalysed the peroxidative oxidation of cyclohexane and cyclopentane to corresponding ketones and alcohols [214].

Kinetics of the thermal reaction between Cr(VI) and Fe(II) was a subject of many studies [11,139,141,167,168]. The pH value favouring the Cr(VI) reduction in the presence of Fe(II) ions appeared to depend also on the  $\text{O}_2$  presence: the reduction rates were reported to increase with increasing pH within 3.5–6.0 for oxic, whereas 3.5–7.2 for anoxic solutions [212]. Apart from pH, also the effect of temperature, ionic strength, reagent concentrations and the role of  $\text{O}_2^{\bullet-}$ ,  $\text{HO}_2^{\bullet}$  radicals and  $\text{H}_2\text{O}_2$  were analysed in details [11,139,168]. The influence of aquifer solids and mechanism of the Cr(VI) reduction by Fe(II) in soils were also investigated [215,216].

Quite an opposite results were presented by Zhang [169,170], who found a possible pathway of light-induced Cr(III) oxidation in the presence of Fe(III) and organic acids in atmospheric waters.

### 5.3. Cu and Cr systems

The recent study of the chromate(VI) photoreduction has shown that the reduction rate is a function of the Cu(I) con-

centration [162]. The rate is affected by increase in pH due to less reactivity of  $\text{CrO}_4^{2-}$  than  $\text{HCrO}_4^-$ , and by the chloride concentration, due to Cu(I) stabilization in form of  $\text{CuCl}_2^-$ . Cu(I) is generated mostly by the  $\text{O}_2^{\bullet-}$  reduction of Cu(II) (Eq. (15)) because the reaction is orders of magnitude faster, than other copper redox reactions, thus also than the Cu(I) oxidation by  $\text{H}_2\text{O}_2$  or  $\text{O}_2$ .

The environmental Cu(I) can originate as well from the photoreduction induced by sunlight. Experiments performed in natural water samples suggest that the photoinduced reduction of chromium(VI) by copper(I) is one of the most important mechanisms of homogeneous abiotic Cr(VI) reduction in atmospheric and sunlit surface waters with low ionic strength and pH, whereas the reaction is of less significance in marine or estuarine waters [162].

The Cr(VI) photoreduction can be accelerated in heterogeneous system, containing copper and  $\text{TiO}_2$  suspension. Conversely, Cr(VI) mediates the Cu(II) reduction to metallic form on the  $\text{TiO}_2$  particles [175].

#### 5.4. Miscellaneous systems

Beside the photocatalytic cycles described above, there are some reports concerning the manganese cycling, in which Mn(IV) undergoes photoreduction to Mn(II) through mediation of humic acids and is next re-oxidized by molecular oxygen. The photochemically induced reduction, at least in part, controls the speciation and thus the biological availability of manganese in surface seawater [217]. Moreover, manganese was found to assist the photodecomposition of bromoxynil herbicide in the solutions containing Fe(III) and Mn(II) and the effect was dependent on the Fe/Mn ratio [208].

The tendency of transition metals to form heterometallic complexes can be also manifested in the environment. Quite a lot of di- or polynuclear complexes is for instance generated by chromate(VI) with such metal cations, as Cu(II), Zn(II), Ni(II) [218–221]. These species would reveal new aspects of environmental photocatalysis; unfortunately, these possibilities have not been explored so far.

Much more is known, however, about interactions between the main cycling metals, i.e. iron, copper and chromium and semiconductors such as  $\text{TiO}_2$ , ZnO, CdS, ZnS and  $\text{WO}_3$ , which cause considerable acceleration of the photoredox processes in the heterogeneous media [151–157,161,178]. Furthermore, different particles and solid phases, especially those with the M–OH bonds, can accelerate the reactions [16,70].

## 6. Concluding remarks

Photocatalysis by transition metal complexes is based on the photoredox process, which gives rise to the reduced metal and the oxidized ligand or an external sacrificial electron donor present in the medium. The quantum yields of these cycles can vary from  $10^{-4}$  to 0.5, depending on the metal and

ligand nature, the presence and concentration of co-ligands and/or sacrificial electron donors, solution pH, aeration status, ionic strength, temperature and irradiation characteristics.

Among the photocatalytic cycles, described here, the iron cycling is of the crucial environmental importance due to Fe high abundance, considerable overlap of the LMCT bands its numerous complexes with the sunlight spectrum and high efficiency of the organic pollutants photodegradation. Copper cycling is also of relevance, but all these parameters, i.e. abundance, overlap and efficiency are at lower level.

Until recently, only half of the chromium cycle, i.e. the photoreduction of Cr(VI) has been identified, whereas photochemistry of Cr(III) complexes was regarded earlier as yielding mostly the photo-substituted species [222–224]. Only in few cases the photoredox reaction of Cr(III) was reported to produce Cr(II) either indirectly [3,4] or directly under UV irradiation [222,225–227]. Just newly, it was found that under natural conditions, the photoreduction  $\text{Cr(III)} \rightarrow \text{Cr(II)}$  can be observed, which is followed by  $\text{O}_2$  re-oxygenation not only to Cr(III) but also to Cr(VI) [134,137,195].

Worthy of notice is the role of oxygen active species, such as  $\text{O}_2^{\bullet-}$ ,  $\text{HO}_2^\bullet$ ,  $\text{OH}^\bullet$ ,  $\text{H}_2\text{O}_2$ ,  $\text{HO}_2^{\bullet-}$ , which are generated in reaction of reduced metal form with molecular oxygen and take part in further redox reactions. They make the photocatalytic processes more efficient and more sophisticated.

Finally, it should be emphasized that the redox processes included in photocatalysis by transition metal complexes are leading just in the opposite outcome as photosynthesis, i.e. an organic matter is oxidized by  $\text{O}_2$  to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , and from that standpoint it could be as well considered as environmentally harmful due to depletion of the organic matter and molecular oxygen with simultaneous production of  $\text{CO}_2$ . The conclusion is vitally important with respect to the environment: it means that as far as transition metal concentrations are relatively low, their photocatalytic cycles are useful as excellent cleaners, but if the level of dissolved metal ions would be much higher (even locally), the consumption of both molecular oxygen and organic matter can exceed the safe level.

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