

Photoredox reactions of environmental chromium

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ABSTRACT. The role of direct photochemical reactions of Cr(VI) and Cr(III) species in the environmental degradation of organic matter was investigated by means of Cr(VI)/alcohol and Cr(III)/EDTA model systems under conditions mimicking the environmental ones. Photoreduction of Cr(VI) proceeds through reductive quenching of chromate(VI) excited within UV-A by an alcohol molecule. Although HCrO_4^- is more susceptible to the quenching than the CrO_4^{2-} ion, and oxygen favours the reverse reaction, the reduction can be easily noticeable at air-saturated natural waters. Photoredox behaviour of $[\text{CrEDTA}(\text{L})]^{n-}$ is more complex: it is initiated also by photoreduction, $\text{Cr}(\text{III}) \xrightarrow{h\nu} \text{Cr}(\text{II})$, which at alkaline medium and a large excess of O_2 over Cr(II) is followed by the $\text{Cr}(\text{II}) \rightarrow \text{Cr}(\text{VI})$ oxidation. Both the photoreductions are accompanied by oxidation of organic matter. Due to the substitutional lability of the $[\text{CrEDTA}(\text{L})]^{n-}$ complexes the conditions can be adjusted under which the Cr(VI)/Cr(III) forms are able to mediate the O_2 oxidation of organic matter in the environmental photocatalytic cycle.

1. INTRODUCTION

The chromium cycle constructed some years ago [1–3] shows the main pathways of Cr(III) and Cr(VI) interconversion when they are in contact with the environmental oxidants and reducers. The cycle was originally proposed for the soil system but it can be easily extended to other environmental compartments, provided that proper oxidants, reducers, ligands and other mediators are accessible.

A more detailed analysis of the cycle shows that these are only organic reducers and atmospheric oxygen, which are consumed in the processes (Figure 1). This means also that molecular oxygen in the catalytic Cr(III)/Cr(VI) system is able to oxidize and thus degrade some organic pollutant. The conclusion is of great environmental importance: it means that the chromium cycle is able to contribute to the self-cleaning environmental processes. Moreover, it suggests that the chromium system can be used for abatement the dissolved and/or volatile organic pollutants even when only one half of the cycle is effective; then the photodegradation of both organic matter and Cr(VI) (dechromification) is expected.

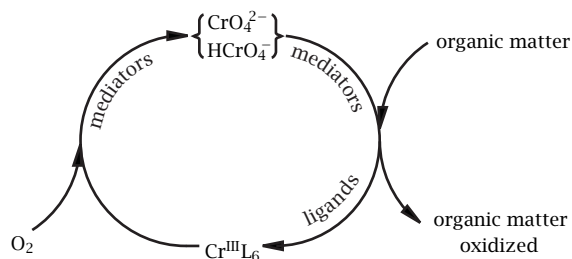


Figure 1. Organic matter degradation in result of the environmental oxidation-reduction Cr cycle (adapted from [3]).

Under environmental conditions the cycle can not 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 reducers, oxidants, ligating agents and other mediators. In both the pathways, however, the actinic radiation impact must be taken into account. It should be of significant importance, as both of the chromium forms are photochemically active and, moreover, chromate(VI) can be photoreduced, whereas the Cr(III) complexes in result of a photoredox reaction could be transferred to Cr(VI). The photochemical behaviour should thus transform the catalytic chromium cycle (Figure 1) into the photocatalytic one.

In earlier investigations the indirect photochemical dechromifications mediated by oxalatoferate(III) complex or semiconductors such as TiO_2 , ZnO , CdS , ZnS and WO_3 were reported [4–10]. Photochemistry of Cr(III) complexes was studied repeatedly and photosubstitution was the main mode described [11–13]. Only in few cases UV irradiation was suggested to result in direct [12, 14–17] or indirect photoredox reactions of Cr(III) [19, 20]. Worthy of notice is the role of iron compounds in the systems, which were found to mediate the Cr photoconversions in both directions [4, 18, 19].

The aim of this study was to recognise a contribution of direct photoreactions to the photocatalytic environmental Cr-cycle. The study was focused on the selected model systems, such as Cr(VI)/alcohol and Cr(III)/EDTA. In the former system the Cr(VI) photoreduction can be performed under aqueous conditions and the environmental aspects easily followed. For the latter model, investigations the $[\text{Cr}^{\text{III}}\text{EDTA}(\text{H}_2\text{O})]^-$ complex has been chosen, because the complex can be easily modified by exchange the weakly bonded water molecule to the selected ligand L; moreover, pho-

todegradation of EDTA mediated by the analogous Fe(III) complex was earlier reported [21, 22].

2. RESULTS AND DISCUSSION

2.1. Cr(VI) photoreduction pathway. Hexavalent chromium has been known for a long time as an effective oxidizer of organic compounds in the dark or in the photochemical processes e.g. [23]. Amongst other reducers, alcohols are known to be oxidized by Cr(VI) in the both ways [24–30] but environmental aspects of the photoredox system have been not investigated as yet. With this end in view, the experiments in this study were performed under conditions mimicking the environmental ones. This means, that radiation range similar to the solar one was used, pH and temperature were kept within the range characteristic of natural waters, chromium concentration in air-equilibrated aqueous solutions was kept at a low level and the impacts of O₂ and some other environmental chemicals were investigated.

Under these conditions, reduction of Cr(VI) by alcohols is not observed in the dark and excitation of chromate(VI) does not lead to any detectable change unless an alcohol or another reducing agent is present in the system (Figure 2). In the presence of alcohols, irradiation with a light from the first UV band (for HCrO_4^- $\lambda_{\text{max}} = 352$ nm) is effective in photoreduction of chromium(VI) (Figure 2).

Then the photochemical behaviour can be interpreted in terms of reductive quenching of the excited Cr(VI) species by a reducer, such as an alcohol molecule.

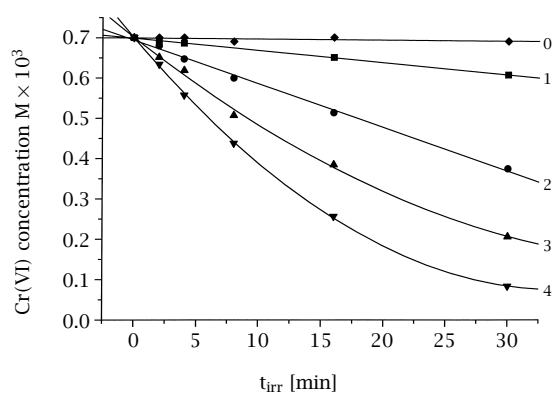
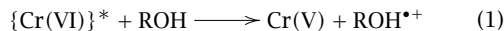
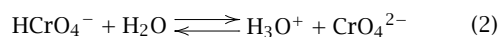


Figure 2. Influence of the alcohol structure on the photoreduction rate of 0.7 mM HCrO_4^- by 70 mM alcohol: methanol (curve 1), ethanol (curve 2), propan-2-ol (curve 3) and butan-2-ol (curve 4); curve 0 represents changes in Cr(VI) concentration vs. t_{irr} without any alcohol; irradiation was performed in Britton-Robinson buffer of pH = 4 using a mercury lamp with a cut-off filter ($\lambda_{\text{irr}} > 320$ nm).



The fate of chromium(V) strongly depends on the system components and usually secondary redox processes yielding Cr(III) and ketones or carboxylic acids as ultimate products [15, 28–30] follow the electron transfer (equation (1)). Different alcohols, such as: methanol, ethanol, propan-2-ol, butan-2-ol, glycol or glycerine can quench the excited Cr(VI) species, and the photoreduction rate depends on the alcohol nature (Figure 2, Table 1). In the case of simple aliphatic alcohols the reaction is the faster the longer hydrocarbon chain and, in fact, the lower its oxidation potential [23], what may be an indication of the environmental sequence of the Cr(VI)-mediated photodegradation of alcohols.

Increased pH reduces strongly the dark reduction rate (e.g. [3, 23]); similar, although less steep, dependence is observed also in the case of the photoreduction rate [28–30]. As a result, in the pH range of natural waters (4–9) only photochemical but not thermal reduction of chromium(VI) by the alcohols is observed and its rate depends considerably on pH (Figure 3, Table 1). The pH-dependent equilibrium



occurring in diluted Cr(VI) solutions is characterised by $\text{pK}_2 = 6.45$ [3, 31] and hence within pH 4–9 both the forms are present, although at $\text{pH} \leq 5$ the HCrO_4^- ion is dominating, whereas at $\text{pH} \geq 8$ it is the CrO_4^{2-} anion. The increased concentration of the protonated form correlates well with the higher photoreduction yield what can be interpreted in terms of higher efficiency of the electron transfer reaction (equation (1)) between an alcohol molecule and excited mono-charged HCrO_4^- , than double-charged CrO_4^{2-} ion. The rate depends also

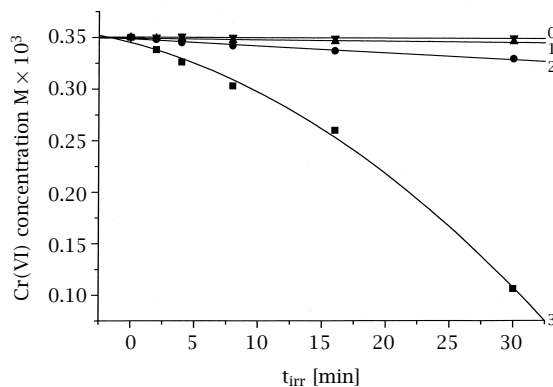


Figure 3. Plots of Cr(VI) concentration vs. irradiation time for 0.35 mM Cr(VI) and 35 mM butan-2-ol in Britton-Robinson buffer at pH = 9.0 (curve 1), 7.0 (curve 2) and 4.0 (curve 3); curve 0 represents dark reaction at pH = 4; temperature 293 K; irradiation by a mercury lamp with a cut-off filter ($\lambda_{\text{irr}} > 320$ nm).

Table 1. Rates of Cr(VI) photoreduction mediated by alcohols; unless otherwise stated the air-equilibrated aqueous solutions in Britton-Robinson buffer of pH = 4 were irradiated at 293 K by mercury lamp light with a cut-off filter ($\lambda > 320$ nm).

alcohol	concentration [mM]		conditions	$k_{\text{obs}} \cdot 10^7$ [s ⁻¹]
	Cr(VI)	alcohol		
methanol				0.58
ethanol				2.14
propan-2-ol	0.7	70		3.99
butan-2-ol				5.49
		17.5		0.92
		35.0		2.17
ethanol ⁽¹⁾	0.7	175.0		7.43
		350.0		14.70
propan-2-ol ⁽²⁾	1.4	140	deoxygenated	0.92
			oxygenated	0.61
butan-2-ol ⁽²⁾	1.4	140	deoxygenated	2.73
			oxygenated	1.45
1,2,3-propantriol	0.7	35	deoxygenated	3.83
			oxygenated	2.87
			pH = 4.0	0.98
butan-2-ol	0.35	17.5	pH = 7.0	0.17
			pH = 9.0	0.06
			283 K	5.40
butan-2-ol	0.7	70	293 K	5.40
			303 K	5.40
butan-2-ol ⁽¹⁾	0.7	35	0.014 mM FeSO ₄ added	3.91
			without any Fe(II)	4.70
butan-2-ol ⁽¹⁾	0.7	35	0.014 mM Fe ₂ (SO ₄) ₃ added	5.20
			without any Fe(III)	5.20

⁽¹⁾ Full light of mercury lamp.

⁽²⁾ $\lambda_{\text{irr}} = 365$ nm.

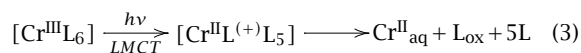
on the alcohol concentration according to the pseudo first order kinetics (Table 1).

Oxygen activates the Cr(VI) regeneration from unstable Cr(V) and Cr(IV) species and therefore photoreduction of Cr(VI) proceeds apparently less effectively in oxygenated than in deaerated solutions (cf. Table 1). Effect of other environmental parameters, such as temperature (within 280–300 K), ionic strength (within 0.04–1.04), and presence of different cations can be neglected. The only exception are Fe(II) cations, which somewhat decrease the photoreduction rate (Table 1) and the known thermal reduction of Cr(VI) by Fe(II) appears to be too slow to interfere with the photochemical process [32–34].

Beside the above-mentioned aliphatic alcohols, also some other environmental reducers were tested as potential mediators in the Cr(VI) photoreduction. Several compounds or ions, such as: phenol and its derivatives, methanal, ethylene glycol, oxalate, tartrate and citrate were found to be active. Among these compounds phenols and chlorinated phenols are widespread pollutants of waste and natural waters. In this case, the direct phe-

nol photolysis under the action of UV light [35, 36] was found to proceed parallel with the sensitized transformation coming up with solar light of much lower energy and in a weakly alkaline medium (pH ~ 8). The system is now under further study.

2.2. Cr(III) photoredox pathway. Transformation of Cr(III) into chromate(VI) on the photochemical way is much more complex than the reverse photoconversion (equation (1)). The process starts from the photoreduction, induced mostly by the LMCT transition [12, 14–17], e.g.



The Cr(II) complex usually releases fast its ligands, and in the presence of oxygen is readily oxidized to Cr(III) species. In alkaline medium, however, and at large excess of O₂ over the Cr(II) concentration, the oxidation proceeds further up to CrO₄²⁻ [15–17].

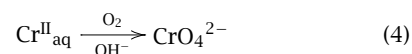


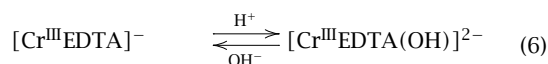
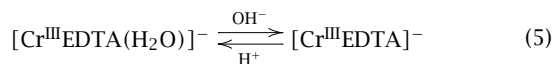
Table 2. Spectral characteristics of the $[\text{Cr}(\text{EDTA})\text{L}]^{n-}$ complexes (all spectra, unless otherwise stated were measured in Britton-Robinson buffer).

ligand L, conditions	λ_{max} [nm] (ϵ_{max} [$\text{M}^{-1}\text{cm}^{-1}$])		
$\text{H}_2\text{O}/\text{none}$ (aqueous, pH ~ 2.5) ⁽¹⁾	541.0 (192)	397.5 (110)	213.5 (5008)
none (pH = 5.4)	544.0 (189)	394.5 (111)	-
OH^- (pH = 9.6)	587.5 (120)	393.0 (83)	-
TEA (1 : 5, pH = 9.6)	587.0 (126)	392.0 (88)	-
$\text{C}_6\text{H}_5\text{O}^-$ (1 : 1, pH = 9.6)	589.0 (122)	393.5 (84)	-
OH^- (pH = 11.5)	587.0 (112)	394.0 (80)	-
OH^- (aqueous, pH ~ 12.5) ⁽¹⁾	-	-	221.0 (4948)

⁽¹⁾ Measured in aqueous solution.

The environmental photoconversion of Cr(III) into chromate(VI) by this way (equations (3) and (4)) is thus conceivable in the case of such Cr(III) complexes which are characterised by the LMCT bands of low energy, i.e. overlapping the actinic radiation range. Humic substances are amongst the optimal ligands due to their easy production of solvated electrons; aminopolycarboxylic acids present a somewhat similar behaviour. Therefore the $[\text{Cr}^{\text{III}}\text{EDTA}(\text{H}_2\text{O})]^-$ complex has been chosen as a model system. Moreover, the complex is substitutionally labile and can be easily modified by exchange the weakly bonded water molecule to the selected ligand L, or even EDTA itself [37–47], what makes the system easy to manipulate.

In aqueous solution, the $[\text{Cr}^{\text{III}}\text{EDTA}(\text{H}_2\text{O})]^-$ complex exists in the pH depended equilibria (equations (5) and (6)) with $[\text{Cr}^{\text{III}}\text{EDTA}]^-$ (containing hexadentate EDTA) and the hydroxo complex, $[\text{Cr}^{\text{III}}\text{EDTA}(\text{OH})]^{2-}$ with $\text{pK}_5 = 1.8$ and $\text{pK}_6 = 7.4$, respectively [44–46].



Their absorption spectrum is characterised by the two LF absorption bands within the visible range and by the LMCT band, which unfortunately lies somewhat outside the actinic radiation region (Table 2). Only one of the visible bands is really sensitive to the ligand nature and is shifted from $\lambda_{\text{max}} \sim 540$ nm (for the aqua complex) to $\lambda_{\text{max}} \sim 590$ nm for the hydroxo one. The shift is accompanied by a small bathochromic shift of the LMCT band and decrease in intensity of both the LF bands (Table 2).

Substitution of the OH^- ligand by $\text{C}_6\text{H}_5\text{O}^-$ or TEA (TEA = triethanolamine) results in insignificant change in the visible spectrum (Table 2), whereas the impact on the LMCT band cannot be assessed due to the strong ligand absorption.

Nevertheless, irradiation of the $[\text{Cr}^{\text{III}}\text{EDTA}(\text{L})]^{n-}$ complexes generates spectral changes characteristic of the CrO_4^{2-} ion (λ_{max} at 373 and 274 nm), provided that

oxygen is present in the system (Figure 4).

The yield of Cr(VI) production depends strongly on the ligand L nature: no photoredox change is observed in the case of the $[\text{Cr}^{\text{III}}\text{EDTA}(\text{H}_2\text{O})]^-$ or for the $[\text{Cr}^{\text{III}}\text{EDTA}]^-$ complex (pH < 8). In alkaline medium, however, i.e. for L = OH^- , $\text{C}_6\text{H}_5\text{O}^-$ or TEA, the Cr(VI) production is detectable. The ligand dependence, as well as necessity of oxygen presence advocates the conception of the primary photoreduction



followed by the Cr(II) oxidation by molecular oxygen (equation (4)).

In the case of TEA, the Cr(VI) yield depends significantly on the ligand concentration: even small TEA additives increase the yield, at the 1 : 1 ratio, however, initial increase is followed by the decrease (Figure 5).

The latter effect (curve 4 in Figure 5) shows that increased TEA concentration accelerates as well the Cr(VI) consumption. This means that the L ligand is able to mediate both photoproduction and photoreduction of chromate(VI). This would be consistent with the previously reported effect of EDTA on the Cr(VI) reduction rate in the photocatalytic TiO_2 system [7].

Study of the Cr(III)/EDTA system indicates that Cr(VI) could be reproduced photochemically from Cr(III), and in consequence the two Cr(VI)/Cr(III) forms are able to mediate the O_2 oxidation of organic matter in the environmental photocatalytic cycle.

3. CONCLUSIONS

The results of this study clearly show that:

- Cr(VI) can be reduced not only in indirect but also in direct photochemical bimolecular reactions. This finding may have a significant application in remediation of Cr(VI) contaminated environmental sites.
- Direct Cr(VI) photoreduction is induced by the $3t_2 \rightarrow 2e$ transition included ($\lambda_{\text{max}} = 352$ nm)

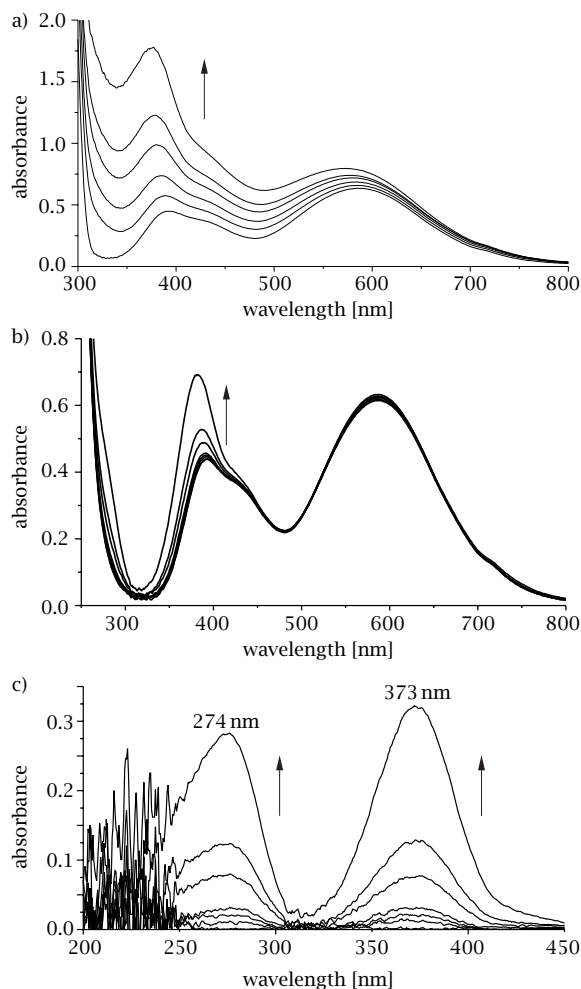


Figure 4. Examples of spectral changes following irradiation of 5 mM $[\text{Cr}^{\text{III}}\text{EDTA}(\text{L})]^{n-}$ complexes in Britton-Robinson buffer at pH = 9.6: (a) in the presence of phenol at the Cr(III)/phenol ratio 1 : 1; (b) in the presence of TEA at the Cr(III)/TEA ratio = 5 : 1; and (c) differential spectra calculated for (b); irradiation was performed using a mercury lamp with a cut-off filter ($\lambda_{\text{irr}} > 300 \text{ nm}$); irradiation times 2–20 min for (a) and 2–60 min for (b) and (c).

within UV-A region easily accessible in the solar light.

- Cr speciation is important in the direct Cr(VI) photoreduction: the reductive quenching of the excited HCrO_4^- form by the alcohol molecule (equation (1)) is much more efficient than that of the CrO_4^{2-} ion.
- As the Cr(III)/EDTA system is sensitive to the nature of the sixth ligand L, its photochemical behaviour should be strongly affected by the components of the environmental compartment and the system could be easily adapted to meet actual requirements.

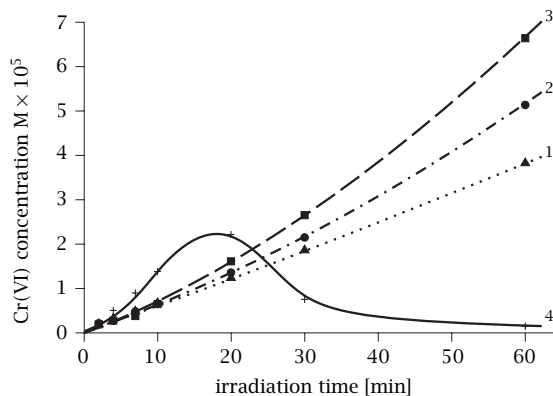


Figure 5. Effect of TEA concentration on the Cr(VI) photo-production rate in 5 mM $[\text{CrEDTA}(\text{L})]^{n-}$ at pH = 9.6: without TEA (curve 1), at Cr(III)/TEA ratio = 10 : 1 (curve 2), 5 : 1 (curve 2) and 1 : 1 (curve 4).

- Contrary to the thermal chromium cycle (Figure 1) the photochemical interconversion of Cr(VI) and Cr(III) in environmental air-equilibrated systems needs only the reducter-ligand mediation, and no oxidant other than O_2 is needed. In consequence, both processes can proceed in the same site. Moreover, in the case of some ligands (TEA or phenol) both the processes can proceed in similar pH range. These behaviours meet the requirements of the photocatalytic cycle. Furthermore, prospects of the environmental photooxidation of organic matter seems to be enhanced by existence in the environment the supported Cr(III) and Cr(VI) compounds as an insoluble support provides a particular enhancing and modifying the reactivity of the bound reagent.

4. EXPERIMENTAL

4.1. Materials and procedures. $\text{Na}[\text{CrEDTA}(\text{H}_2\text{O})]$ was prepared from chromium(III) nitrate and disodium salt of ethylenediaminetetraacetic acid according to the method previously reported [47]. Its purity was checked by UV-VIS spectroscopy. All other reagents used in the experiments were of analytical grade. Solutions of all reagents were freshly prepared for each experiment using demineralized and triply distilled water to prevent potential catalytic effect of iron and/or other metal ion [4]. Alternatively, buffer Britton-Robinson solutions were used as solvents (mixtures of phosphoric, boric and acetic acids and either potassium or sodium hydroxide). All chromium solutions were stored in the dark to avoid light-induced reactions. Anaerobic and aerobic conditions were achieved by 30 min saturation of samples with argon and oxygen, respectively.

4.2. Instrumentation. The UV-VIS spectra were recorded in normal quartz (1 cm) or tandem (0.88 cm)

cells, mainly at 293 ± 0.1 K, using a Shimadzu UV 2100 spectrophotometer. Continuous irradiations were carried out in 1 cm thermostated (± 0.1 K) quartz cells using a high pressure mercury HBO-200 lamp with a glass filters cutting-off the radiation of $\lambda < 300$ nm or $\lambda < 320$ nm. The pH values were measured using a CX-741 (Elmetron) pH-meter with a glass electrode.

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