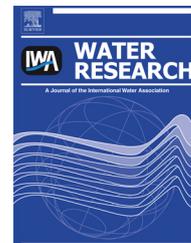Available online at www.sciencedirect.com

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Identifying the factors that influence the reactivity of effluent organic matter with hydroxyl radicals

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ABSTRACT

Advanced oxidation processes (AOPs) are an effective treatment technology for the removal of a variety of organic pollutants in both water and wastewater treatment. However, many background constituents in water are highly reactive towards hydroxyl radicals (HO•) and decrease the efficiency of the process towards contaminant oxidation. Up to 95% of the HO• scavenging can come from dissolved organic matter (OM). In this study, 28 wastewater effluent samples were analyzed to find correlations between the reactivity of HO• with wastewater-derived OM (known as effluent organic matter, EfOM), water quality parameters, treatment train characteristics, and fluorescence-derived data. Rate constants for the reaction between HO• and EfOM ($k_{EfOM-HO}$) were measured using a bench scale UV-based AOP system with methylene blue as an HO• probe and confirmed using an electron pulse radiolysis method for a subset of the samples. The EfOM was characterized using a series of physicochemical parameters, including polarity, average molecular size and fluorescence. The kinetic data were analyzed with principal component analysis and Akaike Information Criterion. Four predictors were identified as dominant: chemical oxygen demand, retention onto NH_2 extraction medium, fluorescence index, and total organic carbon. These four variables accounted for approximately 62% of the variability in the value of $k_{EfOM-HO}$ The average $k_{EfOM-HO}$ value for EfOM in this study was $2.5 \times 10^8 \, M_C^{-1} \, s^{-1}$, which is about 31% lower than the $3.6 \times 10^8 \, M_C^{-1} \, s^{-1}$ value determined for natural organic matter isolates and commonly used in AOP modeling.

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1. Introduction

Advanced oxidation processes (AOPs) have been demonstrated as an efficient treatment technology for the oxidation of a variety of organic contaminants (Huber et al., 2003; Gogate and Pandit, 2004; Rosenfeldt and Linden, 2004; Rosario-Ortiz et al., 2010). Its efficacy arises from the highly reactive and non-selective nature of the hydroxyl radicals (HO•). HO• reacts

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List of abbreviations:

AOP	advanced oxidation process
HO•	hydroxyl radical
OM	organic matter
EfOM	effluent organic matter
TOC	total organic carbon
DOC	dissolved organic carbon
UV	ultraviolet
MB	methylene blue
PCA	principal component analysis
AIC	Akaike Information Criterion
RC	retention coefficient
COD	chemical oxygen demand
SRT	solids retention time
$SUVA_{254}$	specific UV absorbance at 254 nm
MW	molecular weight (weight average)
d	dispersity
FI	fluorescence index
RI	redox index
PS	protein-like fluorescence signal
HIX	humification index
SC	secondary clarifier
TNF	trickling nitrifying filter
DN	denitrifying filter
FE	final effluent

List of symbols:

k	reaction rate constant
$k_{EfOM-HO}$	reaction rate constant between effluent organic matter (EfOM) and HO•, $M_C^{-1}\,s^{-1}$, where M_C is the molar concentration of organic carbon
$k_{HO,MB}$	reaction rate constant between methylene blue (MB) and HO•, $M^{-1}\,s^{-1}$
E_0	average fluence rate, mW/cm^2
F	fluence, mJ/cm^2
k_s	HO• reaction rate constant for a given scavenging compound, $M^{-1}\,s^{-1}$
[S]	concentration of a scavenging compound, M
ε_{254}	molar absorption coefficient at 254 nm, $M^{-1}\,cm^{-1}$
Φ	quantum yield of photolysis, —
U_{254}	254 nm wavelength energy, J/mol

with organic contaminants through different mechanisms, including hydrogen abstraction and addition to electron-rich sites, with reaction rate constants on the order of $10^{8-10}\ M^{-1}\,s^{-1}$ being reported for the reactions with many organic species (Buxton et al., 1988). Although the high reactivity of HO• offers the benefit of oxidizing mixtures of organic compounds, it also has the drawback of reacting with the background water quality components. Carbonate species and dissolved organic matter (OM) are typically the primary HO• scavengers in natural water samples.

The application of AOPs for the oxidation of organic contaminants has been studied as a potential municipal wastewater treatment process for water reuse applications (Huber et al., 2003; Rosario-Ortiz et al., 2010; Keen et al., 2012a, 2012b). Typically, AOP efficiencies for organic compounds vary from no removal to complete oxidation, and are a function of the oxidation kinetics of the compounds and the scavenging capacity of the water matrix (Rosario-Ortiz et al., 2010; Keen et al., 2012b). In AOP systems, only a fraction of HO• will react with the trace contaminants with the majority of the HO• reacting with background scavengers. The consumption of HO• via non-specific reactions is the scavenging capacity of the water matrix. Because of the high level of HO• scavenging in wastewater matrices, AOPs are often viewed as not economical for wastewater treatment. However, some of the recent studies show that it may not be necessary to achieve full mineralization (Keen et al., 2012a). Combined with better ways to predict the process performance, AOPs may become a viable option for wastewater treatment.

In wastewater treatment plant effluents, the main HO• scavenger is effluent organic matter (EfOM), due to both its moderate reactivity with HO• on the order of $10^8\ M_C^{-1}\,s^{-1}$ (Westerhoff et al., 1999; Rosario-Ortiz et al., 2008) and its relatively high concentrations (measured as total organic carbon-TOC). While natural OM isolates and standards were shown to have a relatively constant value for the reaction rate constant with HO• (k_{OM-HO}) (Westerhoff et al., 1999), the reactivity of EfOM ($k_{EfOM-HO}$) has been shown to have variable reactivity with the reported range of values from 1.39×10^8 to $11.5 \times 10^8\ M_C^{-1}\,s^{-1}$ across various studies (Rosario-Ortiz et al., 2008; Westerhoff et al., 2007; McKay et al., 2011; Katsoyiannis et al., 2011; Nagarnaik and Boulanger, 2011) with up to a factor of 4.5 difference in a single study (Rosario-Ortiz et al., 2008). The variable nature of $k_{EfOM-HO}$ has been attributed in part to differences in molecular weight composition across different samples (Westerhoff et al., 2007; Dong et al., 2010). Among other parameters that were previously suggested to influence reactivity of OM towards HO• are specific UV absorbance (absorbance per mg/L of organic carbon) at 254 nm (Westerhoff et al., 1999), polarity measures and fluorescence index (Rosario-Ortiz et al., 2008). These parameters carry information about the structural composition and prevalence of certain functional groups within the bulk OM, such as aromatic rings or hydrophilic functional groups. For example, FI of the sample tends to be higher when more products of microbial activity (more aliphatic in structure) are present (McKnight et al., 2001).

The main objective of this study was to conduct a statistical evaluation of the physicochemical properties of EfOM and of wastewater treatment process variables and their role in the reactivity of EfOM towards HO•. In full-scale AOP systems, it is difficult to measure the concentration of HO• *in situ* or in real time because of its low concentration. Therefore, engineers rely on calculations and safety factors when designing these treatment processes. Part of this study's objective was to develop a model to predict the values of $k_{EfOM-HO}$ to offer a full-scale reactor design tool that could increase confidence in the prediction of performance, and therefore minimize the safety factors and eventual costs associated with AOP treatment.

A number of parameters were evaluated in this study for their ability to predict the value of $k_{EfOM-HO}$. Those parameters