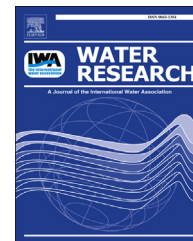




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Trading oxidation power for efficiency: Differential inhibition of photo-generated hydroxyl radicals versus singlet oxygen

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ABSTRACT

The ability of reactive oxygen species (ROS) to interact with target pollutants is crucial for efficient water treatment using advanced oxidation processes (AOPs), and inhibition by natural organic matter (NOM) can significantly reduce degradation efficiency. We compare OH[•]-based degradation (H₂O₂-UV) to ¹O₂-based degradation (Rose Bengal) of several probe compounds (furfuryl alcohol, ranitidine, cimetidine) interacting in water containing background constituents likely to be found in treatment water such as natural organic matter (NOM) and phosphate, as well as in effluent from a waste-water treatment plant (WWTP). Hydroxyl radicals were much more susceptible to hindrance by all three background matrices (NOM, phosphate and WWTP effluent) tested, while ¹O₂ was only slightly inhibited by NOM and not by phosphate or WWTP effluent. A mechanistic model accounting for this inhibition in terms of radical scavenging and inner filter effects was developed, and accurately simulated the results of the NOM interactions. These results underscore the importance of considering the effect of background constituents in the selection of photocatalysts and in the design of AOPs for emerging applications in tertiary treatment of wastewater effluent and disinfection of natural waters.

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1. Introduction

As the demand for clean water continues to grow, the necessity for advanced water treatment and reclamation technologies will continue to increase (Brame et al., 2011; Qu et al., 2012). Advanced oxidation processes (AOP) have great potential to remove many common water pollutants as well as contaminants of emerging concern such as pharmaceutical products, endocrine disrupting compounds, and pesticides (Chong et al., 2010; Herrmann, 1999; Klavarioti et al., 2009).

Reactive oxygen species (ROS) such as hydroxyl radical (OH[•]) and singlet oxygen (¹O₂) that are generated in photocatalytic and photochemical AOPs can oxidize recalcitrant organic and biological contaminants with much lower potential to form carcinogenic disinfection byproducts common to chemical treatment approaches such as chlorination and ozonation (Li et al., 2008; Qu et al., 2012; Toor and Mohseni, 2007). However, the efficiency of AOPs can be hindered by the presence of background constituents in water, such as organic material (e.g., natural organic matter [NOM] or wastewater treatment plant effluent) or inorganic ions (e.g., phosphate)

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(Abdullah et al., 1990; Enriquez and Pichat, 2001; Lee et al., 2011). Such background constituents can interfere with ROS-based degradation processes by absorbing incoming light and by acting as radical scavengers, reducing both the amount of ROS produced and the effective concentration of ROS available for interaction with the target pollutants.

An important factor in whether or not background organic material will significantly affect degradation treatment efficiency is the selectivity of the generated ROS (Hoigné and Bader, 1983; Kim et al., 2012; Lee and von Gunten, 2010). Hydroxyl radicals, which are the primary ROS produced by TiO₂ photocatalysis and H₂O₂/UV oxidation, are very powerful oxidants (2.8 V vs. standard hydrogen electrode (SHE) (Klamerth et al., 2012)), and are therefore able to oxidize a broad range of organic compounds. However hydroxyl radicals are also non-specific, making them susceptible to scavenging by non-target organic and inorganic compounds in water, and their generation requires UV light, which is partially absorbed by organic material in the water (Edzwald et al., 1985; Korshin et al., 1997). Singlet oxygen is produced by visible-light active photosensitizers such as fullerenes (C₆₀), porphyrins and Rose Bengal (RB). Since light absorption by NOM is greatest in the far UV and declines throughout the UV and visible spectrum (Edzwald et al., 1985; Korshin et al., 1997), NOM inner filtering is likely less inhibitory to visible light-activated photocatalysts. Furthermore, ¹O₂ is much more selective than OH•, targeting electron-rich moieties in pollutants such as phenols and activated aromatics (Lee and von Gunten, 2010). Although this specificity could decrease the probability of inadvertent scavenging by organic matter in natural waters, ¹O₂ is a much weaker oxidant (1.1 V vs. SHE (Ahmad and Armstrong, 1984)) than OH•, possibly resulting in partial oxidation of some compounds, including formation of potentially harmful oxidation byproducts (e.g., quinones, nitrophenols, aldehydes, etc. (Chen et al., 1998; Dzengele et al., 1998; Echavia et al., 2009; Topudurti et al., 1998)). A weaker oxidant may also require longer contact times or more photosensitizing material for the same degradation capacity, and not allow degradation of some materials that require strong oxidation.

Most ROS-generating photoreactive and photocatalytic degradation studies are conducted using laboratory-grade deionized water, which ignores these inhibitory effects of background constituents in natural water. Recently, more research has been conducted using non-ideal water sources, specifically focusing on wastewater treatment plant (WWTP) effluent, since tertiary treatment is a likely application scenario for AOP technology (Kim et al., 2012; Klamerth et al., 2012). We recently demonstrated that selective ROS can be more efficient than non-selective ROS in removal of some organic contaminants (Kim et al., 2012), and others have done similar work in wastewater effluent (Lee and von Gunten, 2010), but this tradeoff between oxidative power and specificity in photocatalytic AOPs has not been systematically explored in the literature. This is a critical knowledge gap because inhibition of ROS-mediated degradation by naturally occurring organic matter could have a significant impact on the degradation efficiency of this technology upon implementation.

In this paper we consider two representative types of ROS commonly involved in photo-active AOPs (¹O₂ and OH•) as

produced by homogeneous photoreactive chemicals as part of a larger study to determine the effect and mechanisms of organic matter and inorganic inhibition of ROS-assisted photochemical degradation. Homogeneous photoreactive materials were selected to remove confounding surface effects of heterogeneous photocatalysts (e.g., sorption, charge transfer interference, local vs. bulk ROS scavenging) and focus on the interaction between photo-generated ROS and background organic materials. We explore the extent to which common water constituents such as natural organic matter and phosphate, as well as constituents in WWTP effluent decrease degradation rates and ROS production capacity within the context of water treatment, and develop a mechanistic model to account for the decreased efficiency due to scavenging of ROS and light absorption by NOM (inner filter effect).

2. Materials and methods

2.1. Photo-reactive testing

Hydrogen peroxide (H₂O₂) illuminated by UV light (254 nm) was used to produce hydroxyl radicals (OH•), and Rose Bengal (RB) illuminated by visible light (400–800 nm) was used to produce singlet oxygen (¹O₂). H₂O₂ was 35% H₂O₂ supplied by Fischer Scientific. RB was supplied by Sigma–Aldrich. Photosensitizer (H₂O₂, RB) concentrations were 15 and 25 ppm respectively, which were chosen to match the steady state ROS production of traditional photocatalyst materials in DI water (Brame et al., 2013; Liao et al., 2013) as part of a larger study of ROS production.

Illumination occurred within a photoreactor described previously (Brame et al., 2013; Liao et al., 2013), with UV-C bulbs (H₂O₂, 254 nm) or visible bulbs (RB; 400–800 nm). Photo-reactive materials were stirred vigorously in a quartz reaction vessel with 1 mL sample aliquots taken at various time points for analysis. Degradation of a probe compound easily oxidized by both hydroxyl radicals and singlet oxygen (furfuryl alcohol [FFA], Sigma–Aldrich) was used as a surrogate for ROS production (Buxton et al., 1988; Haag and Hoigne, 1986; Lee et al., 2009, 2010; Minero et al., 2000), which was confirmed using electron paramagnetic resonance (EPR) spectrometry (Liao et al., 2013). Ranitidine (N-(2-[(5-[(dimethylamino)methyl]furan-2-yl)methylthio]ethyl)-N'-methyl-2-nitroethene-1,1-diamine) and cimetidine (2-cyano-1-methyl-3-(2-[(5-methyl-1H-imidazol-4-yl)methylthio]ethyl)guanidine), two pharmaceutical compounds, were also used as representative target pollutants (Sigma–Aldrich). Dark and non-reactive controls were run to ensure that degradation was the result of photoreactive ROS interactions.

2.2. Analysis

Quantification of FFA 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). First order degradation rate constants (*k*_{obs}) were calculated from a linear regression of observed exponential decay. Determination of

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