

**HUMIC SUBSTANCES – EXCITED STATES, QUENCHING BY METAL IONS, AND PHOTSENSITIZED DEGRADATION OF CHLOROPHENOLS**Kamil LANG<sup>a1</sup>, Dana M. WAGNEROVA<sup>a2</sup>, Sarka KLEMENTOVA<sup>b</sup> and Pavel KUBAT<sup>c</sup><sup>a</sup> *Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 160 00 Prague 6, Czech Republic; e-mail: <sup>1</sup> lang@iic.cas.cz, <sup>2</sup> dwagner@iic.cas.cz*<sup>b</sup> *Faculty of Biological Sciences, University of South Bohemia, 370 05 Ceske Budejovice, Czech Republic*<sup>c</sup> *J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, 182 23 Prague 8, Czech Republic; e-mail: kubat@jh-inst.cas.cz*

Received April 8, 1997

Accepted May 3, 1997

*Dedicated to Professor Jaromir Plesek on the occasion of his 70th birthday in recognition of his outstanding contributions to organic, borane and carborane chemistry.*

Alteration of photochemical properties of humic substances (HS) by the addition of metals abundant in natural waters has been investigated. Excited HS states have been characterized by fluorescence spectra and by laser kinetic spectroscopy. The effect of Cu<sup>2+</sup>, Fe<sup>2+</sup>, and Mn<sup>2+</sup> has been explained in terms of static quenching of the HS excited states. In agreement with this, the metal ions were found to inhibit HS sensitized photooxidative degradation of chlorophenols.

**Key words:** Humic substances; Quenching; Excited states; Photooxidative degradation; Chlorophenols.

Humic substances (HS), natural photosensitizers present in surface waters, are known to activate dissolved oxygen and to produce reactive oxidative species as singlet oxygen <sup>1</sup>O<sub>2</sub>, superoxide anion-radicals O<sub>2</sub><sup>-</sup>, hydrogen peroxide, hydroxyl radicals OH<sup>•</sup> and organic peroxides<sup>1,2</sup>; all of them participate in the transformation of organic matter<sup>3</sup>. Humic substances, whose exact structure is unknown, vary in composition, in the nature of chromophores and in the chromophore distribution over the macromolecule. The most common chromophores are aromatic species with phenoxy, carboxy, methoxy, and keto groups, and quinoid species<sup>4</sup>. Considering the non-specific absorption spectrum of HS and the variety of chromophores, one of the few ways to elucidate the mechanisms of HS photoreactions is the use of laser kinetic spectroscopy. Basic information on excited transients, characterization of oxidative species and testing of metal–HS interactions have been the subject of several pioneering works<sup>2,5–8</sup>.

The photosensitizing effect of HS can be affected by metal ions, present as strongly bound “constitutional” components or present in solution and bound to peripheral chro-

mophore groups that, as a rule, have chelating properties<sup>4,9</sup>. Metal ions can either contribute to photochemical reaction by photocatalytic effect<sup>10,11</sup> or suppress it by quenching excited transients<sup>12</sup>.

In the light of current environmental problems, the ability of HS to dispose of anthropogenic substances deserves attention<sup>13</sup>. Chlorophenols, due to their massive utilization in the production of fungicides and herbicides, are frequent pollutants. Their photosensitized degradation is important because they are resistant to microbial degradation and, having only weak absorbance above 300 nm, direct photolysis is insignificant. The HS photosensitized degradation of some of the chlorophenols has recently been reported<sup>14,15</sup>.

In this paper, we have characterized the excited transients and elucidated the effect of added metal ions on the sensitizing properties of two commercial HS. The results were correlated with the effect of metal ions on photooxidative degradation of chlorophenols.

## EXPERIMENTAL

### Chemicals

Commercial humic acids sodium salts, HS (Aldrich, Roth) and sulfonated chloroaluminium phthalocyanine<sup>16</sup>, AISP, were employed without further purification. 4-Chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP) and 2,4,5-trichlorophenol (2,4,5-TCP) (all Riedel de Haen),  $\text{MnSO}_4$ ,  $\text{CuSO}_4$ ,  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$  (all Lachema, Czech Republic) and  $\text{FeCl}_3$  (Cambrian Chemicals) were used as received.

### Laser Flash Photolysis

Fluorescence and kinetic absorption spectra of HS were measured on a laser kinetic spectrometer (Applied Photophysics) equipped with a Lambda Physics excimer laser LPX 200 (wavelength 308 nm, pulse length 28 ns, energy 20 mJ). Experimental details were described previously<sup>16</sup>. The averaging of kinetic profiles measured at 440 nm (20 times) and of the kinetic absorption spectra (8 times) improves significantly the signal-to-noise ratio. All the experiments were carried out in He atmosphere (oxygen removed) at room temperature. The samples were titrated with  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$ . Air- or oxygen-saturated solutions were used only in oxygen-quenching experiments. The Stern-Volmer plots for metal ion quenching of HS (Aldrich) fluorescence were measured on a Perkin-Elmer LS 50 luminiscence spectrometer in air-saturated solutions ( $\lambda_{\text{exc}}$  310 nm,  $A_{310} < 0.1/1$  cm cell, excitation and emission slits 5 nm).

Addition of metal ions does not induce changes in absorption spectra that would indicate aggregation of HS. The HS absorbance at the excitation wavelength  $\lambda_{\text{exc}}$  308 nm matches that in the presence of metal ions; hence, the observed effects do not originate from a different number of absorbed quanta.

### Continuous Irradiation

Two light sources were used for continuous irradiation experiments. A high-pressure mercury lamp HBO 500, 500 W (OSRAM) equipped with band filters transmitting wavelengths in the range of

310–400 nm (4-CP), or of 340–510 nm (2,4-DCP, 2,4,5-TCP) were used in experiments with HS (Aldrich). The filters were chosen to eliminate direct photolysis of chlorophenols. The experiments with AISPC were carried out with a high-pressure sodium lamp SHC, 250 W (Tesla, Czech Republic),  $\lambda_{\max}$  589 nm.

A sample (2.5 ml) was placed in a thermostatted block (25 °C) and bubbled with oxygen to ensure stirring and saturation with oxygen during 120 min irradiation. The initial concentration of chlorophenols was  $5 \cdot 10^{-4}$  mol dm<sup>-3</sup>. The concentration of AISPC was  $1 \cdot 10^{-5}$  mol dm<sup>-3</sup> ( $A_{589} = 0.06/1$  cm). The absorbances of filtered HS (Aldrich),  $c = 71$  mg dm<sup>-3</sup>, were  $A_{360} = 0.8/1$  cm (peak transmittance of the 310–400 nm band filter) and  $A_{405} = 0.5/1$  cm (peak transmittance of the 340–510 nm band filter). The absorption spectrum of HS does not change during irradiation. Fresh stock solutions of Fe<sup>3+</sup>, Fe<sup>2+</sup>, Cu<sup>2+</sup>, and Mn<sup>2+</sup> were prepared before each experiment. No buffer was added to the solutions. The pH of the irradiated solutions was  $6.3 \pm 0.2$  and  $7.7 \pm 0.2$  for chlorophenols in the absence and presence of HS, respectively. The experiments with Fe<sup>3+</sup> were performed at pH  $3.5 \pm 0.2$  to prevent hydrolysis.

UV-VIS spectra were recorded on a PU 8720 spectrophotometer (Philips). The concentration of chlorophenols was determined by HPLC: a Separon SGX C18 (250 × 4 mm, 7 μm) reverse-phase column (TESSEK, Czech Republic), an HPP 4001 pump (Laboratory Instruments, Prague, Czech Republic) and a PU 4025 UV detector (Philips). The eluting solution was 70% methanol in water. The original content of relevant metals in HS was determined by AAS (error 6%).

## RESULTS

### *Laser Flash Experiments*

The fluorescence spectra of both HS (Aldrich and Roth) have a broad band at 425–500 nm. Varying the excitation wavelength from 230 to 333 nm has no effect on the band shape and intensity. The addition of Cu<sup>2+</sup>, Mn<sup>2+</sup>, or Fe<sup>2+</sup> causes a blue shift to 420–450 nm and reduces the fluorescence intensity (Fig. 1).

The Stern–Volmer plots for Cu<sup>2+</sup> titration of HS reveal a downward curvature (Fig. 2) that can be assigned to static quenching of the excited singlet states.

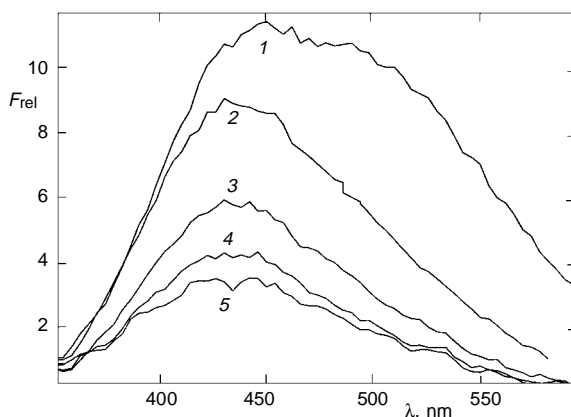


FIG. 1  
Quenching of HS fluorescence by Fe<sup>2+</sup>.  
Concentration of Fe<sup>2+</sup> (mmol dm<sup>-3</sup>):  
1 0; 2 0.11; 3 0.53; 4 2.6; 5 5.4.  
Excitation wavelength 308 nm. HS  
(Roth), 39 mg dm<sup>-3</sup>

After excitation, both HS exhibit similar kinetic spectra. HS (Aldrich) excited by the excimer yields an absorption spectrum featuring a broad band within 350–660 nm with a maximum around 440 nm. The decay profiles measured at 440 nm can be analyzed as a triplicate process and attributed to three distinct transients. The spectrum without specific bands allows the transients to be distinguished only kinetically, not spectrally.

Transient **1** decays too fast (<100 ns) to be characterized in detail. Oxygen does not quench transient **2**; the decay rate constants are  $(5.6 \pm 0.2) \cdot 10^5 \text{ s}^{-1}$  and  $(5.4 \pm 0.3) \cdot 10^5 \text{ s}^{-1}$  for HS (both Aldrich and Roth), respectively (Fig. 3, curve 1). The absorption spectrum attributed to **2** has a peak at 440–450 nm (Fig. 4, curve 1). Unlike **2**, transient **3** is extremely sensitive to oxygen (Fig. 3, curve 2). In oxygen-free solution, **3** lives for hundreds of microseconds, but disappears immediately in an oxygen-saturated solution. In spite of the fact that the absorbance changes of **3** are very low ( $\Delta A_0 \approx 5 \cdot 10^{-4}$  at  $t = 0$ ,  $\lambda_{\text{obs}} 440 \text{ nm}$ ) the decay rate constant was estimated to be  $300 \text{ s}^{-1}$  (HS Aldrich). The absorption band of the transient **3** is depicted in Fig. 4, curve 2.

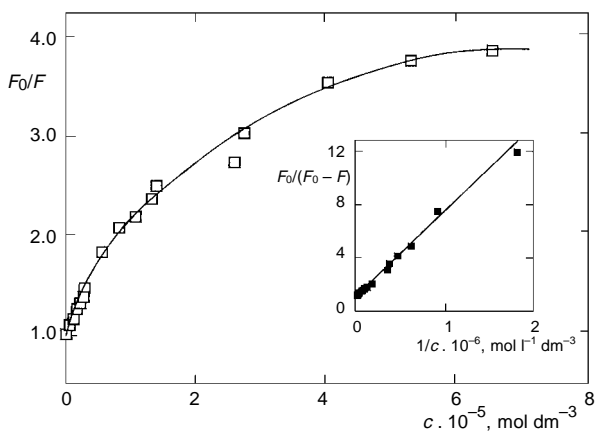


FIG. 2  
Stern-Volmer plot  $F_0/F$  vs concentration of  $\text{Cu}^{2+}$  added. Absorbance at excitation wavelength  $A_{310} = 0.061$ . HS (Aldrich),  $3 \text{ mg dm}^{-3}$ . Insert: linearization according to Eq. (3)

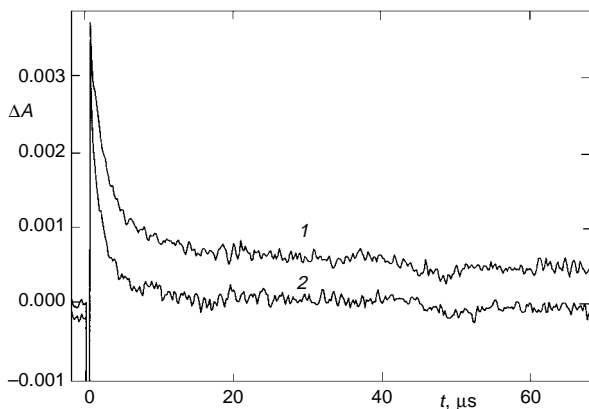


FIG. 3  
Kinetic profiles of transients **2** and **3**: **1** decay in absence of  $\text{O}_2$ ; **2** quenching by  $\text{O}_2$  in oxygen-saturated solution. Excitation wavelength 308 nm, measured at 440 nm, HS (Aldrich),  $21 \text{ mg dm}^{-3}$

The addition of  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  or  $\text{Mn}^{2+}$  reduces the concentration of **2** and **3** (Fig. 5). Whereas the initial concentration of **2** is considerably reduced, the decay rate constant is not affected: the rate constants of HS (Roth) are  $(5.4 \pm 0.3) \cdot 10^5 \text{ s}^{-1}$  and  $(5.6 \pm 0.5) \cdot 10^5 \text{ s}^{-1}$  in absence and presence of  $2.8 \text{ mmol dm}^{-3} \text{ Fe}^{2+}$ . This behaviour is typical of static quenching. The finding is in accordance with fluorescence experiments (*vide supra*). As far as quenching by oxygen and by metal ions is concerned, the transients of HS (Aldrich and Roth) exhibit similar behaviour.

### Continuous Irradiation

The issue of metal ions effect on the photosensitizing activity of HS has been examined using chlorophenols as substrates. Low-yield photooxidative degradation of 2,4-DCP, 2,4,5-TCP occurs in absence of HS, since there is a minor absorption of light by the substrates. 4-CP alone is stable. In the presence of HS, direct photolysis can be excluded considering the fact that more than 99% of the absorbed radiation is absorbed by

FIG. 4  
Absorption spectrum of transient **2** and **3**: **1** transient **2** measured 400 ns, and **2** transient **3** measured 6 ms after the laser pulse. Absorbance at excitation wavelength  $A_{308} = 0.853$ , HS (Aldrich), He atmosphere. Average of 8 measurements

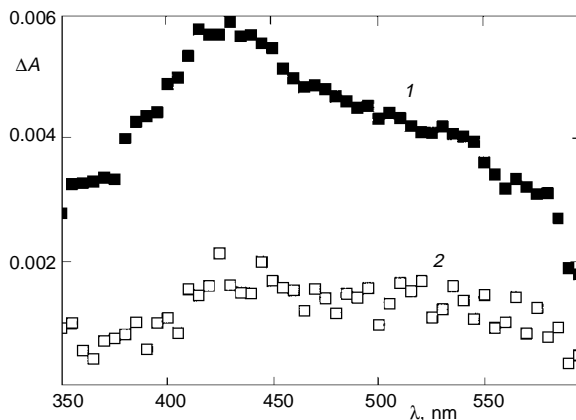
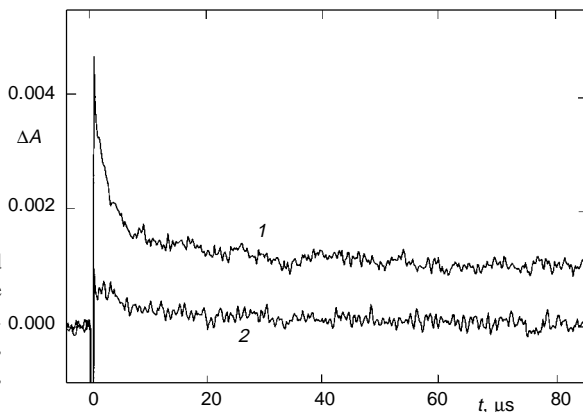


FIG. 5  
Kinetic profiles of transients **2** and **3**: **1** in the absence and **2** in the presence of  $2.8 \text{ mmol dm}^{-3} \text{ Fe}^{2+}$ . Excitation wavelength 308 nm, measured at 440 nm, HS (Aldrich),  $20 \text{ mg dm}^{-3}$ , He atmosphere



HS itself. HS act solely as oxygen-activating sensitizers: neither the "dark reaction" in presence of oxygen, nor photolysis in oxygen free solution proceed to a measurable extent.

The content of relevant metals in the HS is summarized in Table I. The relatively high amount of "constitutional iron" corresponds to concentration of  $0.004 \text{ mmol dm}^{-3}$  Fe in the samples. We did not succeed in removing the metals from HS on an ion exchange column without deteriorating the HS composition. When metal ions are added, their complexation modifies HS-sensitizing properties and, consequently, influences chlorophenol degradation. Of metal ions usually present in surface waters,  $\text{Fe}^{2+}$  and  $\text{Cu}^{2+}$  inhibit, and  $\text{Fe}^{3+}$  supports the degradation (Table II, Fig. 6).  $\text{Mn}^{2+}$  strongly inhibits photodegradation of 2,4,5-TCP (Fig. 6).

Experiments with a synthetic sensitizer AISPc producing  $^1\text{O}_2$  ( $^1\Delta_g$ ,  $\Phi_\Delta = 0.34$ , ref.<sup>17</sup>) have been performed for comparison. 4-CP appears to be least reactive with *in situ* generated  $^1\text{O}_2$  (16% degradation, 120 min of irradiation). Comparable photodegradation for 2,4-DCP and 2,4,5-TCP are 25% and 29%, respectively. The trend is the same as for degradation sensitized by HS (Aldrich).  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Mn}^{2+}$  in the same concentrations as in experiments with HS do not influence chlorophenol photodegradation. (Only  $90 \mu\text{mol dm}^{-3}$   $\text{Cu}^{2+}$  has a weak inhibiting effect.) In the case of AISPc, the metal

TABLE I  
Content of metals in humic substances (relative error 6%)

Humic substance	Fe, $\text{mg g}^{-1}$	Cu, $\mu\text{g g}^{-1}$	Mn, $\mu\text{g g}^{-1}$
HS (Aldrich)	11.4	13.9	9.4
HS (Roth)	10.9	17.5	9.6

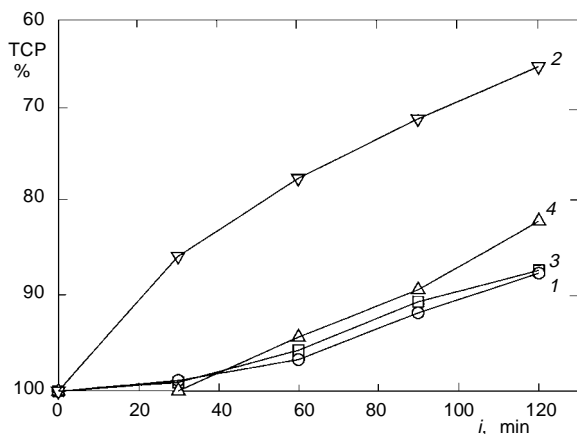


FIG. 6  
Effect of metals on HS photosensitized degradation of 2,4,5-TCP: 1 in the absence of HS; 2 in the presence of HS ( $71 \text{ mg dm}^{-3}$ ). Concentration of added  $\text{Cu}^{2+}$  (3),  $\text{Mn}^{2+}$  (4) was  $90 \mu\text{mol dm}^{-3}$ .  $[\text{2,4,5-TCP}]_0 = 0.5 \text{ mmol dm}^{-3}$ , saturated by  $\text{O}_2$

ions cannot be complexed by the sensitizer and do not compel any changes. Possible complexation of metals by chlorophenols does not influence, under our conditions, the reactivity with singlet oxygen.

## DISCUSSION

Aromatic chromophores distributed over the macromolecule of HS attain high local concentrations and a close face-to-face alignment. This is the reason why HS fluorescence spectra have to be interpreted in terms of excimer and exciplex formation<sup>5,6</sup>, and why the spectra are independent of excitation wavelengths, as we have observed. Similarly, the transient absorption spectrum does not correspond to an individual but to overlapping contributions of species with different fluorescence quantum yields and molar absorption coefficients.

Most chromophores and functional groups of HS have complexing properties and offer a variety of binding sites with high affinity to transition metal ions<sup>9,18</sup>. Binding of extra metal ions definitely induces a new equilibrium as concerns structure of chromophores, aggregation, cooperative interactions, competition among metal ions, interactions between HS and organic contaminants of low molecular weight, *etc.* The changes are too complex to allow any prediction of their effect on the HS photosensitizing activity.

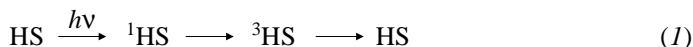
TABLE II

Degradation of 4-CP and 2,4-DCP (in %) photosensitized by HS (Aldrich) after 90 and 120 min irradiation. Relative error 15%. High pressure mercury lamp HBO 500, 500 W (OSRAM), 310–400 nm (4-CP) and 340–510 nm (2,4-DCP) band filters.  $[\text{Substrate}]_0 = 0.5 \text{ mmol dm}^{-3}$ ,  $90 \text{ } \mu\text{mol dm}^{-3}$  added metal, saturated by oxygen, 25 °C

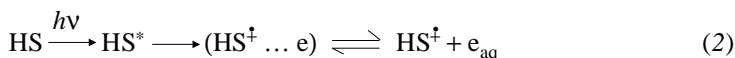
Metal	4-CP, %		2,4-DCP, %	
	90 min	120 min	90 min	120 min
–	5.23 ± 0.02	7.28 ± 0.01	9.9	14.3
Cu <sup>2+,a</sup>	0	0	–	–
Cu <sup>2+</sup>	0	9	6.4 ± 0.8	10.2 ± 2.5
Mn <sup>2+</sup>	4.9 ± 0.7	6.2 ± 0.7	10.1	13.4
Fe <sup>2+</sup>	2.0	4.0	–	–
Fe <sup>3+,b</sup>	24.3	34.2	28.7	36.4
Fe <sup>3+,c</sup>	–	–	12.4	20.0
Fe <sup>3+</sup>	36.7	46.2	–	–

<sup>a</sup> 0.9  $\mu\text{mol dm}^{-3}$  added Cu<sup>2+</sup>. <sup>b</sup> 9  $\mu\text{mol dm}^{-3}$  Fe<sup>2+</sup>. <sup>c</sup> In absence of HS.

Excitation of HS produces primarily excited singlet states (Eq. (1)) and photoionized species (Eq. (2)). Any step in Eqs (1) and (2) can be influenced by metal ions. The direct interaction of HS excited triplet states with chlorophenols can be excluded since the triplet energy of the substrate is much higher than that of HS.



${}^1\text{HS}$  stands for an individual chromophore or an excimer/exciple  ${}^1(\text{A} \dots \text{D})$ .



The fluorophore–metal complexes are usually nonfluorescent. If two fluorophore populations are present and one of them is not accessible to a quencher, then Stern–Volmer plots deviate from linearity<sup>12</sup> (Eq. (3)). The term population embraces in case of HS all fluorophores with a specific behaviour.

$$F_0/(F_0 - F) = 1/(f_a K_{\text{eq}}[\text{Q}]) + 1/f_a \quad (3)$$

$F_0$  and  $F$  are the fluorescence intensities in the absence and in presence of the quencher Q,  $K_{\text{eq}}$  is the association constant. With respect to low concentration of HS in our experiments,  $[\text{Q}]$  equals to the concentration of added  $\text{Cu}^{2+}$ . The blue shift in the HS fluorescence spectrum (Fig. 1) and the Stern–Volmer analysis of  $\text{Cu}^{2+}$  quenching data (Fig. 2) indicate unambiguously static quenching. The fraction of the initial fluorescence accessible to quenching,  $f_a$ , can be determined from the  $F_0/(F_0 - F)$  vs  $1/[\text{Q}]$  plot (Eq. (3)) and amounts to  $(79 \pm 4)\%$ . This set of fluorophores is quenched *via* complex formation and metal-induced changes of HS conformation<sup>19</sup>. The fact that fluorescence of a part of fluorophores remains intact does not necessarily mean that they cannot bind  $\text{Cu}^{2+}$ , but that the binding can be sterically hindered. The lifetimes of HS fluorescence are not changed<sup>20</sup> by  $\text{Cu}^{2+}$ , which is an additional proof of static quenching.

The excited HS absorption spectra are too complex for a complete analysis. The transients can be classified into three classes, according to their kinetics. Transients with the shortest lifetime – excited singlet states and hydrated electrons  $\text{e}_{\text{aq}}$  – form probably the transient **1**. We assume that transient **2** (peak at 440–450 nm) with the lifetime of about 2  $\mu\text{s}$  consists predominantly of cation-radicals. Transient **2** appears to be oxygen-independent, in accordance with the fact that numerous cation-radicals of aromatics do not react with oxygen in aqueous solutions<sup>21</sup>. Transient **2** resembles HS radical-cations formed after immediate electron release<sup>5–7</sup> (Eq. (2)), having a featureless



absorption spectrum with a peak at 475 nm and a lifetime of 1–10  $\mu\text{s}$ . Unlike Fischer *et al.*<sup>7</sup>, we did not observe any dynamic quenching of **2** by dioxygen (Fig. 3); evidently, the contribution of excited triplet states in our samples is less significant. The differences in oxygen quenching and in the absorption spectra probably originate from different HS composition and excitation wavelength ( $\lambda_{\text{exc}}$  355 nm) in refs<sup>5–7</sup>. The long-living transient **3** is a mixture of HS triplet states quenched by oxygen; oxygen-sensitive cation-radicals may also contribute.

The stationary concentration of **2** and **3** decreases as a result of their quenching and/or of quenching of the preceding excited singlet states. This implies that additional binding of metal ions to HS can decrease  $^1\text{O}_2$  ( $\text{O}_2^-$ ) production (Eqs (4a) and (4b)) and suppress the substrate photodegradation.



In spite of the low  $^1\text{O}_2$  quantum yields ( $\Phi_\Delta = 0.005$ , ref.<sup>22</sup>), the decisive role of  $^1\text{O}_2$  in oxidative degradation of some chlorophenols was postulated<sup>23</sup>.

Generally, Cu(II), Fe(II), and Mn(II) are photocatalysts and could accelerate photodegradation of chlorophenols. In our system, however, neither post-irradiation effects nor acceleration have been observed. If  $\text{H}_2\text{O}_2$  were present (low yields for HS were reported<sup>24</sup>),  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$  would have initiated Fenton reaction<sup>25</sup> and accelerate degradation of chlorophenols. Consequently, in our experiments the excited state quenching by  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$  is dominant for HS photosensitizing activity. The combination of both mechanisms, quenching and photocatalysis, accounts for 4-CP and 2,4-DCP insensitivity to  $\text{Mn}^{2+}$ ; in the case of 2,4,5-TCP the quenching, *i.e.* the inhibitive effect, prevails (Fig. 6).

Photosensitized and/or photocatalyzed reactions initiated by direct excitation of unbound Fe(III) in the solution contribute to chlorophenol degradation. This is apparent from the high-rate degradation in absence of HS where all light is exclusively absorbed by Fe(III).

It can be concluded that coordination of metals to HS binding sites modifies considerably its sensitizing properties. The more metal is bound to HS (particularly  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$ ), the less photosensitizing activity can be expected.

*This research was supported by the Grant Agency of the Czech Republic (No. 203/93/0463). The authors wish to thank Mrs J. Brodilova for HPLC and Dr R. Král for AAS analyses.*

## REFERENCES

1. Waite T. D., Sawyer D. T., Zafiriou O. C.: *Appl. Geochem.* 3, 9 (1988).
2. Cooper W. J., Zika R. G., Petasne R. G., Fischer A. M. in: *Advances in Chemistry, Ser. 219, Aquatic Humic Substances* (I. H. Suffet and P. MacCarthy, Eds), p. 333. American Chemical Society, Washington, D.C. 1989.
3. Hoigne J., Faust B. C., Haag W. R., Scully F. E., Zepp R. G.: *Ref.*<sup>2</sup>, p. 363.
4. Murray K., Linder P. W.: *J. Soil Sci.* 35, 217 (1984).
5. Power J. F., Sharma D. K., Langford C. H., Bonneau R., Jousset-Dubien J.: *Photochem. Photobiol.* 44, 11 (1986).
6. Power J. F., Sharma D. K., Langford C. H., Bonneau R., Jousset-Dubien J. in: *ACS Symp. Ser. 327, Photochemistry of Environmental Aquatic Systems* (R. G. Zika and W. J. Cooper, Eds), p. 157. American Chemical Society, Washington, D.C. 1987.
7. Fischer A. M., Winterle J. S., Mill T.: *Ref.*<sup>6</sup>, p. 141.
8. Frimmel F. H., Bauer H., Putzien J., Murasecco P., Braun A. M.: *Environ. Sci. Technol.* 21, 541 (1987).
9. Schnitzer M., Skinner S. I. M.: *Soil Sci.* 103, 247 (1966).
10. Lunak S., Sedlak P., Brodilova J., Lederer P.: *Tetrahedron Lett.* 30, 2277 (1989).
11. Klementova S., Wagnerova D. M.: *Collect. Czech. Chem. Commun.* 59, 1066 (1994).
12. Lakowitz J. R.: *Principles of Fluorescence Spectroscopy*, p. 280. Plenum Press, New York and London 1983.
13. Jaff R.: *Environ. Pollut.* 69, 237 (1991).
14. Kawaguchi H.: *Chemosphere* 25, 635 (1992).
15. Robinson K. C., Novak J. T.: *Water Res.* 28, 445 (1994).
16. Lang K., Wagnerova D. M., Engst P., Kubat P.: *J. Chem. Soc., Faraday Trans.* 88, 677 (1992).
17. Wilkinson F., Helman W. P., Ross A. B.: *J. Phys. Chem. Ref. Data* 22, 113 (1993).
18. *Interaction with Metals, Minerals and Organic Chemicals* (P. MacCharthy, M. B. H. Hayes, R. L. Malcolm and A. S. Swift, Eds). Wiley-Interscience, Chichester 1991.
19. Underdown A. W., Langford C. H., Gamble D. S.: *Environ. Sci. Technol.* 19, 132 (1985).
20. Milne P. J., Zika R. G.: *Marine Chem.* 27, 147 (1989).
21. Joschek H.-I., Grossweiner L. I.: *J. Am. Chem. Soc.* 88, 3261 (1966).
22. Haag W. R., Hoigne J., Gassman E., Braun A. M.: *Chemosphere* 13, 641 (1984).
23. Scully F. E., Hoigne J.: *Chemosphere* 14, 1659 (1985).
24. Cooper W. J., Zika R. G., Petasne R. G., Plane J. M. C.: *Environ. Sci. Technol.* 22, 1156 (1988).
25. Lang K., Wagnerova D. M., Brodilova J.: *Collect. Czech. Chem. Commun.* 59, 2447 (1994).