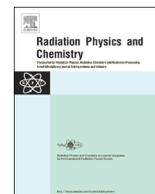




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Determination of the rate constant of hydroperoxyl radical reaction with phenol



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HIGHLIGHTS

- Using formic acid and dissolved O₂ almost all radicals are converted to HO₂[•].
- Using sodium formate and dissolved O₂ almost all radicals are converted to O₂^{•-}.
- The $k_{\text{HO}_2^{\bullet} + \text{phenol}}$ was estimated to be $(2.7 \pm 1.2) \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$.
- HO₂[•] is suggested to contribute significantly to the degradation of phenol.

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ABSTRACT

The rate constant of HO₂[•] reaction with phenol ($k_{\text{HO}_2^{\bullet} + \text{phenol}}$) was investigated. The primary radical set produced in water γ radiolysis ([•]OH, e_{aq}⁻ and H[•]) was transformed to HO₂[•]/O₂^{•-} by using dissolved oxygen and formate anion (in the form of either formic acid or sodium formate). The concentration ratio of HO₂[•]/O₂^{•-} was affected by the pH value of the solution: under acidic conditions (using HCOOH) almost all radicals were converted to HO₂[•], while under alkaline conditions (using HCOONa) to O₂^{•-}. The degradation rate of phenol was significantly higher using HCOOH. From the ratio of reaction rates under the two reaction conditions $k_{\text{HO}_2^{\bullet} + \text{phenol}}$ was estimated to be $(2.7 \pm 1.2) \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$.

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1. Introduction

In the last two decades a large number of papers were published on advanced oxidation processes (AOPs), these methods could complete the traditional water purifying technologies. Using these methods, the mineralization of the target compounds takes place in reactions with reactive free radicals (hydroxyl radical ([•]OH), hydrogen atom/hydrated electron ([•]H/e_{aq}⁻), hydroperoxyl radical/superoxide radical anion (HO₂[•]/O₂^{•-}), etc.).

For the optimization of the degradation pathways accurate knowledge of mechanisms, for example the contribution of the less investigated, low reactivity radicals is needed. Unfortunately, reaction rate values of HO₂[•]/O₂^{•-} are usually reported only for quinone-type compounds or for aromatics compounds at high temperature (e.g. $k_{\text{HO}_2^{\bullet} + \text{toluene}} = (5.5 \pm 1.5) \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$) (Scott and Walker, 2002) and their reaction mechanisms are very diverse (Bielski et al., 1985). Tsujimoto et al. (1993) published a study about the determination of the second-order rate constants of the reaction between O₂^{•-} and various dental phenolic compounds (e.g. phenol) by electron spin resonance spin-trapping technique. In that study the O₂^{•-} was generated by the HPX-XOD (hypoxanthin-xanthin oxidase) reaction system and it was detected as spin adduct (DMPO-O₂^{•-}) of spin-trap agent, 5,5-dimethyl-1-pyrroline-N oxide (DMPO) by ESR spectrometry. The amount of DMPO-O₂^{•-} adduct decreased due to the reaction with phenolic compounds. The rate constants of reaction between O₂^{•-} and phenolic compounds were calculated by the method of kinetic competition with 50% inhibitory dosage of phenolic additives.

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Our study was aimed at the investigation of the reaction of $\text{HO}_2^*/\text{O}_2^{\bullet-}$ with a simple model compound, phenol and at the determination of the HO_2^* +phenol reaction rate constant, since there is no information about it in the literature.

For the method of Tsujimoto et al. (1993) the detection of $\text{O}_2^{\bullet-}$ -adduct was needed; however in case of HO_2^* there is no simply detectable product from the reaction with phenol. Thus another method was found to investigate the reaction between phenol and HO_2^* . In our work a mediate method was used for the determination. The reactive intermediates were produced by the γ -radiolysis of water in dilute phenol solution and the degradation rate of HO_2^* +phenol reaction was utilized for the calculation of rate constant.

During irradiation of water with ionizing radiation $\cdot\text{OH}$, e_{aq}^- and H^* form as reactive radical intermediates (1). In dilute aqueous solution they may react with solute molecules with G values of 0.28, 0.28 and $0.062 \mu\text{mol J}^{-1}$ (Buxton, 2004; Spinks and Woods, 1990).

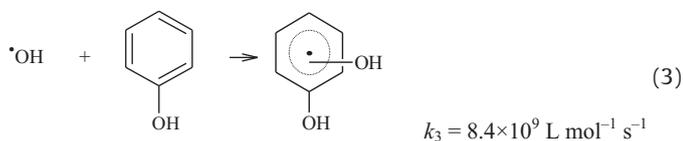


The latter two species are conjugate acid–base pairs (2) with a formal pK_a of 9.6 (Buxton, 2004):

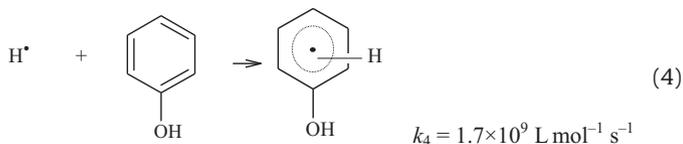


The forward reaction is very slow, $k_2 = 19 \text{ L mol}^{-1} \text{ s}^{-1}$ (Buxton, 2004), while the reversed reaction is very fast, $k_{-2} = 2.3 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ therefore below pH 3, under the usual experimental conditions e_{aq}^- conversion to H^* is practically complete (Hartig and Getoff, 1982).

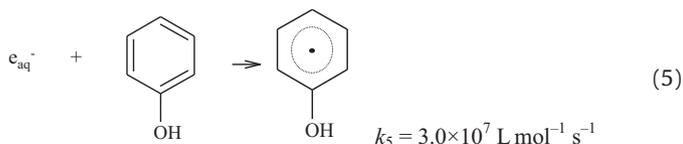
These reactive intermediates react with phenol according to Eqs. (3)–(5) forming dihydroxy cyclohexadienyl radicals and hydroxy cyclohexadienyl radicals:



(Bonin et al., 2007)

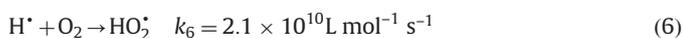


(Buxton et al., 1988)

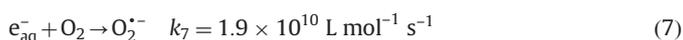


(Lai and Freeman, 1990)

Dissolved O_2 molecule reacts with $\text{H}^*/\text{e}_{\text{aq}}^-$ and transforms these intermediates to $\text{HO}_2^*/\text{O}_2^{\bullet-}$ (6)–(8).



(Buxton et al., 1988)

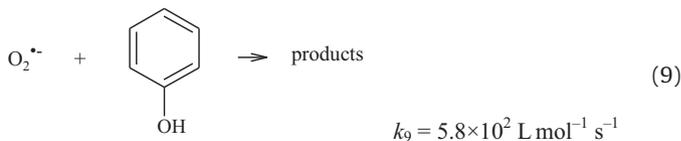


(Buxton et al., 1988)



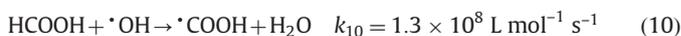
(Bielski et al., 1985)

The effect of $\text{HO}_2^*/\text{O}_2^{\bullet-}$ during the degradation processes is usually neglected, since they are considered to be low reactivity radicals. The rate constant of the reaction between phenol and $\text{O}_2^{\bullet-}$ (9) reported in the literature (Tsujimoto et al., 1993) supports this view.

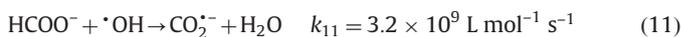


(Tsujimoto et al., 1993)

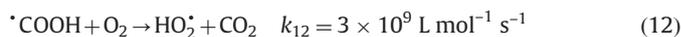
Our measurements were carried out in oxygen saturated formic acid/sodium formate containing solution in order to transform $\cdot\text{OH}$ to $\text{HO}_2^*/\text{O}_2^{\bullet-}$ in the reactions (10)–(13).



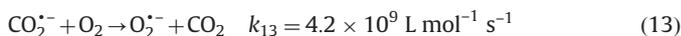
(Bielski et al., 1985)



(Bielski et al., 1985)



(Leitner and Dore, 1996)



(Ilan and Rabani, 1976)

The two carbon centered species ($\cdot\text{COOH}/\text{CO}_2^{\bullet-}$) are conjugate acid–base pairs (14) with a formal pK_a of 1.4 (Leitner and Dore, 1996):



In conclusion, in the presence of both O_2 and formic acid or formate ions all of the primary reactive species transform to $\text{HO}_2^*/\text{O}_2^{\bullet-}$, giving an outstanding possibility for studying the reactions of these intermediates.

In regard to the pK_a value of $\text{HO}_2^*/\text{O}_2^{\bullet-}$ (4.8) (Bielski et al., 1985), the ratio of the concentration of $\text{HO}_2^*/\text{O}_2^{\bullet-}$ could be affected by the pH of the solution. Using low pH (for example in the presence of HCOOH in great excess) HO_2^* will dominate, while at higher pH (neutral or alkaline, using HCOONa in great excess) $\text{O}_2^{\bullet-}$ will be the dominating reactive intermediate.

2. Experimental

2.1. Materials

During our experiments with a ^{60}Co source 250 mL $1.0 \times 10^{-4} \text{ mol L}^{-1}$ (c_0) aqueous phenol (Sigma-Aldrich, $\geq 99\%$) solutions were irradiated in the presence of 0.50 mol L^{-1} formic acid (AnalR NormaPUR, 99–100%) or 0.05 mol L^{-1} sodium formate (FLUKA, 99.0%) prepared in ultrapure MILLI-Q water (ELGA option 4).

2.2. Experimental setup

The 250 mL reservoir was placed near an SSL-01 panoramic type ^{60}Co - γ source to have a dose rate of 1.5 kG y h^{-1} . Since the yield of the primary radicals is $0.28 + 0.28 + 0.062 = 0.622 \mu\text{mol J}^{-1}$ (Spinks and Woods, 1990) and the density of diluted aqueous

solutions is $\sim 1 \text{ kg L}^{-1}$, the rate of radical formation was calculated to be $1500/3600 \text{ J kg}^{-1} \text{ s}^{-1} \times 1 \text{ kg L}^{-1} \times 0.622 \times 10^{-6} \text{ mol J}^{-1} = 2.6 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}$. The solutions were purged with oxygen gas ($> 99.5\%$ purity) ($c_{\text{O}_2} = 12.5 \times 10^{-4} \text{ mol L}^{-1}$) before the reaction for 20 min and throughout the irradiation. The reservoir was thermostated ($25.0 \pm 0.5 \text{ }^\circ\text{C}$) and the solution was continuously mixed by O_2 bubbling. Kinetic investigations were started by lifting up the γ source in the irradiation chamber. Samples were taken from the reservoir at different time intervals. Two parallel measurements were performed in the case of each reaction condition. During the degradation processes the pH of the solution usually changed, thus, the pH of each sample was measured with a METTLER TOLEDO MP225 type pH meter.

2.3. High performance liquid chromatography (HPLC)

The degradation of phenol was followed by an Agilent 1100 Series HPLC equipment with UV detection using a reverse phase LiChroCART[®] 150-4.6, RP-18 column with $5 \mu\text{m}$ particle size. The mobile phase consisted of 35% methanol (VWR, 99.80%) and 65% ultrapure MILLI-Q water (MILLIPORE Milli-Q Direct 8/16). During separation $20 \mu\text{L}$ sample was analyzed using an eluent flow rate of 0.80 mL min^{-1} at $25 \text{ }^\circ\text{C}$ and detection wavelength of 210 nm .

3. Results and discussion

In this research the effect of formic acid/formate ions on phenol degradation was investigated at low pH (using HCOOH) and at high pH (using HCOONa) during the γ radiolysis of oxygenated phenol solutions. In case of using HCOOH the pH of the solution was low, 2.09, and it did not change with the irradiation. In case of HCOONa there was some change in the pH during irradiation, the average pH at low conversion was around 7.88. As it can be seen in Fig. 1, the transformation rate of phenol was significantly higher under acidic conditions (using HCOOH) than in slightly alkaline media (using HCOONa).

The degradation rates of reactions were determined from the slopes of the linear trendlines fitted to the initial values (to 5% phenol conversion). The ratio of the degradation rates was calculated as follows (15):

$$\frac{r_{\text{HO}_2^* + \text{phenol}}}{r_{\text{O}_2^{\cdot-} + \text{phenol}}} = \frac{4.3 \times 10^{-6} \text{ mol L}^{-1} \text{ kG y}^{-1}}{3.3 \times 10^{-6} \text{ mol L}^{-1} \text{ kG y}^{-1}} = 1.3 \quad (15)$$

Since the c_{O_2} ($12.5 \times 10^{-4} \text{ mol L}^{-1}$) was more than one order of magnitude higher than the concentration of phenol, c_0

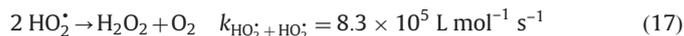
($1.0 \times 10^{-4} \text{ mol L}^{-1}$) and also k_6 and k_7 were with 1–3 orders of magnitude higher than k_4 and k_5 , practically all $\text{H}^*/e_{\text{aq}}^-$ were converted to $\text{HO}_2^*/\text{O}_2^{\cdot-}$. At the beginning of the reactions the actual concentrations of the solutes ([phenol], [HCOOH] and [HCOO^-]) can be considered roughly equal to their initial concentrations (1.0×10^{-4} , 0.50 and 0.05 mol L^{-1} , respectively). Using these concentrations $\cdot\text{OH}$ reacted with the formic acid or formate ion additives with reaction rates approx. 2 orders of magnitude higher than with phenol. Therefore, under our conditions $\cdot\text{OH}$ was also practically entirely converted to $\text{HO}_2^*/\text{O}_2^{\cdot-}$ and the effect of these reactive species to the degradation rate of phenol could be investigated.

Using the dissociation constant of HO_2^* ($K_{\text{HO}_2^*} = 1.6 \times 10^{-5} \text{ mol L}^{-1}$) (Bielski et al., 1985) the HO_2^* and $\text{O}_2^{\cdot-}$ concentrations were calculated by the following relations:

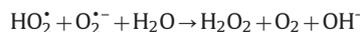
$$[\text{HO}_2^*] = \frac{[\text{H}^+]}{K_{\text{HO}_2^*}} [\text{O}_2^{\cdot-}], \quad [\text{O}_2^{\cdot-}] = \frac{K_{\text{HO}_2^*}}{[\text{H}^+]} [\text{HO}_2^*] \quad (16)$$

Under our conditions at low pH the $\text{HO}_2^*/\text{O}_2^{\cdot-}$ pair was present nearly exclusively in the HO_2^* form, while at the higher pH practically entirely in the $\text{O}_2^{\cdot-}$ form.

The $\text{HO}_2^*/\text{O}_2^{\cdot-}$ radicals either react with phenol or they disappear in self-termination reactions (17)–(19).

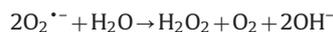


(Bielski et al., 1985)



$$k_{\text{HO}_2^* + \text{O}_2^{\cdot-}} = 9.7 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1} \quad (18)$$

(Bielski et al., 1985)



$$k_{19} < 3 \times 10^{-1} \text{ L mol}^{-1} \text{ s}^{-1} \quad (19)$$

(Bielski et al., 1985)

Since the rate of radical formation, $2.6 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}$, was much higher than the rate of phenol degradation, $1.8 \times 10^{-9} \text{ mol L}^{-1} \text{ s}^{-1}$ and $1.4 \times 10^{-9} \text{ mol L}^{-1} \text{ s}^{-1}$, the $\text{HO}_2^*/\text{O}_2^{\cdot-}$ radicals mainly decayed in self-termination reactions. In other words it was assumed that the presence of phenol did not influence much the steady state concentrations of HO_2^* and $\text{O}_2^{\cdot-}$.

Using the steady state approximation for the concentration of the radicals, the rate of radical formation is equal to the rate of radical recombination. The recombination of the peroxy type radicals ($\text{HO}_2^*/\text{O}_2^{\cdot-}$) depends strongly on the pH (Bielski et al., 1985), therefore in case of HCOOH (due to the low pH value (~ 2.0)) the recombination of two HO_2^* (17) and the reaction

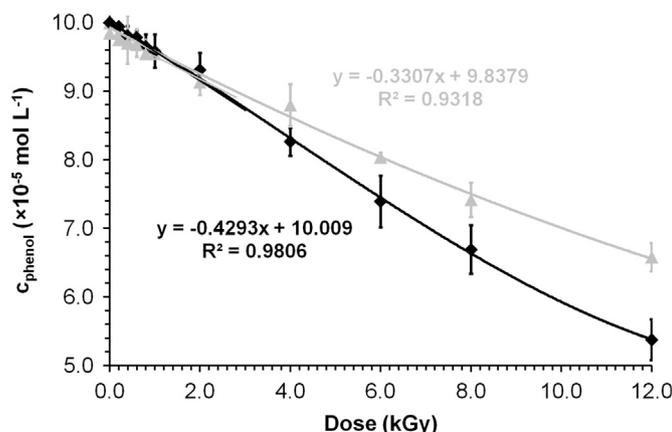


Fig. 1. The concentration of phenol plotted against the absorbed doses in the presence of 0.50 mol L^{-1} HCOOH (◆) or 0.05 mol L^{-1} HCOONa (▲) in O_2 saturated solutions. The error bars show the standard deviation of the measured points. The equations show the slopes of linear trendlines fitted to the initial values.

between HO_2^{\bullet} and $\text{O}_2^{\bullet -}$ (18) should be taken into account. In case of HCOONa (due to the high pH value (> 7.0)) only the reaction between HO_2^{\bullet} and $\text{O}_2^{\bullet -}$ (18) should be considered. The reaction between two $\text{O}_2^{\bullet -}$ (19) is negligible even at extremely high pH (Bielski et al., 1985), therefore this reaction has no influence neither at low nor at high pH.

At low pH (2.09) using HCOOH one may write the following:

$$\begin{aligned} r_{\text{HO}_2^{\bullet} \text{ formation}} &= r_{\text{HO}_2^{\bullet} + \text{HO}_2} + r_{\text{HO}_2^{\bullet} + \text{O}_2^{\bullet -}} \\ &= k_{\text{HO}_2^{\bullet} + \text{HO}_2} [\text{HO}_2^{\bullet}]^2 + k_{\text{HO}_2^{\bullet} + \text{O}_2^{\bullet -}} [\text{HO}_2^{\bullet}] [\text{O}_2^{\bullet -}] \\ &= [\text{HO}_2^{\bullet}]^2 (k_{\text{HO}_2^{\bullet} + \text{HO}_2} + k_{\text{HO}_2^{\bullet} + \text{O}_2^{\bullet -}} (K_{\text{HO}_2} / 10^{-2.09})) \end{aligned} \quad (20)$$

At higher pH (7.88) using HCOONa the following equation describes recombination (21):

$$\begin{aligned} r_{\text{O}_2^{\bullet -} \text{ formation}} &= r_{\text{HO}_2^{\bullet} + \text{O}_2^{\bullet -}} \\ &= k_{\text{HO}_2^{\bullet} + \text{O}_2^{\bullet -}} [\text{HO}_2^{\bullet}] [\text{O}_2^{\bullet -}] \\ &= k_{\text{HO}_2^{\bullet} + \text{O}_2^{\bullet -}} [\text{O}_2^{\bullet -}]^2 \frac{10^{-7.88}}{K_{\text{HO}_2}} \end{aligned} \quad (21)$$

Since all radicals were converted to HO_2^{\bullet} using HCOOH and to $\text{O}_2^{\bullet -}$ using HCOONa , it might be assumed that $r_{\text{HO}_2^{\bullet} \text{ formation}} = r_{\text{O}_2^{\bullet -} \text{ formation}}$. Therefore, using Eqs. (20) and (21) the $[\text{O}_2^{\bullet -}]^{\text{pH}=7.88} / [\text{HO}_2^{\bullet}]^{\text{pH}=2.09}$ ratio could be calculated (22):

$$\begin{aligned} \frac{[\text{O}_2^{\bullet -}]^{\text{pH}=7.88}}{[\text{HO}_2^{\bullet}]^{\text{pH}=2.09}} &= \left(\frac{r_{\text{O}_2^{\bullet -} \text{ formation}} K_{\text{HO}_2} (k_{\text{HO}_2^{\bullet} + \text{HO}_2} + k_{\text{HO}_2^{\bullet} + \text{O}_2^{\bullet -}} (K_{\text{HO}_2} / 10^{-2.09}))}{r_{\text{HO}_2^{\bullet} \text{ formation}} k_{\text{HO}_2^{\bullet} + \text{O}_2^{\bullet -}} 10^{-7.88}} \right)^{0.5} \\ &= \left(\frac{K_{\text{HO}_2} (k_{\text{HO}_2^{\bullet} + \text{HO}_2} + k_{\text{HO}_2^{\bullet} + \text{O}_2^{\bullet -}} (K_{\text{HO}_2} / 10^{-2.09}))}{k_{\text{HO}_2^{\bullet} + \text{O}_2^{\bullet -}} 10^{-7.88}} \right)^{0.5} = 3.6 \end{aligned} \quad (22)$$

The adequate rate equations that describe the reaction of HO_2^{\bullet} and $\text{O}_2^{\bullet -}$ with phenol can be given as

$$\text{HCOOH} : r_{\text{HO}_2^{\bullet} + \text{phenol}} = k_{\text{HO}_2^{\bullet} + \text{phenol}} [\text{HO}_2^{\bullet}]^{\text{pH}=2.09} [\text{phenol}] \quad (23)$$

$$\text{HCOONa} : r_{\text{O}_2^{\bullet -} + \text{phenol}} = k_{\text{O}_2^{\bullet -} + \text{phenol}} [\text{O}_2^{\bullet -}]^{\text{pH}=7.88} [\text{phenol}] \quad (24)$$

On the basis of the ratio of Eqs. (23) and (24), knowing the values of $r_{\text{HO}_2^{\bullet} + \text{phenol}} / r_{\text{O}_2^{\bullet -} + \text{phenol}}$ and $[\text{O}_2^{\bullet -}]^{\text{pH}=7.88} / [\text{HO}_2^{\bullet}]^{\text{pH}=2.09}$ the $k_{\text{HO}_2^{\bullet} + \text{phenol}} / k_{\text{O}_2^{\bullet -} + \text{phenol}}$ ratio could be determined (25):

$$\frac{k_{\text{HO}_2^{\bullet} + \text{phenol}}}{k_{\text{O}_2^{\bullet -} + \text{phenol}}} = \frac{r_{\text{HO}_2^{\bullet} + \text{phenol}} [\text{O}_2^{\bullet -}]^{\text{pH}=7.88}}{r_{\text{O}_2^{\bullet -} + \text{phenol}} [\text{HO}_2^{\bullet}]^{\text{pH}=2.09}} = 4.7 \quad (25)$$

Using the former ratio and the value of $k_{\text{O}_2^{\bullet -} + \text{phenol}}$ from the literature ($5.8 \times 10^2 \text{ L mol}^{-1} \text{ s}^{-1}$) (Tsujimoto et al., 1993) the

$k_{\text{HO}_2^{\bullet} + \text{phenol}}$ could be estimated (26):

$$k_{\text{HO}_2^{\bullet} + \text{phenol}} = 4.7 \times k_{\text{O}_2^{\bullet -} + \text{phenol}} = (2.7 \pm 1.2) \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1} \quad (26)$$

4. Conclusions

The rate constant of reaction between phenol and HO_2^{\bullet} was estimated to be $(2.7 \pm 1.2) \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$. This value is in agreement with the assumption that HO_2^{\bullet} reacts more effectively with phenol than $\text{O}_2^{\bullet -}$. Because in the lower pH range the rate of self-termination is also relatively low, HO_2^{\bullet} might significantly contribute to the degradation processes of phenol. On the other hand the contribution of $\text{O}_2^{\bullet -}$ to the degradation of phenol seems to be negligible because of its low reactivity.

Acknowledgments

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