

# Photodegradation of organic pollutants in aqueous solutions caused by $\text{Fe}(\text{OH})_{\text{aq}}^{2+}$ photolysis: Evidence of OH radical formation

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**ABSTRACT.** Photochemistry of Fe(III) hydroxocomplexes has a great interest because of possibility of hydroxyl radical formation at the primary photochemical step. This mechanism is based mainly on the analysis of the final products of photochemical reactions between light-excited Fe(III) complexes and organic compounds. However, realization of an alternative mechanism of photolysis, based on the intermolecular electron transfer from organic molecules located in the second coordination sphere to the light-excited complex could take place. To distinguish these mechanisms, the experiments on the nanosecond laser flash photolysis of  $\text{Fe}(\text{OH})_{\text{aq}}^{2+}$  in water solutions (pH 3) with organic additives; namely nitrobenzene, N,N-dimethylformamide, and phenol have been performed. And the formation of the organic radicals  $\text{Ph}(\bullet\text{OH})\text{NO}_2$ ,  $\text{HCON}(\text{CH}_2\bullet)(\text{CH}_3)$ , and  $\text{Ph}(\text{OH})_2\bullet$ , was observed, respectively. The rate constants of the formation and decay of the radicals coincide with those found in literature. The results support the formation of the hydroxyl radical upon the photolysis of  $\text{Fe}(\text{OH})_{\text{aq}}^{2+}$ .

## 1. INTRODUCTION

The contamination of natural water systems (oceans, lakes, rivers, precipitation) owing to anthropogenic processes is one of the most urgent ecological problems. One of the factors stimulating the degradation of organic pollutants in natural waters is solar energy. In particular, the photochemical processes involving the ions of transition metals, especially iron, are of importance [1-3].

It is believed that the photolysis of Fe(III) hydroxocomplexes leads to the formation of hydroxyl radical via intramolecular electron transfer from the coordinated  $\text{OH}^-$  anion to the central ion of the light-excited complex. This mechanism was based mainly on the analysis of the final products of photochemical reactions between light-excited Fe(III) complexes and organic compounds [4-16]. Actually, the primary mechanism of the photolysis could not be examined in stationary experiments. In addition to the intramolecular electron transfer, an alternative mechanism of photolysis, based on the electron transfer from organic molecules located in the second coordination sphere to the light-excited complex can take place. In this case, the hydroxyl radical does not occur, but the final reaction products could be the same. The mechanism of intersphere electron transfer is typical of the photoreduction of the complexes of transition metals in polar organic solvents [17-19].

The objective of the present paper was to search for the experimental evidence for hydroxyl radical

formation in the primary photochemical process, using laser flash photolysis.  $\bullet\text{OH}$  radical in water solutions has only a weak absorption in the far UV spectrum region [20]. To detect this species, one needs to use a trap, i.e., a molecule that, in reactions with  $\bullet\text{OH}$  radical, forms an intermediate with a characteristic absorption spectrum. Three compounds, namely nitrobenzene, phenol and N,N-dimethylformamide, were chosen as traps in the current study. Use of several traps allows receiving more reliable information on the mechanism of photolysis.

Recently, the same approach was realized in direct time-resolved experiments on the photolysis of Fe(III) hydroxocomplexes by using a limited number of organic additives [21-24]. The results of all works were interpreted in terms of the  $\bullet\text{OH}$  radical formation.

## 2. EXPERIMENTAL

As a source of Fe(III) ions,  $\text{Fe}(\text{ClO}_4)_3 \times \text{H}_2\text{O}$  (Aldrich) was used. All the experiments were performed in solutions with  $\text{pH} \approx 3$ . In these conditions, the ions of Fe(III) form the complexes  $\text{FeOH}_{\text{aq}}^{2+}$  (85%) and  $\text{Fe}_{\text{aq}}^{3+}$  (15%) [10]. Since the absorption coefficient of hydroxocomplex at the wavelength of laser radiation (308 nm) is much higher than that of  $\text{Fe}_{\text{aq}}^{3+}$ , the only photoactive form was the  $\text{FeOH}_{\text{aq}}^{2+}$  complex.

HPLC grade nitrobenzene, phenol and N,N-dimethylformamide were used without additional purification. Optical absorption spectra of the traps are shown in Figure 1. In spite of a noticeable absorption at 308 nm, nitrobenzene does not display any photochemical

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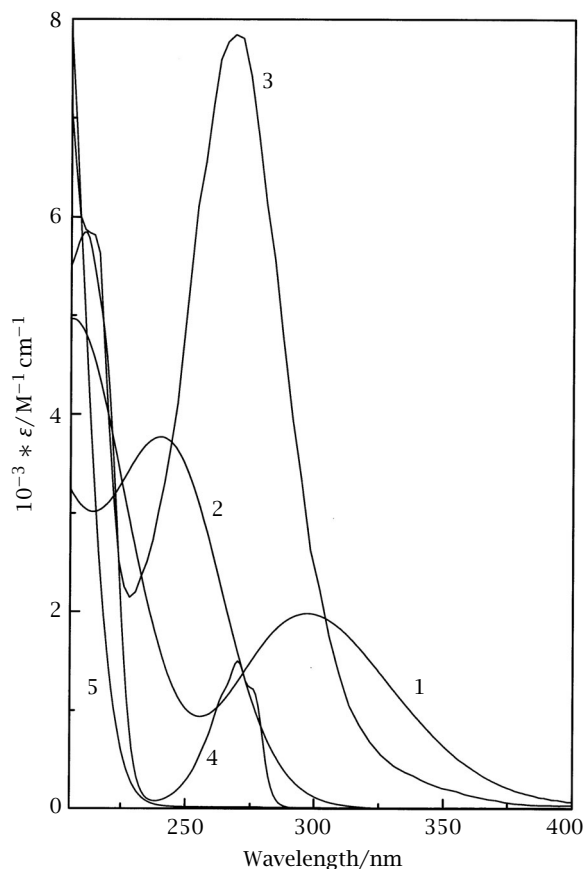


Figure 1. Optical absorption spectra of the reagents in water solution at 298 K: Curves (1–5)—for  $\text{FeOH}_{\text{aq}}^{2+}$ ,  $\text{Fe}_{\text{aq}}^{3+}$ , nitrobenzene, phenol and *N,N*-dimethylformamide, respectively.

activity under excitation at this wavelength, which is necessary for its application as a trap of hydroxyl radicals. Samples were prepared using double-distilled water. Cuvette thickness 1 cm and temperature 298 K were used in all the experiments.

UV absorption spectra were recorded using the HP 8453 spectrophotometer (Hewlett Paccard). A steady-state photolysis was performed using irradiation of a high-pressure mercury lamp with a set of glass filters for the separating the necessary wavelengths.

A set-up for laser flash photolysis with XeCl laser excitation (308 nm, pulse duration 15 ns, mean energy 30 mJ/pulse) was described in detail elsewhere [18]. The experimental kinetic curves were fitted by a numerical solution of the differential equations for reactions describing the systems. The initial concentration of  $\cdot\text{OH}$  radicals was determined from a decrease in absorbance of the  $\text{FeOH}_{\text{aq}}^{2+}$  absorption band (330 nm) just after the laser pulse. The literature rate constants of the reactions of  $\cdot\text{OH}$  radical were used as the fixed parameters of fitting. The molar absorptivities of the bands of

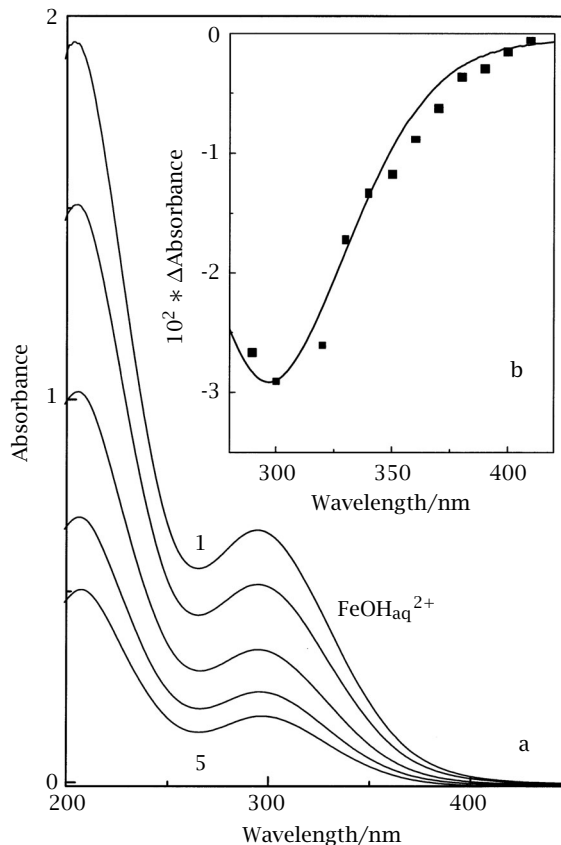
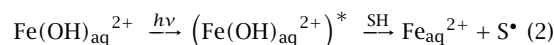
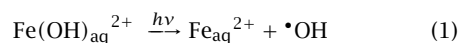


Figure 2. Photolysis of iron(III) perchlorate without organic additives. *a*- steady-state photolysis (313 nm). Curves (1–5) correspond to 0, 1, 3, 10, 25 min of irradiation, pH 2.5, initial Fe(III) concentration  $4.9 \times 10^{-4}$  M. *b*- flash photolysis (308 nm). Transient absorption spectrum just after the laser pulse (points) and inverted absorption spectrum of  $\text{FeOH}_{\text{aq}}^{2+}$  complex (solid line), pH 2.7, initial Fe(III) concentration  $2.1 \times 10^{-4}$  M.

organic radicals and the rate constants of their disappearance were used as variable parameters of fitting.

### 3. RESULTS AND DISCUSSION

**3.1. Photolysis of  $\text{FeOH}_{\text{aq}}^{2+}$  without organic additives.** Stationary irradiation of the  $\text{FeOH}_{\text{aq}}^{2+}$  complex in the region of the long-wave charge transfer band leads to the disappearance of its absorption (Figure 2a). Assume that the primary photochemical process is the intrasphere electron transfer (as was discussed in introduction, in the presence of organic additives SH an alternative mechanism (2) is also possible):



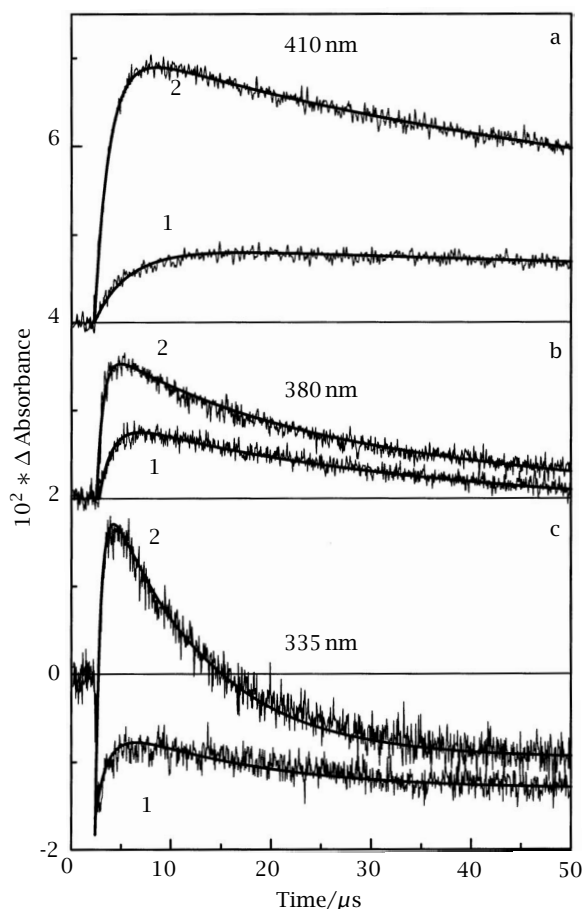


Figure 3. Changes in optical density upon laser flash photolysis (308 nm) of  $\text{Fe}(\text{OH})_{\text{aq}}^{2+}$  in aqueous solutions with additions of nitrobenzene (a), *N,N*-dimethylformamide (b) and phenol (c). Curves (1-2) denote to: a-  $1.6 \times 10^{-5}$  and  $1.3 \times 10^{-4}$  M of nitrobenzene, b-  $2.2 \times 10^{-4}$  and  $6.5 \times 10^{-4}$  M of *N,N*-dimethylformamide, c-  $1.9 \times 10^{-5}$  and  $1.1 \times 10^{-4}$  M of phenol. Smooth curves (a-c) are the best fits by numeric solutions of system of differential equations corresponding to eqs. (3)–(11) with parameters listed in Tables 1, 2.  $\text{Fe}(\text{III})$ :  $5.3 \times 10^{-4}$  M (a),  $4.4 \times 10^{-4}$  M (b),  $4.4 \times 10^{-4}$  M (c). pH: 2.9 (a), 2.8 (b), 2.8 (c).

The complex of Fe(II), namely  $\text{Fe}_{\text{aq}}^{2+}$ , appeared in reaction (1) has only weak absorption in the UV region (the maximum molar absorptivity at 238 nm is  $60 \text{ M}^{-1} \text{ cm}^{-1}$  [25]). In the course of the photolysis, the equilibrium between the two forms of Fe(III) complexes— $\text{Fe}(\text{OH})_{\text{aq}}^{2+}$  and  $\text{Fe}_{\text{aq}}^{3+}$  is established due to the convertible hydrolysis. This is evident from the uniformity of spectral changes in Figure 2a.

Experiments on laser flash photolysis of  $\text{FeOH}_{\text{aq}}^{2+}$  solutions without any organic additives showed only an instant decrease in absorbance in the region of wavelengths  $\lambda > 290 \text{ nm}$ . The spectrum of the decrease

in absorbance is in agreement with the spectrum of  $\text{Fe}(\text{OH})_{\text{aq}}^{2+}$  (Figure 2b). It means that the disappearance of the initial complex occurs in time interval less than the time resolution of the flash photolysis setup (ca. 100 ns). This disappearance was taken into account in calculation of absorption spectra of transient species.

**3.2. Photolysis of  $\text{FeOH}_{\text{aq}}^{2+}$  in the presence of organic additives.** The idea of the experiments was to observe the process of the formation of an organic radical upon the photolysis of  $\text{Fe}(\text{OH})_{\text{aq}}^{2+}$  in the presence of organic additive. If the mechanism (1) is correct, the kinetic curves of the occurrence of organic radical in the reactions between  $\cdot\text{OH}$  radical and organic molecule should be observable in the time region depending on the concentration of the additive. In the case of reaction (2), the formation of organic radical should occur in a time shorter than the resolution time of the experimental setup (ca. 100 ns).

Experiments on the laser flash photolysis of  $\text{Fe}(\text{OH})_{\text{aq}}^{2+}$  in presence of organic additives (nitrobenzene  $10^{-5}$ – $10^{-4}$  M, *N,N*-dimethylformamide  $10^{-5}$ – $10^{-2}$  M and phenol  $10^{-5}$ – $10^{-4}$  M) have demonstrated the formation of an intermediate absorption (Figure 3a–c). A characteristic time of an increase of the signals reduces with enhancing concentration of organic traps. The intermediate absorption spectra have maxima at 410 and 380 nm in presence of nitrobenzene and *N,N*-dimethylformamide and correspond to the  $\text{Ph}(\cdot\text{OH})\text{NO}_2$  [26] and  $\text{HCON}(\text{CH}_2\cdot)(\text{CH}_3)$  [27] radicals (Figure 4a, b). In presence of phenol, the initial intermediate absorption spectrum has a maximum at 335 nm corresponds to that of the radical  $\text{Ph}(\text{OH})_2\cdot$  (Figure 4c) [28]. After formation, the spectrum of  $\text{Ph}(\text{OH})_2\cdot$  is transformed to the new absorption bands with maxima at 380 and 400 nm (Figure 4c). These data are in agreement with those obtained in [28] (pulse radiolysis of aqueous phenol solutions). It is shown in [28], that the  $\text{Ph}(\text{OH})_2\cdot$  radical eliminates a molecule of water with the formation of phenoxy ( $\text{PhO}\cdot$ ) radical.  $\text{PhO}\cdot$  radical has two narrow close-located absorption bands at 380 and 400 nm and rather poorly absorbs in the region of  $\lambda < 350 \text{ nm}$  [28, 29]. The observation of the kinetic curves of the formation of organic radicals for all the systems clearly supports the occurrence of these species in the reactions between  $\cdot\text{OH}$  radical and organic traps.

Although  $\cdot\text{OH}$  radical could be added to a phenol molecule in four different positions to form four isomers, the formation of only ortho and para isomers was observed [30, 31]. However, the data on the difference between the optical spectra of isomers are not available in the literature. Therefore, their spectra were assumed to coincide. The same assumption was made for isomers of  $\text{Ph}(\cdot\text{OH})\text{NO}_2$  radical.

The proposed mechanism of the reactions is described by kinetic scheme ((1), (3)–(11)), which

Table 1. Rate constants ( $k \times 10^{-9}$ ,  $M^{-1} s^{-1}$ ) of reactions (3)–(11).

| Rate constant   | $k_3$ | $k_4$ | $k_5$ | $k_6$ | $k_7$ | $k_8$          | $k_9$           | $k_{10}$ | $k_{11}$                         |
|-----------------|-------|-------|-------|-------|-------|----------------|-----------------|----------|----------------------------------|
| Fitting         | 5.5*  | 0.43* | 4.7*  | 1.7*  | 14*   | $1.4 \pm 0.15$ | $1.15 \pm 0.1$  | 0.013    | $(1.6 \pm 0.2) \times 10^{-4}$   |
| Literature data | 5.5   | 0.43  | 4.7   | 1.7   | 14    | 0.8<br>(pH 1)  | 1.2<br>(pH 5.0) |          | $1.6 \times 10^{-4}$<br>(pH 2.8) |
| Reference       | [20]  | [20]  | [26]  | [27]  | [28]  | [26]           | [27]            |          | [31]                             |

\* fixed literature data were used for fitting.

Table 2. Molar absorptivities ( $\epsilon \times 10^{-3}$ ,  $M^{-1} cm^{-1}$ ) of organic radicals.

| Radical         | Ph( $\bullet$ OH)NO <sub>2</sub> (410 nm) | HCON(CH <sub>2</sub> $\bullet$ )(CH <sub>3</sub> ) (380 nm) | Ph(OH) <sub>2</sub> $\bullet$ (335 nm) |
|-----------------|---|---|--|
| Fitting         | $5.7 \pm 0.2$                             | $1.5 \pm 0.2$   | $3.4 \pm 0.7$                          |
| Literature data | 3.7                                       | 1.6   | 4.4                                    |
| Reference       | [26]                                      | [27]  | [28]                                   |

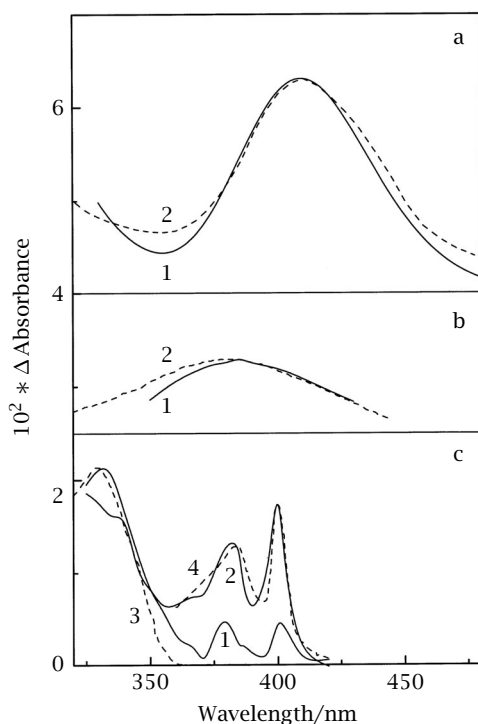
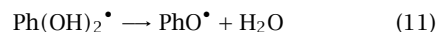
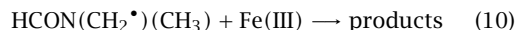
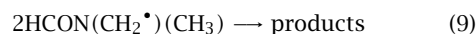
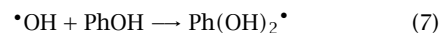
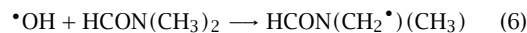
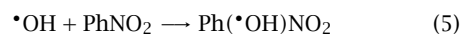
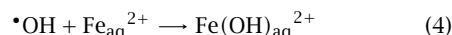


Figure 4. UV absorption spectrum (solid curves) of intermediates arising from laser flash photolysis (308 nm) of  $Fe(OH)_{aq}^{2+}$  in aqueous solutions with additions of nitrobenzene (a, 7.6  $\mu s$  after laser pulse (1), nitrobenzene  $1.1 \times 10^{-4}$  M); *N,N*-dimethylformamide (b, just after the laser pulse (1), *N,N*-dimethylformamide  $1.0 \times 10^{-2}$  M) and phenol (c, 0.8 (1) and 14 (2)  $\mu s$  after laser pulse; phenol  $5.9 \times 10^{-5}$  M). Dot curves: a- spectrum of Ph( $\bullet$ OH)NO<sub>2</sub> radical (2) [26], b- spectrum of HCON(CH<sub>2</sub> $\bullet$ )(CH<sub>3</sub>) radical (2) [27], c- spectra of Ph(OH)<sub>2</sub> $\bullet$  (3) [28] and PhO $\bullet$  (4) [29] radicals. Fe(III):  $3.1 \times 10^{-4}$  M (a),  $6.6 \times 10^{-4}$  M (b),  $2.0 \times 10^{-4}$  M (c). pH: 3.3 (a), 2.9 (b), 2.8 (c).

concludes the primary reaction (1) responsible for the hydroxyl radical formation, reactions of  $\bullet$ OH radical with  $Fe_{aq}^{2+}$  (4), organic traps ((5)–(7)) and self-reaction (3), and reactions of decay of organic radicals ((8)–(11)):



The results of the fitting of experimental curves with different concentrations of organic traps, Fe(III) ions and radical species (varied by change in laser pulse intensity) are summarized in Tables 1, 2. The literature values for the rate constants of the reactions of  $\bullet$ OH radical ((3)–(7)) allow one to get a fair agreement between calculated and experimental kinetic curves (Figure 3a–c).

Reaction (10) was included to the general scheme to describe the apparent decrease in the lifetime of HCON(CH<sub>2</sub> $\bullet$ )(CH<sub>3</sub>) radical with the increase of Fe(III) concentration in the solution. The values of both  $2k_8$  and molar absorptivity of Ph( $\bullet$ OH)NO<sub>2</sub> at 410 nm ( $\epsilon_R^{410nm}$ ) necessary for reaching coincidence between the calculated and experimental kinetic curves exceed those obtained in [26]. However, the  $2k_8/\epsilon_R^{410nm}$  ratio determined for the second-order kinetic curves directly from the experimental data, almost coincides with that measured in [26].

The molar absorptivity of the band of  $\text{Ph}(\cdot\text{OH})\text{NO}_2$  was calculated in [26] using the value of the radiation yield of radicals in water solutions saturated with  $\text{N}_2\text{O}$  (for conversion of  $e_{\text{aq}}^-$  into  $\cdot\text{OH}$  radical). However, a hydrogen atom that can be added to a nitrobenzene molecule to form the  $\cdot\text{Ph}(\text{H})\text{NO}_2$  radical, also contributes to the radiation yield value. The authors [26] suggest that the spectra of the radicals  $\text{Ph}(\cdot\text{OH})\text{NO}_2$  and  $\text{Ph}(\text{H})\text{NO}_2$  fully in agreement with the values of the molar absorptivity. This assumption is not evident and could cause a lower value of absorption coefficient in [26] as compared with that obtained in this work.

#### 4. CONCLUSION

Photolysis of  $\text{FeOH}_{\text{aq}}^{2+}$  in the presence of nitrobenzene, *N,N*-dimethylformamide and phenol results in appearance of organic radicals  $\text{Ph}(\cdot\text{OH})\text{NO}_2$ ,  $\text{HCON}(\text{CH}_2\cdot)(\text{CH}_3)$  and  $\text{Ph}(\text{OH})_2\cdot$ , accordingly. The rate constants of radicals formation and disappearance and  $\cdot\text{OH}$  radical recombination are in agreement with the literature values. This allows concluding that the organic radicals are formed in the reactions between  $\cdot\text{OH}$  radical and organic additives. This is a direct confirmation of the hydroxyl radical formation in the photoreduction of  $\text{Fe}(\text{OH})_{\text{aq}}^{2+}$  complex by the intrasphere mechanism. The high reactivity of  $\cdot\text{OH}$  radical may determine considerable contribution of the photochemistry of *Fe*(III) complexes to the oxidation of organic pollutants in natural waters.

#### ACKNOWLEDGMENTS

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