



Modeling the oxidation of phenolic compounds by hydrogen peroxide photolysis



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HIGHLIGHTS

- A mechanism for oxidation of phenolic compounds by hydroxyl radicals is presented.
- Hydroxyl radical scavenging by intermediates reduces effectiveness of process.
- Kinetic model of the full mechanism is necessary for prediction of reactor performance.

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ABSTRACT

Hydrogen peroxide UV photolysis is among the most widely used advanced oxidation processes (AOPs) for the destruction of trace organics in waters destined for reuse. Previous kinetic models of hydrogen peroxide photolysis focus on the dynamics of hydroxyl radical production and consumption, as well as the reaction of the target organic with hydroxyl radicals. However, the rate of target destruction may also be affected by radical scavenging by reaction products. In this work, we build a predictive kinetic model for the destruction of *p*-cresol by hydrogen peroxide photolysis based on a complete reaction mechanism that includes reactions of intermediates with hydroxyl radicals. The results show that development of a predictive kinetic model to evaluate process performance requires consideration of the complete reaction mechanism, including reactions of intermediates with hydroxyl radicals.

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1. Introduction

Alkylphenol ethoxylates are non-ionic surfactants commonly used to formulate products such as detergents, paints, dispersing agents, wetting products, pesticides, and lubricants (Nagarnaik and Boulanger, 2011). These compounds are converted into alkylphenols in bioreactors used in wastewater treatment (Ahel et al., 1996), leading to their presence in surface waters (Scullion et al., 1996; Dong et al., 2015), groundwater (Swartz et al., 2006), municipal and industrial wastewater (Loyo-Rosales et al., 2007), aquatic sediments and marine shellfish (Lye et al., 1999). The most commonly detected metabolite, *p*-nonylphenol, induces breast tumor cell proliferation (Soto et al., 1991) and is a recognized endocrine disrupter (Lee and Lee, 1996). Therefore, the fates of *p*-nonylphenol and other phenolic compounds during wastewater

treatment and following the release of treated wastewater into the environment is of practical importance.

Advanced oxidation processes (AOPs) are effective treatments for phenolic compounds due to their high rates of reaction with hydroxyl radicals (second-order rate constants in the range 10^9 – 10^{10} $\text{M}^{-1} \text{s}^{-1}$; Buxton et al., 1988). The UV photolysis of hydrogen peroxide (UV/H₂O₂) is among the most widely used AOPs in water treatment. Various models have been developed to simulate process kinetics. Common elements in these models include: (i) the kinetics of radical production from the direct photolysis of hydrogen peroxide, and hydroxyl radical scavenging by hydrogen peroxide and other radicals; (ii) reaction of hydroxyl radicals with the target compound and, although to a lesser extent, (iii) radical scavenging by reaction byproducts and intermediates (Lay, 1989; Glaze et al., 1995; Liao and Gurol, 1995; Stefan et al., 1996; Crittenden et al., 1999; Murcia et al., 2015; Rojas et al., 2010, 2011).

The first step in the reaction mechanism for radical oxidation of phenolic compounds is OH addition to the ring (Wojnárovits et al.,

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2002). The position of OH addition is controlled by substitutions on the ring, but *para*- and *ortho*-hydroxylation normally predominate due to the electrophilic nature of the hydroxyl radical (Omura and Matsuura, 1968; Matsuura and Omura, 1974). Further oxidation of the resulting dihydroxy compound occurs via abstraction of a hydrogen atom to form benzoquinones, after which the ring can be cleaved to yield aliphatic acids (Scheck and Frimmel, 1995).

Previous efforts on the kinetic modeling of the UV/H₂O₂ process generally include a complete description of the chemistry behind radical formation, but rarely consider reaction intermediate and by-products. Glaze et al. (1995) proposed a kinetic model containing the most important elements of UV/H₂O₂ photolysis to predict the time-dependent concentration of a halogenated target. They used a quasi-steady-state assumption (QSSA) to calculate the time-dependent concentrations of free radicals. Their model did not account for CO₂ evolution/pH change and neglected the role of all radical scavenging species except H₂O₂. Stefan et al. (1996) followed a similar approach, but assumed that the target compound (in their case acetone) was transformed to oxalic and formic acids and then to CO₂. Subsequently, Crittenden et al. (1999) modeled UV/H₂O₂ process without reliance on a quasi-steady-state assumption for radical concentrations. Their work showed that the QSSA tends to under-predict hydroxyl radical concentrations in some cases and therefore the rates of target compound decomposition. Furthermore, their model included radical scavenging reactions.

The model of Song et al. (2008) accounted for time-dependent radical concentrations, pH changes due to product formation (CO₂ and low molecular weight acids), and radical scavenging by H₂O₂ and natural organic matter.

More recent modeling efforts of oxidation of phenolic compounds usually include a full formulation of the dynamics of radical formation, but very few or no details of the influence of intermediate compounds and by-products over target compound degradation. De Luis et al. (2011) presented a model of phenol and cresol degradation during the UV/H₂O₂ process that considered possible reactions of the organic compounds with produced radicals, but without considering intermediate compounds and by-products. A similar approach was followed by Rojas et al. (2010, 2011) to model the UV/H₂O₂ and Fenton's reaction processes. Moreira et al. (2012) developed a phenomenological model to simulate the TiO₂ photocatalysis of phenol, which includes specific details about the reaction mechanism.

In this work, *p*-cresol was selected as an example of a substituted phenolic compound. Even though *p*-cresol itself is not a common trace organic in wastewater effluent, it has chemical structure and reactivity with hydroxyl radicals similar to *p*-nonylphenol, which is a common endocrine disrupter compound widely present in wastewater effluent. A mechanism for radical-dependent UV/photolysis was proposed and calibrated based on time-dependent measurements of *p*-cresol and a number of reaction products/intermediates in a batch reactor. The model accounts for changes in ionic strength and pH due to reactant conversions. Reactor fluence rate and the *p*-cresol quantum yield during direct photolysis were considered in the kinetic model. The calibrated model was employed to predict the evolution of concentrations of *p*-cresol and reaction intermediates under various experimental conditions.

2. Materials and methods

2.1. Chemicals

All chemicals were obtained from commercial sources and used without further purification, including *p*-cresol (Acros, 99+%), 4-

methylcatechol (Acros, 98%), hydrogen peroxide (Acros, 50 wt%), titanium sulfate (Pfaltz&Bauer, 30%), formate (Fluka, 1000 mg/L ± 4 mg/L), acetate (Fluka, 1000 mg/L ± 4 mg/L), oxalate (Fluka, 1000 mg/L ± 4 mg/L), and TOC standard (Fluka, 50 mg/L ± 2 mg/L). Methanol (Fisher Chemical, HPLC Grade) and acetonitrile (Fisher Chemical, HPLC Grade) were solvents for HPLC analyses. Milli-Q water (resistivity ≥18.0 mΩ cm⁻¹) was obtained from a Barnstead NANOpure II system. Glassware was washed and heated overnight at 550 °C prior to use.

2.2. Experimental procedure

All experiments were conducted in a cylindrical (14-cm diameter, 950-mL) glass batch reactor, equipped with low pressure (LP) UV lamp, UV fluence meter (Hamamatsu, H8025-254) and magnetic stirrer. Stock solutions of *p*-cresol were prepared one day before use. 4-Methylcatechol stock solutions were prepared a half hour before use in amber glass containers. The UV lamp (43-cm long) was turned on two hours before the experiments. The lamp position was 21 cm above the liquid level in the reactor. A quartz sleeve covered the lamp to cut-off wavelengths below 185 nm. Solution volume was 300 mL in all experiments (liquid depth was 1.95 cm). Experiments were initiated by exposing the reactor to UV light. Experiment duration depended on the initial *p*-cresol concentration but ranged from one to three hours. Samples were analyzed immediately after withdrawal. Dilution was frequently necessary to maintain concentrations within the recommended analytical range. Temperature was maintained at T = 24.5 ± 0.5 °C. The trajectory of solution pH was determined in each experiment.

2.3. Analytics

The concentration of *p*-cresol was measured by fluorescence spectrometry (PerkinElmer LS 55). The inner filter effect (IFE) caused by light absorption and reabsorption of light-absorbing compounds was corrected mathematically, accounting for the absorption spectrum of the sample (MacDonald et al., 1997). Solution spectra were measured using a UV-Vis spectrophotometer (Thermo Science, Genesys 10s). Even though the reaction intermediate 4-methylcatechol is produced in concentrations that are comparable in order of magnitude to *p*-cresol, independent measurements showed that its fluorescence intensities were negligible compared to those of *p*-cresol in the relevant range of wavelengths.

Analysis of primary intermediates, particularly 4-methylcatechol, was carried out by HPLC (Agilent Technologies, 1200 Series) with a Polar-RP, 80 A column (15 cm × 4.6 mm × 4 μm) (Phenomenex) and UV/VIS detector at 280 nm. Elution solvents were 10% methanol in water (A) and acetonitrile (B), Q = 0.4 mL/min. The mobile phase initially consisted of 45% vol. B, linearly ramped to 65% vol. B at 15 min and then restored to the initial condition.

Formate, acetate and oxalate were measured via ion chromatography (Dionex, ICS-5000) equipped with an AS18 column (2 × 250 mm) (Dionex IonPac™), an AG18 guard column (2 × 50 mm) (Dionex IonPac™), and an AS-DV (Dionex) autosampler. Ions were detected by suppressed conductivity of the eluent using an ASRS-2mm self-regenerating suppressor (Dionex). The eluent (KOH solution; Q = 0.4 mL/min) was programmed as follows: 1 mM for 8 min, ramped (linearly) to 30 mM in 20 min, then immediately restored to 1 mM.

Hydrogen peroxide was measured using a modified peroxytitanic (colorimetric) method (Boltz and Holwell, 1978). Absorbance was measured spectrophotometrically (Thermo Science, Genesys 10s) at 407 nm. Samples were diluted to maintain absorbance values within linear limits. TOC was monitored using a Total

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