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Comparative study of the UV and UV/VUV-induced photolysis of phenol in aqueous solution

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Abstract

The UV (254 nm) and UV/VUV (254/185 nm) photolysis of phenol and the distribution of the products in solutions saturated with oxygen or nitrogen were investigated and compared. The initial rate of degradation of phenol in UV/VUV-irradiated solutions exceeded that determined in UV-irradiated solutions, but the difference decreased dramatically with increase of the initial phenol concentration. The effects of methanol as $HO^{\bullet}$ scavenger demonstrated that the relative contribution of the $HO^{\bullet}$-based reactions to the decomposition of phenol in UV/VUV-irradiated solutions decreased strongly with increase of the initial phenol concentration. The same aromatic (1,2- and 1,4-dihydroxybenzene) and aliphatic (maleic, malic, tartaric and oxalic acids) intermediates were detected in UV- and UV/VUV-irradiated solutions saturated with oxygen. The decompositions of 1,2- and 1,4-dihydroxybenzene, 1,4-benzoquinone and oxalic acid were also investigated both in UV/VUV- and in UV-irradiated solutions.

Keywords: 254 nm; 185 nm; Hydroxyl radical; Phenoxyl radical; Phenol

1. Introduction

The potential of advanced oxidation processes to remove both organic and inorganic compounds from water or air is currently being intensively studied. These processes include direct ultraviolet (UV) and vacuum-ultraviolet (VUV) photolysis, which are promising methods for the production of drinking water or ultrapure water without the addition of other reagents. These methods can be successfully applied to remove aromatic pollutants such as phenols. It should be noted, however that UV irradiation alone cannot be used as an effective procedure for the total mineralization of organics, whereas it is quite efficient for water disinfection [1]. At the same time, the $HO^{\bullet}$ generated from water by VUV light is one of the most reactive and nonselective species, which can react at high rates with almost any organic substances. Thus, a number of technologies are based on the $HO^{\bullet}$-initiated reactions for the complete removal of organic pollutants from aqueous solutions.

The commercially available low-pressure mercury vapour lamp is a light source widely applied in water purification and disinfection technologies. This light source has its main output at 254 nm, with a small amount (6% of the total intensity of irradiation) at 185 nm [2]. The generally low quantum yield and the relatively small molar absorptivity of the target compounds at 254 nm are factors that limit the efficiency, and therefore the applicability of direct photolysis process in water remediation [3]. The extinction coefficient for phenol at 254 nm is $516\ \mathrm{mol^{-1}\ dm^{3}\ cm^{-1}}$ and the quantum yield of phenol photooxidation in aerated solutions has been found to vary in the interval 0.12–0.02 at pH 1.6–13.2, with a minimum value at pH 11.1 [4].

The excitation of phenol leads to the formation of its first excited singlet state (1), which can decay by fluorescence (298 nm) (2) [5,6], radiationless internal conversion to the ground state (3), intersystem crossing to the triplet state (4) [6], chemical dissociation into phenoxyl radical ($ArO^{\bullet}$) and $H^{\bullet}$ (5) [7,8], photoionization (6) [9,10] and product formation (7). Naturally, the relative contributions of these reactions to the decay of the excited state depend strongly on the experimental parameters:

$$\text{phenol} + h\nu \rightarrow {}^{1}\text{phenol} \tag{1}$$

$$^{1}\text{phenol} \rightarrow \text{phenol} + h\nu' \tag{2}$$

$$^{1}\text{phenol} \rightarrow \text{phenol} \tag{3}$$

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$$^{1}\text{phenol} \rightarrow {}^{3}\text{phenol} \tag{4}$$

$$^{1}\text{phenol} \rightarrow ({}^{3}\text{phenol}) \rightarrow \text{ArO}^{\bullet} + {}^{\bullet}\text{H} \tag{5}$$

$$\begin{aligned} &^{1}\text{phenol} \rightarrow {}^{3}\text{phenol} \xrightarrow{h\nu} \text{ArOH}^{\bullet+} + \text{e}_{\text{aq}}{}^{-} \\ &\xrightarrow{\text{H}_2\text{O}/\text{H}^+} \text{ArO}^{\bullet} + \text{H}^{+} + \text{e}_{\text{aq}}{}^{-} \rightarrow \text{ArO}^{\bullet} + {}^{\bullet}\text{H} \end{aligned} \tag{6}$$

$$^{1}\text{phenol} \rightarrow \text{products} \tag{7}$$

$$^{3}\text{phenol} + \text{O}_2 \rightarrow \text{phenol} + {}^{1}\text{O}_2 \tag{8}$$

$$^{3}\text{phenol} + \text{O}_2 \rightarrow \text{ArO}^{\bullet+} + \text{O}_2{}^{\bullet-} \tag{9}$$

The quantum yield of $\text{H}^{\bullet}$ formation (5) and photoionization (6) depend on the nature of the solvent, on the pH of the solution and on the wavelength of excitation [8]. In neutral or acidic aqueous solutions (pH 7–2) excitation to singlet-state phenol at 266 nm leads primarily to photoionization. Besides this, $\text{H}^{\bullet}$ formation (5) is a very minor path likely because homolytic cleavage of the O–H bond of phenol is suppressed by H-bonding with water molecules. Most phenoxyl radical cations are generated via a biphotonic process [7,11] in neutral and acidic solutions if a second photon is absorbed by the triplet state of the phenol molecule. The radical cation formed is not stable in aqueous solutions, it rapidly deprotonation yielding a phenoxyl radical [12]. Besides decaying to the ground state by fluorescence and photoionization, the triplet-excited state of phenol can be quenched by oxygen. A fraction of this reaction can lead to the formation of singlet oxygen ($^{1}\text{O}_2$) (8) or $\text{O}_2{}^{\bullet-}$ (9).

VUV light generates $\text{HO}^{\bullet}$ from water. In water, homolysis to $\text{HO}^{\bullet}$ and $\text{H}^{\bullet}$ takes place with a quantum yield ($\Phi_{\text{HO}^{\bullet}}$) at 185 nm of 0.33 [13]. The penetration depth for VUV light in water is very short, about 0.1 mm. During the degradation of aromatic compounds, the first step is generally nucleophilic addition of $\text{HO}^{\bullet}$ to the aromatic ring [13].

Dissolved oxygen strongly influences the quality and quantity of the reactive species in irradiated aqueous solutions. This can open up the pathway for the formation of peroxyl-type organic radicals ($\text{R}^{\bullet} + \text{O}_2 \rightarrow \text{ROO}^{\bullet}$), $\text{HO}_2{}^{\bullet}$ ($\text{H}^{\bullet} + \text{O}_2 \rightarrow \text{HO}_2{}^{\bullet}$, $k = 1.4 \times 10^{10}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ [14]), or $\text{O}_2{}^{\bullet-}$ ($\text{O}_2 + \text{e}^- \rightarrow \text{O}_2{}^{\bullet-}$, $k = 1.9 \times 10^{10}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ [15]). $\text{HO}_2{}^{\bullet}$ is in equilibrium with its conjugated base, $\text{O}_2{}^{\bullet-}$; $\text{p}K = 4.8$ [15]. The further transformation of the organic peroxyl-type radicals involves $\text{HO}_2{}^{\bullet}$ and $\text{O}_2{}^{\bullet-}$ elimination [16]. Thus, in oxygen-containing aqueous solution, the direct photooxidation of organics has a quite complex chemism.

In the present work, the direct photolysis of phenol in aqueous solutions was investigated by using low-pressure mercury vapour lamps immersed in the irradiated solution. The aims were to compare the efficiencies of two different low-pressure mercury lamps in the decomposition of phenol and its intermediates in solutions saturated with oxygen or in oxygen-free solutions, and to investigate the relative contributions of $\text{HO}^{\bullet}$-based reactions and the direct photolysis-initiated decompositions of phenol in UV/VUV-irradiated solutions.

2. Materials and methods

Both of the low-pressure mercury vapour lamps applied were made by LightTech (Hungary, Dunakeszi) and had identical geometry (307 mm long and a 20.5 mm external diameter sleeve) and electric parameters (15 W electric and 4.0 W UV output). The lamp emitting at 254 nm (GCL307T5VH/CELL) was covered with a commercial quartz sleeve (UV lamp). The lamp emitting at both 254 and 185 nm (GCL307T5/CELL) was covered with a Suprasil sleeve (UV/VUV lamp). The emitted photon flux of the light sources was measured by potassium ferrioxalate actinometry [17]. The photon flux of the 254 nm component of both lamps was independent of the material of the sleeve, and was found to be $3.45 \pm 0.09 \times 10^{-5}\ \text{mol}_{\text{photon}}\ \text{s}^{-1}$. The actinometric measurements were carried out by using the same volume as that of the irradiated phenol solutions in the reactor. The emission spectra of the low-pressure mercury lamps, measured with a T3000-RT-UV-VIS photometer in the wavelength range 200–890 nm, were found to be identical for the two lamps. The photon flux of the 185 nm component of the light emitted by UV/VUV lamp was estimated to be $2.1 \times 10^{-6}\ \text{mol}_{\text{photon}}\ \text{s}^{-1}$ according to the data given by LightTech.

The decomposition and mineralization of phenol were investigated under four different conditions: irradiation with UV or UV/VUV light, in solutions saturated with oxygen or nitrogen. The initial concentrations of phenol were adjusted in the range $(0.1–2.0) \times 10^{-3}\ \text{mol dm}^{-3}$.

The effects of methanol as $\text{HO}^{\bullet}$ scavenger were also investigated. Phenol of analytical grade from Sigma was dissolved in ultrapure water without any buffering. Methanol was of HPLC grade from Scharlau. In each experiment ultrapure water obtained from a Millipore purifier (Milli-Q) was applied.

The experimental apparatus is shown in Fig. 1. The low-pressure mercury lamp (3) was centred in the water-cooled,

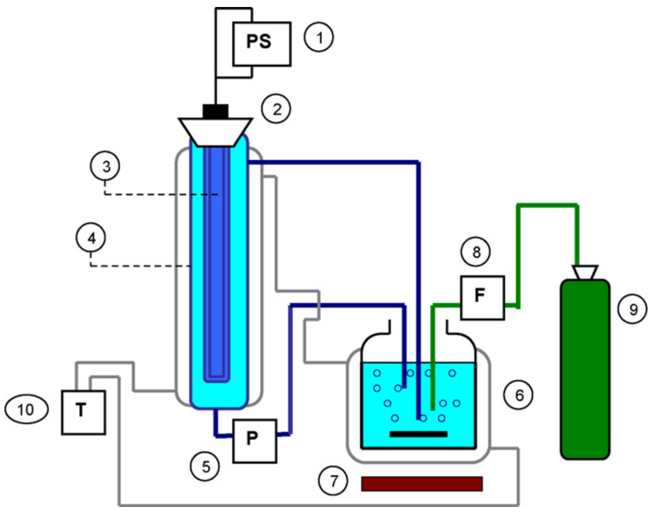

Fig. 1. Experimental apparatus: (1) power supply; (2) Teflon packing ring; (3) UV or UV/VUV lamp; (4) reactor; (5) pump; (6) reservoir; (7) magnetic stirrer; (8) flow meter; (9) oxygen or nitrogen cylinder; (10) thermostat.