Photooxidation of phenol in aqueous nanodispersion of humic acid

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Abstract

Photooxidation of phenol sensitized by Aldrich humic acid (AHA) has been studied in an aqueous solution at neutral and basic pH. Solutions containing phenol and AHA of various concentrations were irradiated with monochromatic light at 253.7 nm or with polychromatic light within the wavelength range of 310–420 nm. The quantum yields of phenol photodegradation under these conditions were determined. At the wavelength of 253.7 nm direct degradation of phenol was much more effective than that sensitized by AHA. With polychromatic light the photooxidation was found to be strongly dependent on pH of aqueous solution and independent on AHA concentration.
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1. Introduction

Humic substances (HS) are ubiquitous, heterogeneous polymeric organic materials, which play an important role in the photochemical processes occurring in surface waters. Humic acids (HA) belong to a subclass of HS, which consists of the fraction of humic substances that is precipitated from aqueous alkaline extracts of soil when the pH is decreased below two [1]. Upon electronic excitation, HA produce reactive species, which can transform a great variety of organic compounds [2]. There is a growing interest in studies of the role of HA as the photosensitizers or photoinitiators in the degradation of pollutants present in water [3].

Phenols are widely spread and very common contaminants of water. Several various methods including ultrasound/H_2O_2 or ozone, UV/H_2O_2 or ozone, ozone/H_2O_2, sonophotochemical oxidation, photo-Fenton processes, catalytic advanced oxidation processes have been proposed for the treatment of wastewater containing phenolic pollutants [4]. There have been a number of attempts to use HA to enhance photodegradation of phenolic compounds in aqueous solution [5–11]. But the majority of the studies were done at acidic pH. There is also little quantitative data, such as quantum yields, in literature concerning degradation of phenol photosensitized by HA. Therefore, the aim of this work was to obtain quantitative data on the efficiency of oxidation of phenol photosensitized by HA. A commercial Aldrich humic acid (AHA) was chosen as a model photosensitizer. The photoinductive properties of the humic material arise from the present chromophores and are not greatly influenced by the origin of the material [7]. The effect of various parameters such as the wavelength of the light used for irradiation, pH of the aqueous solution (especially pH >7), and concentration of AHA was studied. The quantum yields of the processes occurring in the system were determined.

2. Experimental details

2.1. Materials and methods

Humic acid sodium salt was obtained from Aldrich Chemical Co. (Milwaukee, WI). Phenol (PhOH) (POCh, Gliwice; pure for analysis) was purified by sublimation before use. *p*-Benzoquinone (BQ) (POCh, Gliwice, pure) was crystallized from hexane. Hydroquinone (POCh, Gliwice, pure), resorcinol (99%, Aldrich), pyrocatechol (≥99%, Aldrich), *N,N*-dimethyl-4-nitrosoaniline (RNO, Aldrich, 97%) and imidazole (Aldrich; 99%) were used without further purification. K[Cr(NH_3)$_2$(SCN)$_4$] was obtained from the commercial Reinecke's salt and purified according to the procedure in the

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literature [12]. Aqueous solutions of the reactants were prepared using deionized doubly distilled water. The pH of the solutions was adjusted by using 10 mM phosphate buffer solutions.

The solutions of AHA were prepared according to the following procedure. A desired amount of AHA was dissolved in buffer solution. The solution was sonicated for 10 min at 20 °C in a Bronsonic ultrasonic bath and filtered over a 0.45 μm membrane filter to remove non-dissolved aggregates. The effective concentration of the dissolved AHA was determined from the absorption spectrum using the specific ultraviolet absorbance at 254 nm (SUVA254) of 0.067 cm^{-1}/mg of organic carbon [13] and the organic carbon contents of 41.9 wt.% [8].

2.2. Apparatus and procedures

UV–vis absorption spectra were recorded at room temperature using a Hewlett-Packard 8452A diode array spectrophotometer equipped with a HP 89090A Peltier temperature control accessory. A Malvern Nano ZS light-scattering apparatus (Malvern Instrument Ltd., Worcestershire, UK) was used for dynamic light scattering (DLS) measurements. The samples were illuminated with a 633 nm laser, and the intensity of light scattered at an angle of 173° was measured by an avalanche photodiode. The z-average diameter (dz) and the polydispersity index (PD) of the samples were automatically provided by the instrument using cumulant analysis.

2.2.1. Irradiation of the samples

The samples were irradiated using the Rayonet RPR-100 photoreactor equipped with lamps emitting UV radiation at 253.7 or the polychromatic light within the wavelength range 310–420 nm with a maximum located at 350 nm. The photochemical experiments were carried out as follows. In a typical experiment, 10 cm^3 of aqueous solution of phenol (1×10^{-3} mol dm^{-3}) and required amount of AHA was placed in the reaction vessel (a quartz tube RQV-7, Rayonet, 175 mm × 13 mm). The tube was placed in the center of the reactor. A distance between the tube and lamps was 100 mm. Oxygen gas was bubbled continuously through the solution during irradiation.

For irradiations carried out with polychromatic light (310–420 nm), the photon flow emitted by the lamp was determined using the potassium reineckate actinometer, K[Cr(NH$_3$)$_2$(SCN)$_4$] [12]. The concentration of potassium Reinecke's salt was 1.24×10^{-2} mol dm^{-3} at 5.3 <pH<5.5 and the solution was bubbled with argon during irradiation. The rate of reaction in the actinometer solution, V_r, was measured. That rate can be expressed as follows:

$$V_r = I_{350} \int_\lambda \phi_R(\lambda) F_{350}(\lambda)(1 - 10^{-A_R(\lambda)}) \, d\lambda \qquad (1)$$

where $\phi_R(\lambda)$ is quantum yield of the reaction, $A_R(\lambda)$ the absorbance of Reinecke salt and $F(\lambda)$ is the spectral distribution of the light emitted by the lamp given as $I(\lambda) = I_{350} F_{350}(\lambda)$. The spectral distribution is shown in Fig. 1.
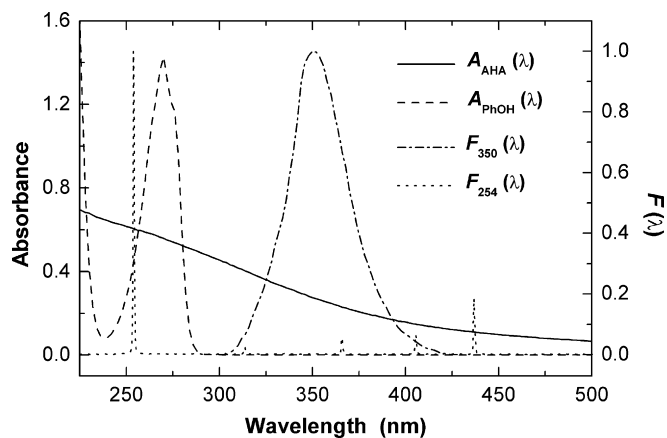

Fig. 1. Spectral characteristics of the studied system; $A_{AHA}(\lambda)$ and $A_{PhOH}(\lambda)$ are absorption spectra of AHA ($c_{AHA} = 0.02$ g dm^{-3}, pH 6.9) and phenol ($c_{PhOH} = 1 \times 10^{-3}$ mol dm^{-3}, pH 6.9), respectively; $F_{254}(\lambda)$ and $F_{350}(\lambda)$ are the spectral distributions of the light emitted by the lamps emitting UV radiation at 253.7 nm and within the wavelength range 310–420 nm, respectively.

2.2.2. HPLC chromatography analyses

The analyses of the systems during irradiation were performed by means of an HPLC Waters system equipped with a Symmetry C-18 column (15 cm length), a Waters 518 isocratic pump and a Waters 2487 Dual λ Absorbance detector. A mixture (50/50, v/v) of methanol and 0.1% aqueous solution of phosphoric acid was used as an eluent. Concentrations of phenol were calculated from calibration equation determined prior to the analysis.

3. Results

The electronic absorption spectrum of AHA aqueous solution ($c = 0.02$ g dm^{-3}) is shown in Fig. 1. AHA shows broad and featureless absorption in the range of 200–400 nm. For the wavelength higher than 400 nm the absorption gradually decreases with an increase of the wavelength. There are no changes in the shape of the spectrum with increasing the solution pH from 6.9 to 10.

3.1. Irradiation at 253.7 nm

Oxygen-saturated solutions of phenol (1×10^{-3} mol dm^{-3}) and AHA (0–0.5 g dm^{-3}) buffered at pH 6.9 or 9.1 were irradiated at 253.7 nm. The experimental details are presented in Table 1. The reaction was followed by the HPLC analyses. Fig. 2 shows HPLC traces obtained for the solution after various times of irradiation of solution **3** (see Table 1 for details). It was observed that irradiation resulted in a decrease in concentration of phenol (peak 'd' at the retention time of 4.35 min). Simultaneously, new peaks appeared in the chromatograms of the irradiated solutions at retention times of 1.98, 2.39 and 2.86 min. The products were identified as hydroquinone, resorcinol and pyrocatechol, respectively, by comparison with the standard substances. The arising photoproducts are derivatives of phenol and therefore they can undergo further oxidation under these con-

Table 1
Experimental data for photosensitized oxidation of phenol in solution irradiated at 253.7 nm

Solution	pH	AHA (g dm^{-3})	f_{PhOH}	f_{AHA}	$k_r \times 10^4$ (s^{-1})	$V_r^0 \times 10^7$ (mol dm^{-3} s^{-1})
1	6.9	0	0.5995	0	2.58 ± 0.04	2.56 ± 0.05
2	6.9	0.005	0.522	0.2133	2.47 ± 0.03	2.40 ± 0.04
3	6.9	0.01	0.4586	0.3789	2.29 ± 0.03	2.25 ± 0.04
4	6.9	0.05	0.2131	0.9421	1.57 ± 0.03	1.55 ± 0.04
5	6.9	0.1	0.1224	1.1269	0.988 ± 0.02	0.959 ± 0.022
6	6.9	0.15	0.0856	1.2009	0.690 ± 0.024	0.670 ± 0.025
7	6.9	0.5	0.0276	1.2936	0.286 ± 0.024	0.279 ± 0.024
8	9.1	0			2.94 ± 0.04	2.61 ± 0.05
9	9.1	0.1			1.20 ± 0.02	1.20 ± 0.03

ditions. As can be seen in Fig. 2, they were consumed when irradiation was prolonged.

Fig. 3 shows the changes in the concentration of phenol observed during irradiation of aqueous solutions containing different amounts of AHA. Plots of ln([PhOH]$_0$/[PhOH]) versus irradiation time were linear, indicating that the kinetics of the reaction is first-order with respect to the substrate. Apparent first-order rate constants (k_r) were obtained by linear regression and the values are collected in Table 1. They decrease with an increase of AHA concentration. An effect of pH can be noticed; the values of k_r are slightly higher at pH 9.1 than those at pH 6.9 for the same concentration of HA. The initial rates of reaction,

V_r^0, were determined from the rate constants for early stage of the reaction. The results are listed in Table 1.

The incident radiation is absorbed by both PhOH and AHA (see Fig. 1). Thus there are two pathways of substrate disappearance: direct photodegradation and photodegradation induced by excitation of the humic acid. The rate of phenol consumption can be given as follows:

$$-\frac{d[PhOH]}{dt} = I_{abs}^{PhOH}\phi_d + I_{abs}^{AHA}\phi_i \qquad (2)$$

ϕ_d and ϕ_i are the quantum yields of direct and induced degradation of phenol; I_{abs}^{PhOH} and I_{abs}^{HA} are the photon flows absorbed by PhOH and humic acid, respectively, which can be calculated according to Eq. (3)

$$I_{abs}^k = I_{254} \int_\lambda \frac{A_k(\lambda)}{A(\lambda)} F_{254}(\lambda)(1 - 10^{-A(\lambda)})d\lambda = I_{254} f_k$$

$$(k = AHA \text{ or } PhOH) \qquad (3)$$

where $A(\lambda)$ is the sum of absorbance of AHA ($A_{AHA}(\lambda)$) and PhOH ($A_{PhOH}(\lambda)$) at given wavelength; $F_{254}(\lambda)$ is the spectral distribution of the light emitted by the lamps given as $I(\lambda) = I_{254} F_{254}(\lambda)$. $F_{254}(\lambda)$ is normalized to unity at wavelength of 253.7 nm. f_{AHA} and f_{PhOH} are the fraction of the light absorbed by AHA and PhOH, respectively. The calculated values of f_k are
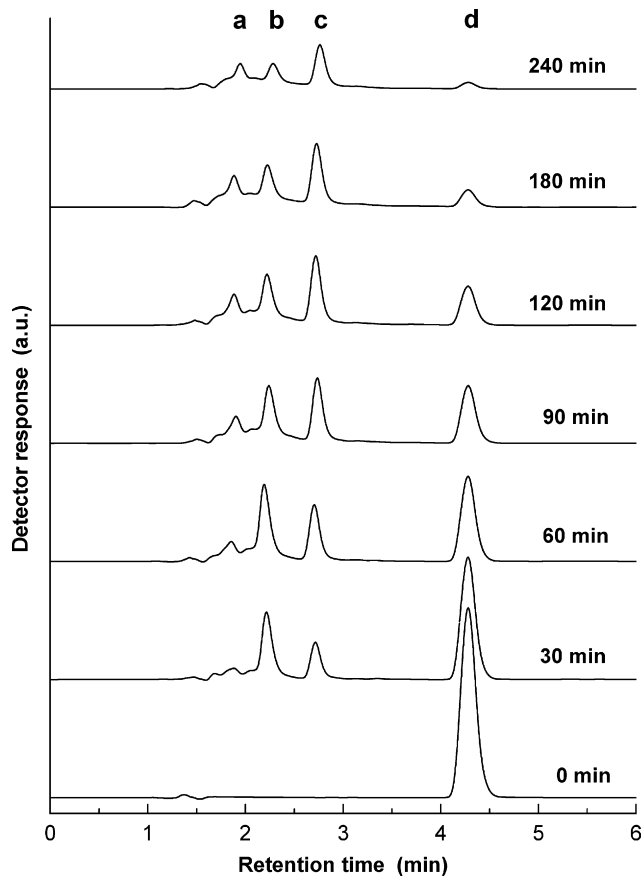
Fig. 2. HPLC chromatograms taken after irradiation at 253.7 nm of the solution **3** ($c_{PhOH} = 1 \times 10^{-3}$ mol dm^{-3}, $c_{AHA} = 0.01$ g dm^{-3}, pH 6.9); (a) hydroquinone, (b) resorcinol, (c) pyrocatechol and (d) phenol.
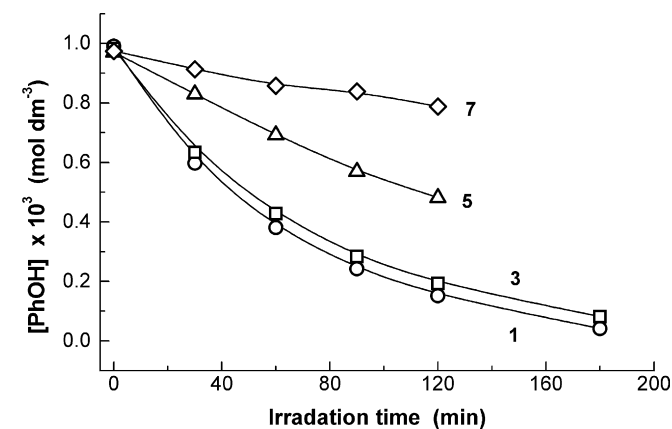
Fig. 3. Changes in the concentration of phenol on irradiation time ($\lambda = 253.7$ nm) of aqueous solutions (pH 6.9) containing various concentrations of HA: (solution **1**) 0.0 g dm^{-3}; (solution **3**) 0.01 g dm^{-3}; (solution **5**) 0.1 g dm^{-3}; (solution **7**) 0.5 g dm^{-3}.

Table 2
Experimental data for photosensitized oxidation of phenol in solution irradiated with polychromatic light (310–420 nm)

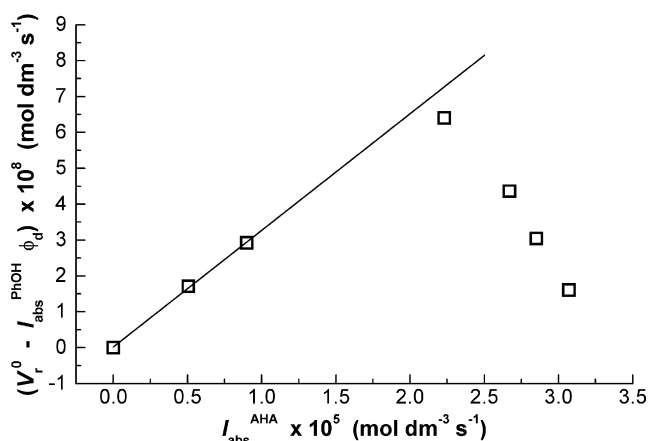| Solution	pH	AHA (g dm^{-3})	$k_r \times 10^4$ (s^{-1})	$V_r^0 \times 10^7$ (mol dm^{-3} s^{-1})	$\phi_i \times 10^3$ ($\pm 10\%$)
10	6.9	0.1	–	0.256[a]	0.96
11	9.1	0.1	–	0.433[a]	1.6
12	10.8	0.01	0.405 ± 0.008	0.40 ± 0.01	5.4
13	10.8	0.1	1.27 ± 0.02	1.23 ± 0.03	4.6
14	10.8	0.5	2.28 ± 0.03	2.16 ± 0.04	7.6

[a] Values estimated from the dependencies of phenol concentration on irradiation time for early stage of the reaction.

Fig. 4. Dependence of the left side of Eq. (4) on the light intensities absorbed by humic acid (irradiation at 253.7 nm).

collected in Table 1. The quantum yield of direct degradation of phenol with UV light at pH 6.2 was found earlier to be 0.018[1] [14]. Thus, we have used the solution **1** as an actinometer system to determine I_{254}.

For early stage of the reaction we can rearrange Eq. (2) as follows:

$$V_r^0 - I_{abs}^{PhOH}\phi_d = I_{abs}^{AHA}\phi_i \qquad (4)$$

according to the above equation a plot of $V_r^0 - I_{abs}^{PhOH}\phi_d$ versus the photon flows absorbed by humic acid should be linear with slope equal to the quantum yield of degradation of PhOH induced by AHA. Fig. 4 shows the dependence of the left side of Eq. (4) on I_{abs}^{AHA}.

Indeed, for the solution where the concentration of AHA was lower than 0.05 g dm^{-3} the dependence is linear with the slope being 3.25×10^{-3}. That value corresponds to the quantum yield of degradation of PhOH photoinduced by AHA. One can observe that when the concentration of AHA increases, the value of the left side of Eq. (4) drops off dramatically.

The value of ϕ_i determined in this work compares quite well with the literature values found for 4-nitrophenol [6]. The quantum yields of degradation of 4-nitrophenol induced by Aldrich HA at pH 6.5 in oxygen-saturated solution irradiated at 253.7 nm was found to be 1.6×10^{-3}.

3.2. Irradiation with polychromatic light in the wavelength range 310–420 nm

Oxygen-saturated solutions of phenol (1×10^{-3} mol dm^{-3}) and AHA at various concentrations buffered at pH 6.9, 9.1 or 10.8 were irradiated with light in the range of 310–420 nm. The details are presented in Table 2. The reaction was followed by the HPLC analyses. Fig. 5 depicts the changes in the concentration of phenol on irradiation time. Plots of ln([PhOH]$_0$/[PhOH]) versus irradiation time (not shown) are linear, indicating that the reaction is first-order with respect to the substrate. The values of the apparent first-order rate constants of the process increase with an increase of AHA concentration. The initial rates of reaction, V_r^0, for the solutions at pH 10.8 were determined from the rate constants for early stage of the reaction. In the case of lower pH plots of ln([PhOH]$_0$/[PhOH]) versus irradiation time were not linear (data not shown) and the values of V_r^0 were estimated from the dependencies of phenol concentration on irradiation time for early stage of the reaction. The results are listed in Table 2. The kinetics of the process is strongly dependent on concentration of AHA and pH of the irradiated solution.
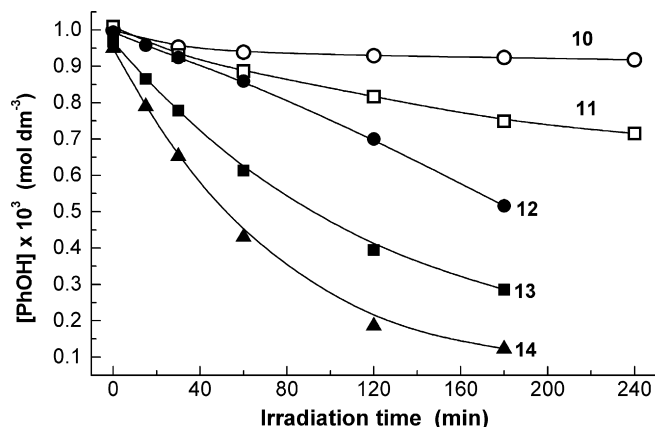

Fig. 5. Changes in the concentration of phenol on irradiation time (310 nm $\leq \lambda \leq$ 420 nm) of aqueous solutions at different pH and containing various concentrations of HA: (solution **10**) pH 6.9, [HA] = 0.1 g dm^{-3}; (solution **11**) pH 9.1, [HA] = 0.1 g dm^{-3}; (solution **12**) pH 10.8, [HA] = 0.01 g dm^{-3}; (solution **13**) pH 10.8, [HA] = 0.1 g dm^{-3}; (solution **14**) pH 10.8, [HA] = 0.5 g dm^{-3}.

Under current experimental conditions the incident light is absorbed only by AHA (see Fig. 1). As a consequence, the photodegradation of PhOH in the presence of AHA is only attributable to photosensitized reactions. Phenol does not absorb light above 300 nm thus the direct photolysis can be excluded. The quantum yield of photooxidation of phenol, ϕ_i, can be calculated using Eq. (5):

$$\phi_i = \frac{V_r^0}{I_{abs}^{AHA}} \tag{5}$$

The mean photon flow absorbed by HA, I_{abs}^{AHA}, was calculated according to the following equation:

$$\bar{I}_{abs}^{AHA} = I_{350} \int_{\lambda} F_{350}(\lambda)(1 - 10^{-A_{AHA}(\lambda)})\, d\lambda = I_{350} f_{AHA} \tag{6}$$

where $A_{AHA}(\lambda)$ is the absorbance of AHA and $F(\lambda)$ is the spectral distribution of the light emitted by the lamps given as $I(\lambda) = I_{350} F_{350}(\lambda)$. The spectral distribution is shown in Fig. 1.

The determined values of ϕ_i are collected in Table 2. From these values it can be concluded that the quantum yield increases with an increase of the pH and it is constant (within the error limits) with changes of sensitizer concentration.

It is difficult to find a suitable literature data for PhOH to compare with our results. The value of quantum yield of 2,4,6-trimethylphenol (TMP) degradation induced by Aldrich HA at pH 6.5 was determined to be 6.9×10^{-3} [8].

3.3. Singlet oxygen formation by AHA in the aqueous solution

The quantum yield of singlet oxygen formation (Φ_Δ) by AHA in aqueous environment was determined using the spectrophotometric method described in the literature [15,16]. The procedure is based on a secondary bleaching of RNO induced by the reaction of $^1O_2$ with imidazole. The intermediate product of the reaction of $^1O_2$ with the imidazole, a transannular peroxide, causes the bleaching of RNO. The kinetics of the degradation of RNO was followed by the measurement of decrease of absorbance at 440 nm.

The irradiation of solutions containing AHA (0.01 g dm^{-3}), imidazole (8×10^{-3}–1×10^{-2} mol dm^{-3}) and RNO (the initial concentration was 5×10^{-5} mol dm^{-3}) with the polychromatic light were carried out. Under our experimental conditions, imidazole being in large excess and changes of RNO being kept under 10% of its initial concentration, zero order kinetics for decay were observed with a slope proportional to the quantum yield of singlet oxygen formation. The value of Φ_Δ can be calculated using the following expression:

$$[RNO] = [RNO]_0 - I_{abs}^{AHA} \Phi_\Delta t \tag{7}$$

Fig. 6 shows the dependence of the concentration of RNO on irradiation time. The dependence is linear. Based on the above presented experimental data, the quantum yield of singlet oxygen formation by AHA was determined to be 7.89×10^{-4} and 6.52×10^{-4} for imidazole concentration of 8×10^{-3} mol dm^{-3} and 1×10^{-2} mol dm^{-3}, respectively. The values of Φ_Δ are
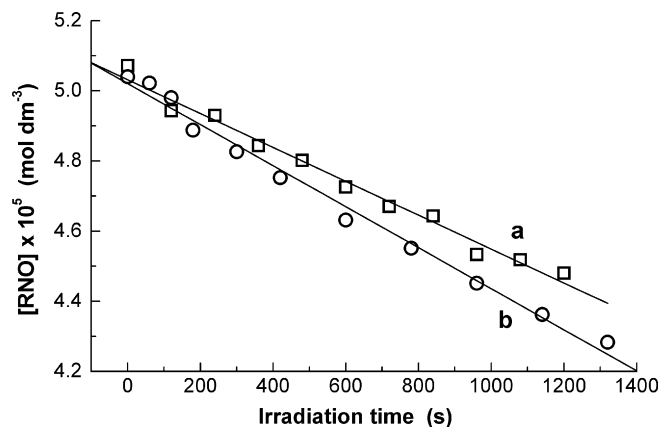

Fig. 6. Changes in the concentration of RNO on irradiation time (310 nm < λ < 420 nm) of aqueous solutions containing AHA (0.01 g dm^{-3}) and various concentrations of imidazole: (a) 1×10^{-2} mol dm^{-3} and (b) 8×10^{-3} mol dm^{-3}.

comparable with that evaluated for AHA to be about 10^{-3} at 404 nm in air-saturated solutions with furoin as a singlet oxygen acceptor reported by Aquer and Richard [6]. But they are lower than that found by the same authors later; the quantum yields of production at 365 nm irradiance were evaluated to be 0.002 in air-saturated solution and 0.0045 in oxygen-saturated medium [7].

3.4. DLS measurements of AHA

Because of their amphiphilic nature, the HS molecules tend to organize spontaneously in aqueous solution forming micelle-like structures [17]. We have used a dynamic light scattering method to determine the size and polydispersity of AHA material dispersed in aqueous solution. The measurements were done for solution at relatively low concentration of 0.01 g dm^{-3} at pH 7. The intensity weighted mean size (dz) of AHA aggregates was 101.5 nm with the polydispersity being of 0.279.

The hydrodynamic diameter of AHA particles is comparable to that reported for Gray humic acids [18]. Concentration of humic material has little effect on particle dimensions [19]. However, a general trend towards decreased sizes with increased pH values was observed [18].

4. Discussion and conclusions

The photochemical reactivity of HA is complex due to its complicated chemical structure and depends on the experimental conditions under which studies are performed, in particular on the excitation wavelength. HA were shown to act as sensitizers or precursors for the production of reactive species able to degrade organic chemicals [10]. Photooxidants such as hydroxyl radicals, singlet oxygen, peroxyl radicals and oxidant triplet states were shown or proposed to be formed on excitation of HA. As a result, phototransformation of phenol sensitized by HA is rather a complex process and several reactive species are involved in the transformation of phenol. In the present study, we focus rather on the efficiency of photodegradation of phenol induced by humic acid. Since the kind of reactive species generated by
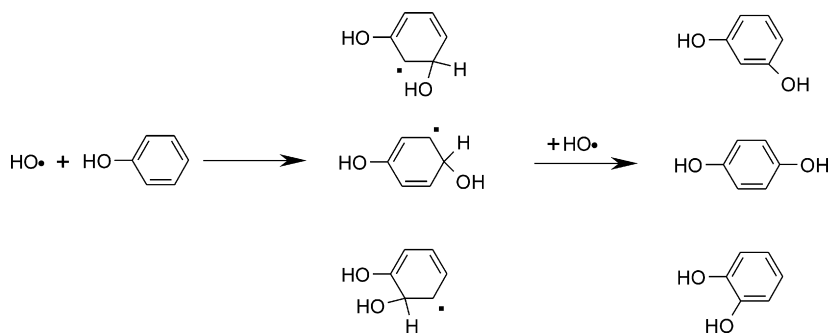
Scheme 1.

HA during excitation depends on a wavelength of the incidental light, we divided our study in two parts.

In a first step, the photodegradation process induced by 253.7 nm irradiation was studied. Both direct and photoinduced processes were observed. In both cases, the identified products were the same, namely hydroquinone, resorcinol and pyrocatechol. The nature of the photoproducts suggests the involvement of hydroxyl radicals in the photoinduced transformation at this wavelength. In the case of the direct phototransformation, it is well known that the irradiation of the phenol results in ejection of an electron from the phenolate ion to produce a phenoxyl radical and a solvated electron [20,21]. In oxygenated solution, these electrons were found to be transformed into hydroxyl radicals [6]. In the latter case, it is well established that irradiation of homogenous solution of humic acid at $\lambda = 254$ nm leads to the formation of the hydrated electrons which are converted into hydroxyl radicals in aerated or oxygenated solutions [2]. The reaction of phenol and HO$^\bullet$ was previously investigated by Rodríguez et al. [22]. They suggested that it could take place according to Scheme 1. The following steps are involved: (i) addition of HO$^\bullet$ radicals to substrate and formation of HO$^\bullet$-PhOH adducts with the rate constant close to the diffusion limit; (ii) hydrogen abstraction from HO$^\bullet$-PhOH adducts by HO$^\bullet$ and formation of dihydroxybenzene isomers.

It has been previously reported that a humic-like material can be synthesized by irradiation of phenol at 253.7 nm [6,7]. This can explain our results presented in Fig. 2. The prolonged irradiation of the reaction mixture leads to the disappearance of the photoproducts.

As was shown in the Fig. 4 the value of the left side of Eq. (4) drops off when the concentration of AHA exceeded 0.05 g dm^{-3}. This can be explained in two ways. Firstly, the Eq. (4) is only true assuming that the kinetics of direct oxidation of phenol is not affected by addition of AHA. Oxidant species produced from directly excited PhOH cannot only react with phenol, but also disappear in other processes. AHA can compete with phenol for reaction with the oxidant species. As a result, the initial rates of reaction of phenol degradation are lowered with increasing concentration of AHA. As was mentioned above, the irradiation of phenol results in the generation of hydroxyl radicals. HA, which are polyphenolic compounds with multiple carboxyl, carbohydrate and peptide moieties, can act as a HO$^\bullet$ scavenger, decreasing this way the rate of direct degradation. Another explanation is connected with an overestimation of I_{abs}^{PhOH} calculated

according to Eq. (3) for high content of AHA. The incident light is scattered by the particles of AHA. The intensity of the scattered light is a function of both the particle number and their size. As was mentioned above the size is almost constant with concentration of HA at given pH. At low concentration of AHA the light scattering should be negligible, but for higher concentration it may reduce the intensity of incident light. As a consequence, the light intensity absorbed by PhOH is lower than that calculated with Eq. (4).

Analyzing the data in Table 1, one can notice the effect of pH on the rate of reaction. The apparent first-order rate constant for direct oxidation of phenol increased with an increasing value of pH. That observation can be explained considering that higher pH increases the fraction of phenol present as phenolate. The phenolate ions, which have the oxidation potential lower than that of undissociated phenol (see below), should release an electron more efficiently than phenol upon excitation.

In the next step, we used the polychromatic light within the range of 310–420 nm for AHA sensitized degradation of PhOH. There is some discrepancy in literature concerning the type of oxidants responsible for phenolic substrate transformation induced by the polychromatic light in those wavelength ranges. Canonica et al. [5] have shown that phenolic pollutants are readily phototransformed by various natural organic materials present in water (aquatic humic and fulvic acids) and model sensitizers-like aromatic ketones. They studied the phototransformation of several phenolic substrates at pH 7 and 8 irradiated with light at $\lambda > 320$ nm and proposed that this reaction involved mainly excited triplet states of sensitizers. Vialaton et al. [9] investigated the photooxidation of 4-chloro-2-methylphenol (CMP) in natural and humic substances containing waters. Samples were irradiated with the polychromatic light in the wavelength range 300–450 nm. They concluded that the oxidation of CMP sensitized by HS involves reactive triplet states of sensitizers capable of abstracting the phenolic hydrogen atoms. That hydrogen atom is further transferred onto oxygen with formation of HO$_2^\bullet$/O$_2^\bullet$ and regeneration of the starting HS chromophores. Aguer and Richard [2] have also studied degradation of CMP in solution of HA at pH 6.5 irradiated with the polychromatic light in the wavelength range 300–450 nm. They have shown that under these conditions the hydroxyl radicals are the main species responsible for the transformation of the substrate. They have argued that the oxidation by reactive triplet states is a very minor pathway as shown by the fact that the
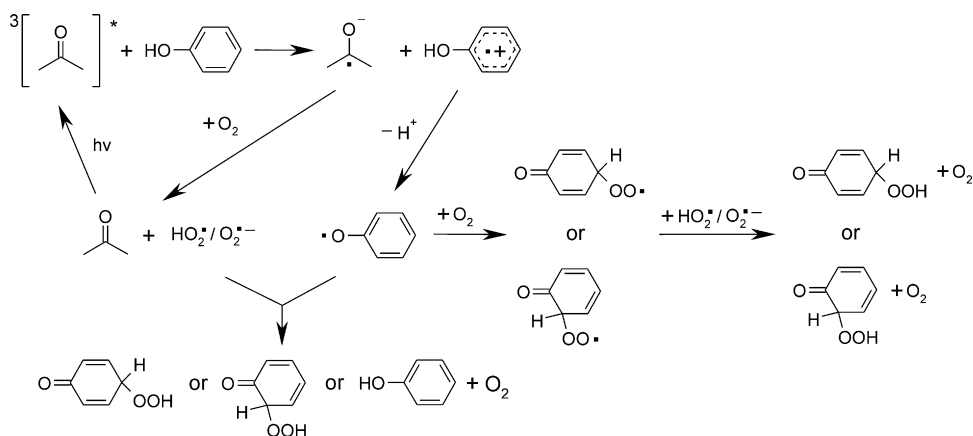
Scheme 2.

reactions are drastically inhibited by 2-propanol. That conclusion should be treated with some reservation. It is known that 2-propanol acts as efficient scavenger of hydroxyl radicals but it is also very efficient reductant of carbonyl compounds in their excited triplet states [23]. In the next paper, Vialaton and Richard [11] have shown that 2-propanol had no effect on the consumption of CMP in photoprocess sensitized by HA irradiated under natural sunlight and they suggested that CMP was oxidized by reaction with excited triplet states of sensitizers. The detailed study by Canonica et al. [24] has shown that reaction between phenolic substances and excited triplet states of a carbonyl compounds occur by electron transfer and not by H atom transfer.

It has been previously shown that HA contains chromophores capable of sensitizing the production of singlet oxygen and excitation of HA produces singlet oxygen [7,8]. But experiments with heavy water (D_2O) as a solvent [5] and azide anions as a scavenger [7,11] have shown that singlet oxygen do not participate in photodegradation of phenols sensitized by HS. On the other hand, Aguer and Richard [7] have shown that phenols can significantly inhibit the photoproduction of singlet oxygen by HA. Thus, the formation of singlet oxygen can be attributed to chromophoric groups present in humic acids the same which are responsible for the degradation of phenol. We have confirmed that AHA can form singlet oxygen when irradiated with the polychromatic light within range 310–420 nm. However, our results have shown that the ability of AHA to generate the singlet oxygen is lower then it was previously reported. Phenols are known to react readily with singlet oxygen. The rate of that reaction is strongly pH dependent as the rate constants for phenol and phenolate anion are considerably different [25]. It was found that in the case of mechanism in which singlet oxygen is involved the change of pH from 7.2 to 10.3 causes a 42-fold increase in the quantum yield. This increase is almost 10 times higher than that observed in the present work (4.8).

Taking into account all above mentioned findings we believe that phototransformation of phenol sensitized by AHA irradiated with polychromatic light involves a type I photosensitized oxidation. The Scheme 2 shows the possible pathways of reaction. An electron transfer process from a phenol to the excited triplet state of a carbonyl group present in AHA structure yields

a protonated phenoxyl radical ($PhOH^{\bullet+}$) and a deprotonated ketyl radical ($R1R2–C^{\bullet}–O^-$) [24]. Because of very low dissociation constant ($pK_a = -2$) the $PhOH^{\bullet+}$ radical undergoes dissociation forming phenoxyl radical ($PhO^{\bullet}$). As a result of reaction between oxygen and the deprotonated ketyl radicals, the carbonyl groups are regenerated and $HO_2^{\bullet}/O_2^{\bullet}$ radicals are created [5]. The $HO_2^{\bullet}/O_2^{\bullet}$ radicals react with $PhO^{\bullet}$ with formation of the hydroperoxycyclohexadienone as a primary product. Such a scheme of reaction is supported by the observation of pronounced influence of pH on the rate of photosensitized reaction. The value of V_r increases with an increase of pH of irradiated solution (see Table 2). That effect can be explained considering the dissociation of phenol and the higher reactivity of PhO^- than $PhOH$ towards the excited triplet states of HA. A one-electron oxidation potential of phenol, $E_{ox}(PhOH/PhOH^{\bullet+})$ in aqueous solution was calculated to be 1.5 V versus NHE [24]. However, the oxidation potential of the anions, $E_{ox}(PhO^-/PhO^{\bullet})$, was determined to be 0.79 V versus NHE [24]. Previously, it was shown that the values of the apparent first-order rate constants increase with the oxidizability of the phenolic substrates [7].

To summarize, our results demonstrate that the addition of HA to phenol solution affects its oxidation. Depending on the wavelength of irradiation and the concentration of HA it can enhance or inhibit oxidation of PhOH. At the 253.7 nm the ϕ_i value is low compared to ϕ_d; the sensitized phototransformation of phenol was a minor pathway. However, photooxidation of phenol with light within the wavelength range of 310–420 nm is effectively sensitized by HA. The quantum yield of that process is pH dependent and it is considerably higher in alkaline than in a neutral solution.

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