

Efficiency of singlet oxygen generation by fulvic acids and its influence on UV photodegradation of herbicide Amitrole in aqueous solutions

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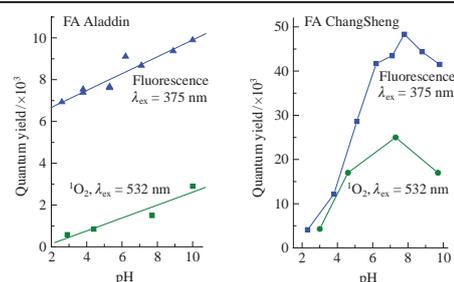
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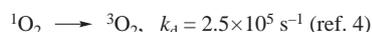
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DOI: 10.1016/j.mencom.2017.07.028

pH-dependent efficiency of singlet oxygen ($^1\text{O}_2$) generation by fulvic acids (FAs) from different sources was estimated by time-resolved luminescence technique. All FAs turn up the highest quantum yields of $^1\text{O}_2$ for neutral and alkali solutions [$\phi^{532}(^1\text{O}_2) = (0.3\text{--}2.5)\times 10^{-2}$] and 3–5-fold decrease in $\phi^{532}(^1\text{O}_2)$ for acidic solutions. Potential of FA ChangSheng (the best $^1\text{O}_2$ generating agent among investigated FAs) in relation to photodegradation of non-UVA-absorbing herbicide Amitrole (3-amino-1,2,4-triazole) was demonstrated.



Humic and fulvic acids (or more generally humic substances, HS) are the common components of natural waters which are involved in variety of photochemical processes under sunlight irradiation.¹ As a primary active species, aquated electrons and triplet states (^3HS) were formed *via* the irradiation of HS and subsequently transformed to so-called reactive oxygen species (ROS, *i.e.* singlet oxygen, hydrogen peroxide, $\cdot\text{OH}$ and HO_2 radicals).^{1,2} Participation of these species in oxidation of different contaminants, including pesticides in natural waters, was investigated previously.³ Among all ROS, the singlet oxygen is produced in the highest rate and this species exhibits the rather high steady-state concentration in sunlit natural waters.² Singlet oxygen is produced in reaction of ^3HS with dissolved oxygen and its decay in aqueous solution is mainly determined by interaction with the solvent.



Although formation of singlet oxygen *via* excitation of HS was demonstrated repeatedly,^{2,5,6} little attention was paid both to pH influence on singlet oxygen photoproduction rate and correlation between fluorescence and $^1\text{O}_2$ quantum yields for these compounds. Such correlation gives a possibility to use common steady-state fluorimetry instead of relatively rare near-IR luminescence technique (for direct $^1\text{O}_2$ detection) or time-consuming HPLC technique (for indirect $^1\text{O}_2$ detection with the use of chemical traps).

The aim of this work was to obtain quantitative information regarding the quantum yields of fluorescence and $^1\text{O}_2$ production for a number of fulvic acids (FAs),[†] to explore the correlation between these parameters, and to estimate the possibility of photo-oxidation of non-UVA-absorbing herbicide Amitrole (3-AT) in the presence of these FAs in aqueous solution. This particular herbicide was chosen due to the following reasons. (1) 3-AT is a

well-known non-selective herbicide which is often used in weed control⁷ and largely employed to substitute some banned herbicides. Due to its good solubility in water, it could be found in relatively considerable amount in natural waters. (2) Up to now, only one work concerning influence of HS on degradation of 3-AT was published without any details regarding mechanism of this process.⁸ (3) 3-AT is a heterocyclic organic compound, *viz.*, 3-amino-1,2,4-triazole. It is known that $^1\text{O}_2$ reacts effectively with triazoles and similar compounds by 1,4-cycloaddition to give unstable endoperoxides.⁹

Absorption and fluorescent (excitation at 375 nm) spectra of FAs at pH 7 are presented in Figure 1.[‡] Typical of HS practically exponential decrease in structureless absorption with increasing of wavelength¹⁵ was observed for all FAs. The only exception is CS demonstrating a rather well-pronounced shoulder at ~470 nm.

[†] Fulvic acids (AL, Aladdin Industrial Corporation, H108498, CAS: 1415-93-6; CS, Henan ChangSheng Corporation; NA, Nordic Acid, IHSS reference, 1R105F; WP, Waskish Peat, IHSS reference 1R107F) and 3-amino-1,2,4-triazole (95%, Sigma Aldrich, CAS 61-82-5) were used without additional purification. All compounds are fully soluble in water at concentrations $< 500 \text{ mg dm}^{-3}$ in pH range 3–10. pH value was controlled by an Anion-4100 ionometer (Infrapak-Analit, Russia) with combined electrode ESK-10614. NaOH or HClO_4 (analytical grade) were used for pH adjustment. Deionized water was used for solution preparation.

[‡] UV spectra were recorded using an Agilent 8453 spectrophotometer (Agilent Technologies). The fluorescence spectra and kinetics were measured using a FLSP920 spectrofluorimeter (Edinburg Instruments). As excitation sources, ozone free xenon lamp Xe900 ($\lambda_{\text{ex}} = 375 \text{ nm}$) and diode laser EPL-375 (Edinburg Instruments, $\lambda_{\text{ex}} = 375 \text{ nm}$, pulse duration of 75 ps) were used. The fluorescence quantum yields of FAs was determined as described¹⁰ using solutions of quinine sulfate in 0.5 M H_2SO_4 ($\phi_{\text{fl}} = 0.546$) as a standard. Stationary photolysis was performed in a quartz cell with an optical path 1 cm at 298 K using high-pressure mercury lamp (DRSh-500) with water and glass filters for separating the 365 nm mercury line. Lamp intensity was determined by a ferrioxalate actinometer in the same photochemical cell.¹¹

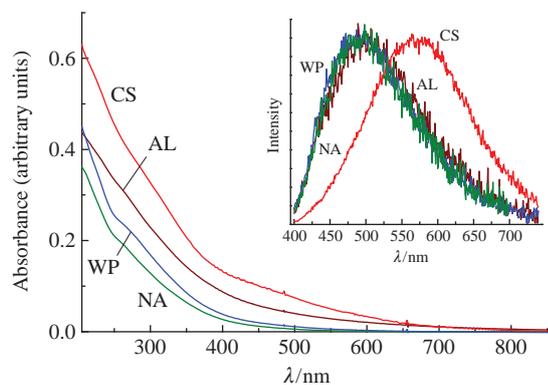


Figure 1 Absorption spectra of FAs at pH 7. Insert: their fluorescence spectra. The concentrations of FAs are 10 mg dm^{-3} .

Table 1 Fluorescence maximum ($\lambda_{\text{fl}}^{375}$), fluorescence quantum yield (ϕ_{fl}^{375}), and singlet oxygen quantum yield [$\phi^{532}(^1\text{O}_2)$] at pH 3 and 10 for investigated FAs. The accuracy of quantum yield measurement is about 10%.

Acid	pH 3			pH 10		
	$\lambda_{\text{fl}}^{375}/\text{nm}$	ϕ_{fl}^{375}	$\phi^{532}(^1\text{O}_2)$	$\lambda_{\text{fl}}^{375}/\text{nm}$	ϕ_{fl}^{375}	$\phi^{532}(^1\text{O}_2)$
CS	540	0.008	0.0044	570	0.040	0.0170
AL	475	0.070	0.0006	515	0.100	0.0029
NA	485	0.015	0.0019	500	0.015	0.0058
WP	480	0.014	0.0010	490	0.018	0.0036

For all FAs both quantum yield of fluorescence (ϕ_{fl}^{375}) and emission maximum ($\lambda_{\text{fl}}^{375}$) are pH-sensitive and increase of pH from 3 to 10 generally results in 3–5-fold enhancement of fluorescence intensity and fluorescence maximum shift of 10–40 nm (Table 1). That is probably attributed to the acid-base equilibria of the chromophores of FAs and the quenching of the singlet excited states of chromophores by protons in media as well.

Note that CS demonstrates the highest ϕ_{fl}^{375} value of 0.05 at pH 7 and exhibits a red-shift of emission maximum of about 70 nm in comparison with other FAs (Table 1).⁸ In our recent publication¹⁶ the maximum of triplet state generation upon excitation of CS at 355 nm also appeared to be under neutral pH. This fact indicates that, possessing high quantum yields of fluorescence and triplet state generation, this FA readily forms the singlet states at pH ~ 7.

The quantum yield of singlet oxygen generation at excitation wavelength of 532 nm [$\phi^{532}(^1\text{O}_2)$] turns up pH-dependence which is similar to that observed for ϕ_{fl}^{375} (Figure 2, Table 1). Moreover, the values obtained are within the typical range of $\phi(^1\text{O}_2)$ for HS.^{5,6} That is due to close correlation between quantum yields of fluorescence and singlet oxygen production [and, apparently, triplet state formation quantum yield (ϕ_{T})] for FAs. If this correlation is of general character it can serve as a good approach to the fast estimation of relative ϕ_{T} and $\phi(^1\text{O}_2)$ values using simple and wide-spread fluorescence technique.

High value of singlet oxygen quantum yield found for CS fulvic acid [$\phi^{532}(^1\text{O}_2) = 2.5 \times 10^{-2}$ at pH 7] allows one to propose efficient 3-AT photodegradation in the presence of this FA. It should be expected that decrease in excitation wavelength from 532 to 365 nm would result in twofold increase in $\phi(^1\text{O}_2)$ value.⁵

⁸ Kinetics of singlet oxygen luminescence was detected with the use of the installation based on a laser fluorimeter, designed in the Institute of Physics of NASB.¹² Excitation of samples was accomplished by Nd:YAG-laser (DTL-314QT, Laser-export Co. Ltd, Russia) pulses (duration of pulse 10 ns, energy 20 μJ , frequency 2.5 kHz at $\lambda = 532 \text{ nm}$). The band-pass interference filter (maximum at 1272 nm, halfwidth 34 nm) was used for spectral selection. Quantum yields of singlet oxygen formation $\phi^{532}(^1\text{O}_2)$ were determined as described¹³ using *meso*-tetra(*N*-methyl-4-pyridyl)porphyrin (TMpyP) tosylate as a standard, $\phi^{532}(^1\text{O}_2) = 0.77$.¹⁴

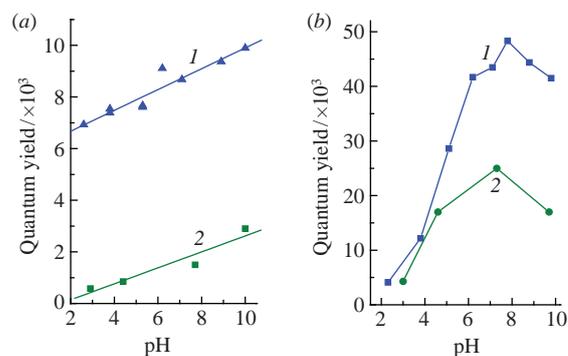


Figure 2 pH-dependence of (1) fluorescence (excitation at $\lambda = 375 \text{ nm}$) and (2) singlet oxygen (excitation at $\lambda = 532 \text{ nm}$) quantum yields for (a) AL and (b) CS.

Indeed, steady-state irradiation of air-equilibrated solution of 3-AT (8.4 mg dm^{-3}) and CS (3.6 mg dm^{-3}) at 365 nm leads to disappearance of 3-AT absorption peak at 200 nm and formation of photoproducts with absorption at 233 and ~260 nm (Figure 3). Note that absorption of CS itself also disappeared after UVA irradiation indicating that the fulvic acid was partially oxidized by reactive species generated upon its excitation.¹⁷ 3-AT itself ($\lambda_{\text{max}} = 198 \text{ nm}$, $\epsilon_{\text{nm}}^{198} = 5200 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) exhibits negligible absorption at wavelengths higher than 250 nm and it is stable under UVA irradiation.

Therefore, $^1\text{O}_2$ can be considered as a key intermediate in photooxidation of 3-AT in the presence of CS and other FAs. Note that primary active species (the aquated electron, the triplet state) or other ROS (hydrogen peroxide, $\cdot\text{OH}$ and $\text{HO}_2\cdot$ radicals) probably participate in the photodegradation process as well.^{1,2,18,19} Determination of detailed mechanism, quantum yields, and final products of 3-AT photodegradation is out of scope of the current work and will be a subject of next publications.

In conclusion, pH-dependent efficiency of $^1\text{O}_2$ generation by several fulvic acids (FAs) under visible (532 nm) light has been studied by the time-resolved luminescence technique. All investigated FAs demonstrate the highest quantum yields of $^1\text{O}_2$ for neutral and alkali solutions and their 3–5-fold decrease for acidic solutions. pH dependences of the quantum yield of FAs fluorescence and $\phi^{532}(^1\text{O}_2)$ are similar to each other indicating that the last one correlates with efficiency of internal conversion in the singlet excited state of FAs. Potential of these FAs toward photodegradation of non-UVA-absorbing herbicides like 3-AT upon irradiation at 365 nm has been demonstrated.

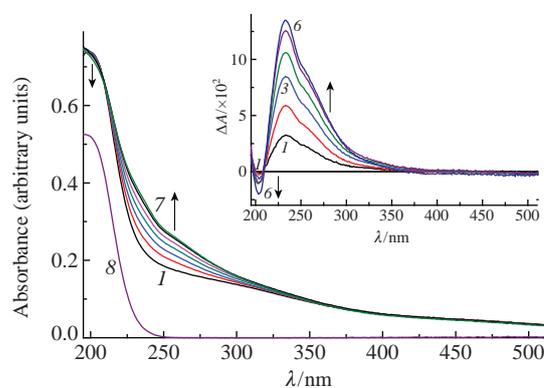


Figure 3 Absorption spectra of 3-AT (8.4 mg dm^{-3}) and CS (3.6 mg dm^{-3}) aqueous solutions at pH 6.3 during steady-state irradiation ($\lambda = 365 \text{ nm}$): (1–7) 0, 30, 60, 90, 120, 150 and 180 min of irradiation, respectively, (8) absorption spectrum of 3-AT solution (8.4 mg dm^{-3}). Insert: differential absorption spectra under the same conditions (1) 30–0 min, (2) 60–0 min, (3) 90–0 min, (4) 120–0 min, (5) 150–0 min and (6) 180–0 min. Incident light energy is 1.8 J min^{-1} . CS absorbs 17% of incident energy at 365 nm.

This work was supported by the Russian Foundation for Basic Research (grant nos. 15-03-03376_a, 14-03-00692_a and 16-33-00335 mol_a) and the Belarusian Republican Foundation for Fundamental Research (joint project BRFFR–SB RAS no. F15SO-036).

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Received: 24th November 2016; Com. 16/5102