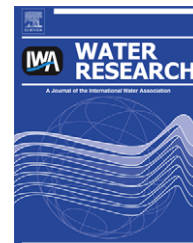


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Fenton's oxidation of pentachlorophenol

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ABSTRACT

The combination of H₂O₂ and Fe(II) (Fenton's reaction) has been demonstrated to rapidly degrade many organics via hydroxyl radicals. However, few studies have related hydroxyl radical generation rates with measured organic chemical degradation data. The goals of this work were to investigate the kinetics, stoichiometry, and intermediates of pentachlorophenol (PCP) degradation in the Fenton's reaction and to develop a mathematical model of this reaction system. Batch reaction experiments were performed to assess both initial transients and steady states, and special attention was given to the analysis of intermediates. Solutions of PCP (55 μM) and Fe(II) (200 μM) were treated with variable levels of H₂O₂ (<850 μM), and the concentrations of these reactants and their products were measured. Partial PCP degradation and near stoichiometric dechlorination were observed at low initial H₂O₂ concentrations. Higher H₂O₂ doses achieved at most 70% dechlorination even though nearly all of the PCP was degraded. The reaction intermediates tetrachlorohydroquinone and dichloromaleic acid accounted for up to 5% of the PCP degraded. Organic carbon mineralization (transformation to CO₂) was not observed. The 'OH scavenging effects of the PCP-by-products mixture were characterized as a lumped parameter in the reaction kinetics model, which provided reasonable predictions of experimental results at different oxidant concentrations and reaction time.

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1. Introduction

Fenton's reaction generates hydroxyl-radicals (OH) by means of the reaction of H₂O₂ with ferrous ion. Due to the high oxidation potential, fast reaction kinetics, and relative lack of selectivity of the 'OH toward most organic compounds (Venkatadri and Peters, 1993), Fenton's reaction produces a range of intermediates upon treatment of aromatic and chloroaromatic compounds, including chlorophenols. The elementary reaction produces cyclohexadienyl radicals, which upon stabilization yield the corresponding quinones (Anbar et al., 1966; Bunce et al., 1997; Chen and Pignatello, 1997; Kang et al., 2002; Pera-Titus et al., 2004; Potter and Roth, 1993; Sedlak and Andren, 1991). Further oxidation induces ring cleavage and

leads to the formation of organic acids such as formic, acetic, and oxalic acids (e.g., Pera-Titus et al., 2004; Pignatello et al., 2006).

The degradation of pentachlorophenol (PCP) via AOPs appears to be consistent with that of other aromatics, as ozonation/photocatalytic oxidation and Fenton's-like reactions (using multiple solid iron forms) has been reported to initially generate mixtures of tetrachlorobenzoquinone, tetrachlorohydroquinone, and tetrachlorocatechol (Benitez et al., 2003; Hirvonen et al., 2000; Luo et al., 2008; Mills and Hoffman, 1993). Strong AOP oxidation of PCP has been shown to generate ring-opened (often partially substituted) by-products (i.e., chloromaleate) and ultimately small organic acids such as oxalate and formate (Czaplicka, 2006; Sen Gupta

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et al., 2002; Hirvonen et al., 2000; Hong and Zeng, 2002; Weavers et al., 2000; Wong and Crosby, 1981). As this reaction pathway progresses, strong AOP treatment (i.e., using high oxidizer doses and/or long treatment time) of PCP-contaminated media can achieve complete substrate degradation, reduced waste toxicity and increased biodegradability (Gonze et al., 1999; Hanna et al., 2005; Mandonado et al., 2007). However, dimerization of the organic free radicals can occur under some conditions (particularly at high substrate concentrations), generating concern due to the increased toxicity of the intermediates. For example, polychlorinated dibenzo dioxins and furans have been reported to be formed upon photolysis and photo-Fenton's degradation of PCP (Czaplicka, 2006; Fukushima and Tatsumi, 2001; Hirvonen et al., 2000).

Mathematical models that can predict the degradation kinetics of the parent compound by Fenton's oxidation are less abundant than reports of experimental work. Reactions incorporated into kinetics models fall into three types (Kang et al., 2002): Group I reactions between inorganic species involved in the Fenton's system (H_2O_2 , Fe(II)/Fe(III) and initiation/propagation reactions involving the radicals $\cdot\text{OH}$, $\cdot\text{O}_2\text{H}/\cdot\text{O}_2^-$); Group II termination reactions between free radicals and organic molecules; and Group III reactions of organics and their by-products affecting the redox cycle of iron. Reactions in Group I were the main focus of earlier studies (Evans et al., 1949; Walling, 1975), although recent kinetics studies have developed a more complete understanding of the iron speciation and complexation mechanisms that can affect the kinetics (DeLaat and Gallard, 1999; Kwan and Voelker, 2002). Reactions in Group II involve the second-order degradation of organic molecules (and their by-products) by the $\cdot\text{OH}$ radicals, some of which have been available for decades (for example, see Buxton et al., 1988). Reactions in Group III include the Fe(II) regeneration effects (i.e. reduction of Fe(III)) due to hydroquinones, common intermediates of phenolics degradation that can enhance the parent compound degradation (Chen and Pignatello, 1997; Kang et al., 2002; Rivas et al., 2001).

Due to the difficulties of obtaining parameters for comprehensive kinetic models, simplifications that might limit the predictive capabilities of the model are often assumed, such as pseudo-first-order or pseudo second-order simplifying approaches (Zazo et al., 2005). More rigorous models incorporate reactions for at least Groups I and II, achieving considerable predictive capabilities (Pignatello et al., 2006). For example, the degradation of formic acid, a molecule with a well-known, short reaction pathway to CO_2 , has been described with 11 elementary steps and their corresponding reaction rates, some of which depend on the concentration of formic acid (Duesterberg et al., 2005; Duesterberg and Waite, 2006). Many of these studies assume that a complete degradation pathway is necessary to predict the degradation of the parent compound. Thus, most studies that included successful predictive kinetic models still required assumption of elementary steps and reaction rates, the latter obtained by extrapolation of data for similar molecules. Unfortunately, application of the same approach for the development of detailed kinetic models (i.e., accounting for each possible intermediate, its stoichiometry, and kinetics) for less-studied substrates with unknown or incomplete

degradation pathways (and the associated kinetic constants) becomes overwhelmingly complex. Furthermore, for molecules with relatively unknown reactivities, the assumption of detailed reaction pathways and reaction rates would introduce large uncertainties. Thus, as much as a complete kinetics model is desirable, there is a strong need to develop a reaction kinetics model that retains predictive capabilities under different reaction conditions (typically different oxidant concentrations).

The traditional Fenton's treatment (referred to as "thermal" Fenton's by Pignatello and collaborators (Pignatello et al., 2006) consists of a reaction in the dark using soluble iron (typically Fe(II) and H_2O_2), with an optimal pH around 3 (for example, Hong et al., 2008; Pignatello et al., 2006; Venkatadri and Peters, 1993). Although Fenton's and Fenton's-like degradation of PCP have been reported, the experimental conditions used to obtain these data preclude modeling under a traditional Fenton's approach due to different limitations: (a) heterogeneous catalysis by solid forms of iron (Liao et al., 2007; Liou et al., 2004; Luo et al., 2008; Mecozzi et al., 2006); (b) use of additional $\cdot\text{OH}$ -generating mechanisms such as photolysis or electricity (Hanna et al., 2005), or (c) PCP concentrations exceeding the PCP solubility at low pH (55 μM) (Liou et al., 2004; Mandonado et al., 2007; Fukushima and Tatsumi, 2001; Mecozzi et al., 2006). Information on the degradation of dissolved PCP by the traditional Fenton's treatment (based on Fe(II) at pH 3-4) at H_2O_2 doses resulting in partial PCP degradation is scarce. The goal of this work was to measure the kinetics and extent of the degradation of PCP in aqueous solution upon variable concentrations of the Fenton's reaction reagents, to investigate the nature of the PCP-by-products, and to model the kinetics of this reaction system. Concentrations of key species were measured during initial transients and after the reactions had reached completion, and special attention was given to the analysis of intermediates (including a mass balance on organic carbon and chloride). The resulting information was incorporated into a kinetics model that retained reasonably detailed rates of initiation and propagation for the hydroxyl- and other radicals and used simplified forms of the rates of termination reactions with organics by lumping the hydroxyl free radical-scavenging effects of all reaction by-products of the parent compound. This allowed the evaluation of a reaction kinetics modeling approach that is more tractable than the detailed mechanistic models in which all reaction by-products and their reactivities are included, and that provides more predictive capability than pseudo-first-order kinetic models.

2. Experimental section

2.1. Chemicals

Pentachlorophenol (99%), the extraction surrogate (dibromophenol, 95%) and the internal standard (dibromobenzene, 98%) were purchased from Sigma. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (99%+) was purchased from Baxter. H_2O_2 (non-stabilized, 31.4%), sodium chloride (99.9%) and sulfuric acid (conc.) were all purchased from Fisher. Sulfuric acid (0.1 N) was used for pH adjustment. Pesticide-grade chloroform and ethyl acetate used as

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