

Role of photochemical and microbial degradation of phenol in water

O. Tchaikovskaya,^{1,†} I. Sokolova,¹ L. Kondratieva,^{2,‡} and E. Karetnikova²

¹*Siberian Physical Technical Institute, 1, Novo-Sobornaia Sq., Tomsk 634050, Russia*

²*Institute of Water and Ecological Problems of the Russian Academy of Sciences,
65, Kim-Yu-Chen St., Khabarovsk 680000, Russia*

ABSTRACT. The present work is aimed at spectroscopic and luminescent investigations of the microbial cleavage efficiency of phenol in the water solution upon expose to UV light. With increasing time of irradiation of phenol in the saline solution, the absorption intensity increases throughout the spectrum. The efficiency of photoalteration of phenol in the saline solution is higher compared to that in water. The results obtained have shown that the efficiency of complex photobiological phenol destruction increases sharply compared to the photochemical or microbial destruction.

1. INTRODUCTION

Research on the impact of UV light on an aquatic system was initiated in reply to the discovery of the ozone hole over the Antarctic region. The ozone depletion leads to increased penetration of UV-B radiation (280–320 nm) through the atmosphere [1]. In this connection, a study of the interaction between UV radiation and microorganisms becomes urgent.

It is well known that phenol compounds enter pools with the sewage of woodworking enterprises, oil refining complexes, and coal mining and chemical industries. However, a huge variety of phenol compounds are generated *in vivo*. Natural compounds in surface waters are encountered not only as free dissolved species: they also take part in condensation and polymerization reactions and produce humic complexes and polyaromatic compounds. The phenol concentration in aquatic ecosystems depends on the season. The phenol compounds differ by their toxic and organoleptic properties, chemical inertness, and sensitivity to microbiological cleavage. Therefore, some of them are rapidly oxidized in the aquatic environment or are metabolized by microbial communities, whereas others remain unchanged for a long time or are accumulated in a pool, thereby bringing the actual threat to microorganisms [2]. It is customary to assume that the volatile low-molecular phenol compounds, for example, monophenol, cresol, xylenol, and thymol, are the most toxic ones. The natural self-purification from phenol pollutants occurs in the presence of organic matter. The phenol cleavage in the presence of enzymes includes a complex of physicochemical processes, among them the photolysis. At present, the action of UV radiation is one of the most important technologies of sewage

purification from organic molecules, since it is accompanied by the photolysis of ecotoxicants. The degree of ecological hazard of various technologies of natural water purification from the phenol compounds is determined by mechanisms of their cleavage. A comparative analysis of the efficiency of microbiological cleavage of various phenol compounds by microbial communities and individual bacterial strains in the presence of co-substrates was conducted in [3] for different temperatures to refine the methods for detoxication of the phenol compounds. It was demonstrated that the temperature regime influences significantly the destruction rate of phenol compounds. As the temperature decreased down to 12 °C, the cleavage of phenol compounds by the examined strains almost vanished. Microbiological investigations demonstrated different mechanisms of destruction of the aromatic compounds incorporated into the remains of decomposed plants and of the phenol compounds of technogenic origin by active monophenol destructors. We have already studied the photolysis of phenol in water solutions upon exposure to UV radiation in [4–6]. It was shown that the photolysis of phenol in water solutions depends on the pH of the medium and the exciting radiation power and wavelength [7].

The present work is aimed at spectroscopic and luminescent investigations of the microbial cleavage efficiency of phenol in the water solution upon expose to UV light.

2. MATERIALS AND METHODS

The standard procedure was used to record the absorption and fluorescence spectra by a Specord M40 spectrophotometer and a Hitachi M850 spectrofluorimeter. An OKN-11M high-pressure mercury vapor lamp ($W = 1 \text{ MW/cm}^2$) was used as a source of UV and visible light to perform photochemical investigations.

[†]E-mail: tchon@phys.tsu.ru

[‡]E-mail: kondr@fe.ru

Table 1. Spectroscopic and luminescence properties of phenol and its photoproducts.

	pH	Absorption		Fluorescence
		λ_1 , nm	λ_2 , nm	λ_{\max} , nm
Phenol in water	6.3	210	270	296 ($\lambda_{\text{exc}} = 270$ nm)
Phenol (10^{-1} mol·L $^{-1}$) in the saline solution	6.3	210	270	304 ($\lambda_{\text{exc}} = 270$ nm)
Phenol (6×10^{-4} mol·L $^{-1}$) in the saline solution	6.3	210	270	345 ($\lambda_{\text{exc}} = 270$ nm)
Phenol in water + 10^{-1} mol·L $^{-1}$ KOH	12.5	230	290	345 ($\lambda_{\text{exc}} = 300$ nm)
Hydroquinone in water	6	210	290	330 ($\lambda_{\text{exc}} = 280$ nm)
Hydroquinone + 10^{-1} mol·L $^{-1}$ KOH	11.5	260	310	440 ($\lambda_{\text{exc}} = 300$ nm)
<i>p</i> -benzo-quinon	6.2	250	294	No fluorescence

We examined phenol in the saline solution of the following composition (g/l): KNO₃ (1):MgSO₄ (0.2):NaCl (1):K₂HPO₄ (1). The time of preliminary irradiation varied from 1 to 80 min. The pH values of the medium were measured by a pH-673 meter. The phenol concentration in the solution varied in the range 10^{-3} – 10^{-5} mol·L $^{-1}$. The phenol-resistant group of bacteria extracted from natural waters of the Amur Lagoon by the passage methods in agaric nutrient media was utilized in the present work. Microorganisms-destroyers were extracted by the method of cumulative cultures. Phenol was dissolved in the saline solution and then irradiated by the light from the mercury lamp. Bacteria were added to this solution and held for the fixed time. Then the solution was filtered out, and its absorption and fluorescence spectra were recorded.

3. RESULTS AND DISCUSSION

3.1. Spectral characteristics of phenol in the saline solution before and after irradiation. Phenol exists in water as neutral species which generates absorption bands with maxima at 210 and 270 nm and a fluorescence band with the maximum at 296 nm [4]. The following specific features were established for the spectral characteristics of phenol in the saline solution compared to those in the water solution without irradiation:

1. The maximum of the fluorescent band of neutral species was shifted toward longer wavelengths from 296 to 304 nm (Table 1). The shift of the band maximum and the low band intensity demonstrate that the neutral phenol species in the saline solution exists in the form of an H-bound complex with the solvent molecules. In this case, the shift of the maximum toward longer wavelengths is explained by the fact that phenol donates positive protons, that is, it shares with the solvent a hydrogen atom of the OH group of phenol [8].
2. The fluorescence intensity of neutral phenol species in the saline solution depends on the phenol concentration. The fluorescence of neutral species was not recorded when the phenol

concentration was less than 6×10^{-4} mol·L $^{-1}$. Only anionic phenol species produces the fluorescence band with the maximum at 345 nm (Table 1). The neutral species produces the low-intensity fluorescence band when the phenol concentrations exceed 6×10^{-4} mol·L $^{-1}$.

3. With increasing time of irradiation of phenol in the saline solution, the absorption intensity increases throughout the spectrum. This is associated with the formation of several photoproducts (Figure 1). The increase of the absorption intensity in the 240–260 nm wavelength range is due to the formation of compounds having the quinone structure. The well defined maximum around 400 nm, whose spectral characteristics were presented in [9], is attributed to the *p*-benzo-quinone absorption (Table 1). The intensity of this absorption band increases with irradiation time.

When the test phenol solution was irradiated, the intensity of the fluorescence band with the maximum at 304 nm decreased. Simultaneously, bands with maxima at 330 and 400 nm appear (Figure 2), whose intensities also increase with irradiation time. The band with

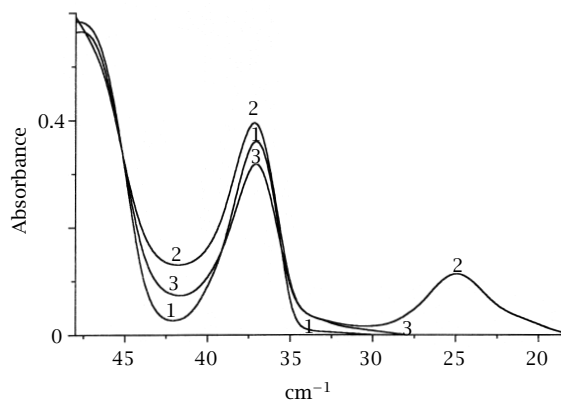


Figure 1. Absorption spectra of phenol in the water (1) and saline (2) solutions after 40 min irradiation and 24 h destruction by microbial communities of the phenol solution irradiated for 40 min (3).

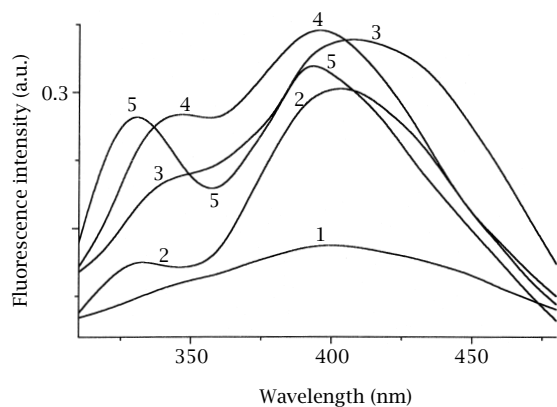


Figure 2. Fluorescence spectra (with a wavelength of the fluorescence excitation of 300 nm) of phenol in the saline solution irradiated during 0 (1), 15 (5), 40 (2 and 4), and 80 min (3). The phenol concentrations were $8 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ (1-3) and $10^{-4} \text{ mol} \cdot \text{L}^{-1}$ (4 and 5).

the maximum at 330 nm is associated with the hydroquinone fluorescence (Table 1). We succeeded in recording the band with the maximum at 400 nm attributed to the photoproduct when we studied the phenol photolysis in a highly alkaline solution [3] in which phenol existed as anionic species. Thus, upon irradiation of phenol in the saline solution, a positive proton of the OH group of phenol may move to the solvent, and phenol may be further decomposed with the participation of anionic species as intermediate products. The efficiency of photoalteration of phenol in the saline solution is higher compared to that in water (pH = 6.3). This is explained by the fact that the multichannel mechanism of phenol photolysis is realized, with the participation of ionic species as intermediate photoproducts and hydroquinone.

3.2. Microbiological destruction of nonirradiated and irradiated solutions. The following specific features were observed after microbial destruction (for 1–50 h) of nonirradiated phenol solutions:

1. The intensity of the main absorption band with the maximum at 270 nm decreases, which points to the phenol destruction. Simultaneously, the absorption intensities in the bands between 240–260 and 300–350 nm, associated with destruction products, increase.
2. After microbial destruction of the nonirradiated test phenol solution, the absorption band with the maximum at 400 nm disappeared (Figure 3).
3. In the fluorescence spectra, the main band with the maximum at 304 nm, associated with the emission of the H-bound phenol complex, decreased after microbial destruction (Table 2).

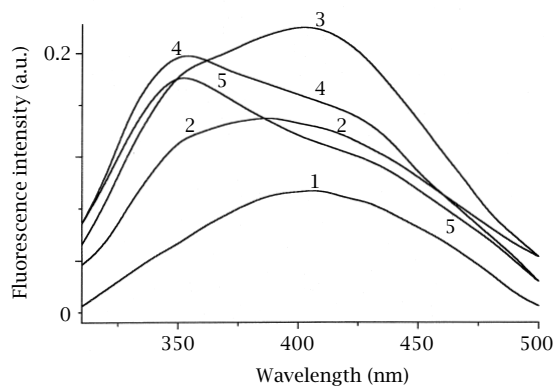


Figure 3. Fluorescence spectra (with a wavelength of the fluorescence excitation of 300 nm) of phenol in the saline solution after microbial destruction during: 0 (1), 1 (2), 6 (3), 24 (4), and 50 h (5).

Table 2. Change of the 400 nm relative fluorescence intensity of phenol in the saline solution after irradiation and microbial destruction (I/I_0 , where I is a current relative fluorescence intensity and I_0 is the relative fluorescence intensity of nonirradiated phenol in the saline solution).

Time of solution irradiation (min)	Time of microbial destruction of the irradiated solution (h)				
	0	1	6	24	50
0	1	1.4	2.1	1.7	1.4
1	2.5	2.4	2.4	2.1	2
15	2.3	5	5	5	5
40	1.9	8.5	6	6	6

4. In addition to the main band, complex bands with the maxima between 310–440 and 450–550 nm (Figures 2, 4 and 5) were detected in the fluorescence spectra. The fluorescence band with the maximum between 450–550 nm generated by photoproducts disappears after UV irradiation of phenol in the aquatic and saline solutions. We recorded this photoproduct after irradiation of phenol in the alkaline solution by the high-power XeCl-laser radiation ($170 \text{ MW}/\text{cm}^2$) with an exciting radiation wavelength of 308 nm [7]. It is most likely that the nature of the product formed upon exposure to high-power laser radiation or after microbial destruction of phenol in the water solution is the same. It can be caused by the fact that the microbial destruction of phenol leads to the cleavage of the benzene ring during the metabolism.

The following changes in the spectroscopic and luminescence properties were recorded after microbial destruction (during 1–50 h) of irradiated (for 1–40 min) phenol solutions:

1. The absorption intensities in the 240–260 and

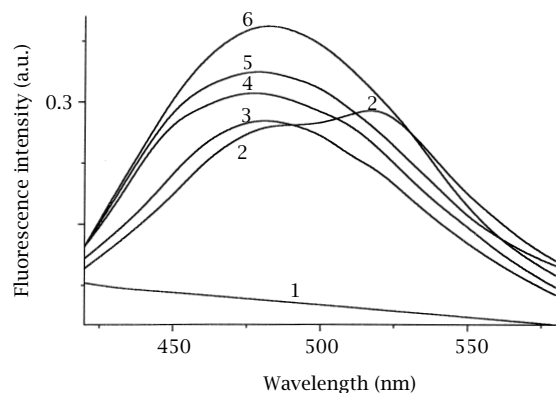


Figure 4. Fluorescence spectra (with a wavelength of the fluorescence excitation of 400 nm) of phenol in the saline solution after microbial destruction during: 0 (1), 6 (4 and 5), 24 (6), and 50 h (2 and 3). Solutions 3, 5, and 6 were preliminary irradiated for 15 min.

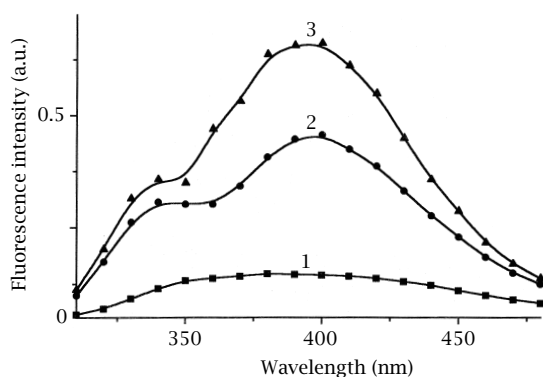


Figure 5. Fluorescence spectra (with a wavelength of the fluorescence excitation of 300 nm) of phenol in the saline solutions nonirradiated (1) and irradiated for 15 (2) and 40 min (3) after the phenol destruction by microbial communities for 1 h.

300–350 nm wavelength ranges decreased, which may be attributed to the destruction of phenol photolytes by microbial communities. The absorption band with the maximum at 400 nm disappeared from the absorption spectra after the microbial destruction of the irradiated phenol solutions.

2. The intensity of the fluorescence band with the

maximum at 304 nm in the fluorescence spectra decreased as the time of the strain interaction with the irradiated phenol solution increased. Simultaneously, the fluorescence intensity in the 310–450 nm wavelength range increased (Table 2).

3. The emission band with maxima between 450–550 nm was observed in the fluorescence spectra.

4. CONCLUSIONS

Thus, the results obtained have shown that the efficiency of complex photobiological phenol destruction increases sharply compared to the photochemical or microbial destruction.

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