



Inhibitory effect of natural organic matter or other background constituents on photocatalytic advanced oxidation processes: Mechanistic model development and validation



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ABSTRACT

The ability of reactive oxygen species (ROS) to interact with priority pollutants is crucial for efficient water treatment by photocatalytic advanced oxidation processes (AOPs). However, background compounds in water such as natural organic matter (NOM) can significantly hinder targeted reactions and removal efficiency. This inhibition can be complex, interfering with degradation in solution and at the photocatalyst surface as well as hindering illumination efficiency and ROS production. We developed an analytical model to account for various inhibition mechanisms in catalytic AOPs, including competitive adsorption of inhibitors, scavenging of produced ROS at the surface and in solution, and the inner filtering of the excitation illumination, which combine to decrease ROS-mediated degradation. This model was validated with batch experiments using a variety of ROS producing systems ($\cdot\text{OH}$ -generating TiO₂ photocatalyst and H₂O₂-UV; ¹O₂-generating photosensitive functionalized fullerenes and rose bengal) and inhibitory compounds (NOM, *tert*-butyl alcohol). Competitive adsorption by NOM and ROS scavenging were the most influential inhibitory mechanisms. Overall, this model enables accurate simulation of photocatalytic AOP performance when one or more inhibitory mechanisms are at work in a wide variety of application scenarios, and underscores the need to consider the effects of background constituents on degradation efficiency.

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1. Introduction

Photochemical and photocatalytic processes offer unique capabilities to treat many common water pollutants as well as recalcitrant contaminants of emerging concern, including pharmaceutical products, endocrine disrupting compounds, and pesticides (Qu et al., 2012; Chong et al., 2010; Klavarioti et al., 2009; Brame et al., 2011). These advanced oxidation processes (AOPs) rely primarily on the strong oxidation potential of produced reactive oxygen species (ROS) such as hydroxyl radicals ($\cdot\text{OH}$; 2.8 V vs. SHE (Klamerth et al., 2012)) or singlet oxygen (¹O₂, 1.1 V vs. SHE (Ahmad and Armstrong, 1984)). Photocatalysis offers a potentially cost-effective avenue for contaminant removal through extensive

material reuse, use of solar illumination energy and utilization of existing UV disinfection infrastructure to achieve more efficient treatment.

Photocatalytic processes must account for and overcome various inhibition mechanisms in complex water matrices to enable implementation as a viable water treatment technology. For example, non-target organics can scavenge produced ROS, shade the photocatalytic materials from incoming photons (inner filter effect (Guillard et al., 2005)), and adsorb to the photocatalyst surface where they both displace adsorption of the target contaminants and potentially interfere with ROS production processes. We recently developed an analytical model to account for the inhibitory effect of background constituents such as dissolved organic matter and inorganic ions on the efficiency of homogeneous photo-reactive AOP systems (Brame et al., 2014a). In this paper we expand this model to consider more common heterogeneous photocatalytic systems, in which additional inhibition mechanisms may interplay. Specifically, we consider ROS scavenging both in solution and at the photocatalyst surface, competition for surface adsorption

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sites between target contaminants and background materials, and light occlusion effects due to inner filtering.

To accurately predict AOP inhibition in natural waters, models must account for all of these processes—both surface and bulk phenomena—since inhibitory mechanisms are likely to affect not only bulk ROS concentration, but also surface concentrations and generation mechanisms. However, existing models of photocatalytic processes are limited by assumptions of either bulk degradation of contaminants by a steady state ROS concentration or surface degradation following adsorption of the contaminant to the photocatalyst surface (i.e., Langmuir–Hinshelwood kinetics, (Konstantinou and Albanis, 2004)). Herein we develop a model to account for both bulk and surface inhibition mechanisms simultaneously, allowing prediction of photocatalytic AOP inhibition due to non-target compounds present in treatment water, such as background natural organic matter (NOM). Validation of the model was carried out using several different combinations of photocatalysts, ROS probes and inhibitory compounds, to investigate the sensitivity of the model to variations in parameters such as adsorption capacity, ROS generation rate, type (OH• and ¹O₂) and scavenging potential.

2. Materials and methods

2.1. Photo-reactive testing

Both homogeneous and heterogeneous photoactive systems were used to validate the model and ensure its applicability to a wide variety of photo-active AOPs. Hydroxyl radical-producing materials used were titanium dioxide (TiO₂) as a heterogeneous system and UV-hydrogen peroxide (H₂O₂) as a homogeneous system. TiO₂ was Degussa P25 with a nominal particle size of 30 nm and surface area of 50 m²/g (Jafry et al., 2010). H₂O₂ (35 wt%) was supplied by Fischer Scientific. Singlet oxygen-producing materials used were functionalized fullerenes (heterogeneous system) and rose bengal (RB; homogeneous system). The fullerene photocatalyst (Si–C₆₀) was an amine-functionalized C₆₀ material covalently attached to a silica gel substrate by amide bonds. RB was supplied by Sigma–Aldrich. Photocatalyst loading (TiO₂, Si–C₆₀) was set at 0.5 g/L to simulate potential treatment conditions (Brame et al., 2013; Lee et al., 2010), and homogeneous photosensitizer concentrations (H₂O₂, RB) were chosen to match the steady state ROS production of the photocatalyst materials (15 mg/L, and 25 mg/L respectively). While other ROS species (e.g., super oxide) could be generated by photo-reactive materials, electron paramagnetic resonance (EPR) analysis showed that our systems primarily generate •OH and ¹O₂, respectively (Brame et al., 2014a, 2013; Lee et al., 2010; Liao et al., 2013).

All photocatalytic tests were conducted using a box photo-reactor described extensively in previous works (Brame et al., 2013; Lee et al., 2010; Liao et al., 2013; Kim et al., 2012). Illumination was provided by six 4 W bulbs with UV-A (TiO₂, 350–400 nm), UV-C (H₂O₂, 254 nm) or visible (Si–C₆₀, RB; 400–800 nm) illumination spectra, with measured light intensities of 18 mW cm⁻² (Brame et al., 2013), 165 mW cm⁻² (Lee et al., 2010), and 1.105 mW cm⁻² (Lee et al., 2011), respectively. Photo-reactive materials were stirred vigorously at room temperature in the 50 mL quartz reaction vessel with 1 mL sample aliquots taken at various time points for analysis. Probe compounds used as representative target pollutants included furfuryl alcohol (FFA, Sigma–Aldrich) and 4-chlorophenol (4CP, Sigma–Aldrich) (Brame et al., 2014a; Lee et al., 2010; Lee et al. 2009; Haag and Hoigne, 1986; Minerio et al., 2000; Buxton et al., 1988; Brame et al., 2014b). These probe compounds were chosen due to their disparate properties (e.g., sorption, ROS reaction kinetics) to validate the model under a wide range of degradation

circumstances. ROS (OH• and ¹O₂) production was confirmed previously using electron paramagnetic resonance (EPR) spectrometry, with typical values of 5.5 × 10⁻¹⁴ mg/L (•OH) and 5.64 × 10⁻¹³ mg/L (¹O₂) (Brame et al., 2014a).

2.2. Analysis

Quantification of FFA and 4CP concentration was carried out with a Shimadzu Prominence HPLC (Shimadzu Corp., Columbia MD) using a C18 column with acetonitrile and 0.1% (w/v) phosphoric acid as mobile phase solvents (70:30, FFA; 55:45, 4CP). Pseudo first order degradation rate constants (*k_A*) were estimated (±standard deviation) from a linear regression of observed exponential decay of compound concentrations as a function of time. To avoid influence of degradation byproducts, rate constants were calculated using only the early time data, representing the first 30% of degradation. All HPLC solvents were analytical-grade and obtained from Sigma–Aldrich.

2.3. Inhibitory compounds

Two different compounds were used to probe inhibitory mechanisms. Suwannee River NOM was used as a representative organic material, and was obtained from the International Humic Substances Society (St. Paul, MN, USA, (Hyung et al., 2006)). A second inhibitory compound, tert-butyl alcohol (t-BuOH), was used as a non-adsorbing comparison material, and was obtained from Sigma–Aldrich. Concentration ranges for inhibition compounds were chosen based on preliminary studies (data not shown) and previous findings (Brame et al., 2014a).

2.4. Kinetic model of ROS-mediated degradation

The initial ROS-mediated degradation of aqueous organic target compound A in water (prior to degradation product formation) can be modeled as a second order reaction:

$$\frac{dC_A}{dt} = k_A C_{ROS} C_A \quad (1)$$

Here *C_A* represents the concentration of the target compound being degraded (e.g., FFA), *C_{ROS}* represents the steady state ROS concentration in the system, and *k_A* is the reaction rate constant for a specific ROS compound reacting with target contaminant A in water. Literature values of *k_A* for a variety of compounds are available for both •OH (Buxton et al., 1988) and ¹O₂ (Wilkinson et al., 1995).

When degradation takes place on the photocatalyst surface, the same second order rate law is assumed with respect to the surface-bound concentrations of ROS and the target pollutant (*C_{ROS,S}* and *C_{A,S}*, respectively). *C_{A,S}* is a ratio of the occupied surface sites compared to the total number of surface sites, and is assumed to be in instantaneous equilibrium with the bulk aqueous phase concentration *C_A*, and is quantified using the Langmuir adsorption equilibrium model, which assumes a limited number of surface adsorption sites that can be filled to a monolayer of surface coverage in instantaneous equilibrium with the bulk concentration of the adsorbing compound (*C_A*):

$$C_{A,S} = q_A = \frac{K_A C_A}{1 + K_A C_A} \quad (2)$$

Where *q_A* is the equilibrium surface loading of A and *K_A* is the Langmuir adsorption constant. Inserting eq. (2) into eq. (1) yields an expression for ROS-mediated degradation at the surface of a

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