

Selective Oxidative Degradation of Organic Pollutants by Singlet Oxygen-Mediated Photosensitization: Tin Porphyrin versus C₆₀ Aminofullerene Systems

Heechan Kim,[†] Wooyul Kim,[‡] Yuri Mackeyev,[§] Gi-Seon Lee,^{||} Hee-Joon Kim,^{||} Takashi Tachikawa,[⊥] Seokwon Hong,[†] Sanghyup Lee,[†] Jungbae Kim,[#] Lon J. Wilson,[§] Tetsuro Majima,[⊥] Pedro J. J. Alvarez,[▽] Wonyong Choi,[‡] and Jaesang Lee^{†,*}

[†]Water Research Center, Korea Institute of Science and Technology, Seoul 136-791, Korea

[‡]Environmental Science and Engineering, Pohang University of Science and Technology, Pohang 790-784, Korea

[§]Chemistry, Smalley Center for Nanoscale Science and Technology, Rice University, Houston, Texas 77005, United States

^{||}Applied Chemistry, Kumoh National Institute of Technology, Gumi 730-701, Korea

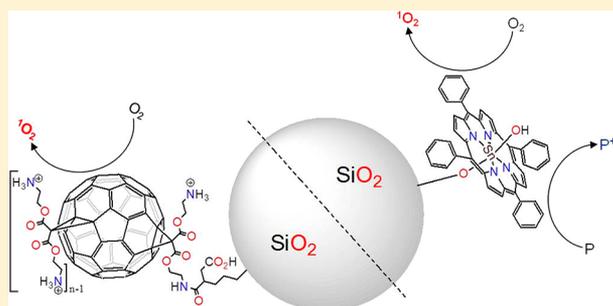
[⊥]The Institute of Scientific and Industrial Research, Osaka University, Osaka 567-0047, Japan

[#]Chemical and Biological Engineering, Korea University, Seoul 136-701, Korea

[▽]Civil and Environmental Engineering, Rice University, Houston, Texas 77005, United States

Supporting Information

ABSTRACT: This study evaluates the potential application of tin porphyrin- and C₆₀ aminofullerene-derivatized silica (SnP/silica and aminoC₆₀/silica) as ¹O₂ generating systems for photochemical degradation of organic pollutants. Photosensitized ¹O₂ production with SnP/silica, which was faster than with aminoC₆₀/silica, effectively oxidized a variety of pharmaceuticals. Significant degradation of pharmaceuticals in the presence of the 400-nm UV cutoff filter corroborated visible light activation of both photosensitizers. Whereas the efficacy of aminoC₆₀/silica for ¹O₂ production drastically decreased under irradiation with λ > 550 nm, Q-band absorption caused negligible loss of the photosensitizing activity of SnP/silica in the long wavelength region. Faster destruction of phenolates by SnP/silica and aminoC₆₀/silica under alkaline pH conditions further implicated ¹O₂ involvement in the oxidative degradation. Direct charge transfer mediated by SnP, which was inferred from nanosecond laser flash photolysis, induced significant degradation of neutral phenols under high power light irradiation. Self-sensitized destruction caused gradual activity loss of SnP/silica in reuse tests unlike aminoC₆₀/silica. The kinetic comparison of SnP/silica and TiO₂ photocatalyst in real wastewater effluents showed that photosensitized singlet oxygenation of pharmaceuticals was still efficiently achieved in the presence of background organic matters, while significant interference was observed for photocatalyzed oxidation involving non-selective OH radical.



INTRODUCTION

Photochemical production of reactive oxygen species (ROS) by a number of diverse natural materials under sunlight irradiation can initiate the transformation of organic compounds in waters.^{1–4} For example, sunlight-induced photochemical reactions of ferric ion or its carboxylate complexes present in the environment are involved in formation of hydrogen peroxide and its catalytic decomposition to hydroxyl radical ([•]OH), resulting in the oxidation of aquatic organic substances.^{3,5} Nitrate-induced production of OH radical leads to pollutant degradation in atmospheric and surface waters upon sunlight irradiation.⁴ Natural organic matter (NOM), a prevalent constituent of natural waters, causes oxidative transformation through the photochemical reactions involving production of ROS such as [•]OH^{6,7} and singlet oxygen (¹O₂).^{1,8}

The underlying mechanisms of such photosensitized oxidation reactions, especially those induced by natural precursors of [•]OH (e.g., iron polycarboxylates, clay minerals), offer potential insights into photochemical remediation strategies to treat industrial and municipal effluents contaminated with recalcitrant substances.^{9,10}

It is well recognized that photochemically generated ¹O₂ acts as a primary oxidant in the photosensitized transformation of organic substances^{11,12} and inactivation of viruses^{13–15} in natural waters. Organic pollutants including polycyclic aromatic

Received: May 3, 2012

Revised: July 16, 2012

Accepted: August 1, 2012

Published: August 1, 2012

hydrocarbons,¹⁶ chlorophenols,¹⁷ and pesticides¹⁸ were found to be considerably vulnerable to singlet oxygenation, which occurs through the energy transfer from the photoexcited NOM to oxygen. Previous findings demonstrated that ¹O₂ produced upon irradiation of NOMs with sunlight was responsible for the enhanced inactivation of MS-2 coliphage in natural waters under sunlight illumination.^{13,14} On the basis of the high reactivity of ¹O₂ and its widespread occurrence in the naturally-occurring photooxidation reactions, photochemical remediation approaches, exploiting the oxidizing capacity of ¹O₂, have significant application for water treatment and disinfection processes.

As electrophilic ¹O₂ preferentially oxidizes electron-rich olefins, dienes, sulfides, and aromatic hydrocarbons,^{19–21} ¹O₂ production capability of photosensitizers such as macrocyclic dyes, aromatic hydrocarbons, and transition metal complexes enables photochemical pollutant oxidation and microbial disinfection. Among various photoactive ¹O₂ generating agents, porphyrin and fullerene derivatives (both are highly effective for ¹O₂ production in response to visible light) have been employed for photosensitized phenol oxidation,²² dye decoloration,²³ and bacterial/viral disinfection²⁴ in water. Photochemical ¹O₂ generation by functionalized porphyrins led to oxidative degradation of endocrine-disrupting contaminants (e.g., pentachlorophenol, butylparaben),^{25,26} as aqueous dispersions of C₆₀ fullerenes surface-modified with hydrophilic groups enabled photodynamic disinfection of *Escherichia coli* and MS-2 bacteriophage.²⁷ Our recent findings^{28,29} also demonstrated that C₆₀ aminofullerenes chemically anchored to the functionalized silica induced rapid degradation of pharmaceuticals (e.g., ranitidine and cimetidine) and inactivation of MS-2 bacteriophage.

Photosensitized singlet oxygenation potentially offers advanced opportunities for oxidation processes in terms of (1) rapid degradation of electron-rich moieties ubiquitously present in organic pollutants, (2) effective ¹O₂ production through the visible-light-induced photosensitization, and (3) targeting of high priority pollutants in complex water matrices due to the selective nature of ¹O₂. Whereas previous studies have demonstrated the possible singlet oxygenation of pollutants and microbes by photosensitizing agents,^{22,24–26} the potential applicability has not been systematically investigated. In order to address the critical knowledge gap in the applicability assessment, this study shows application of tin porphyrin and hexakis C₆₀ aminofullerene (as representative ¹O₂ photosensitizers) immobilized on silica support (referred to herein as SnP/silica and aminoC₆₀/silica, respectively) for photochemical degradation of diverse pharmaceutical and endocrine-disrupting pollutants. In addition to the efficacy of ¹O₂ yield, the activity of both photosensitizing agents in the photochemical oxidation is evaluated in terms of (1) the kinetics for visible-light-induced degradation of pharmaceuticals, (2) active wavelength region for photosensitized ¹O₂ production, (3) charge transfer mechanism for photoinduced phenol oxidation, and (4) potential for multiple use scenarios as photocatalyst. In particular, we compare performance of SnP/SiO₂ as a ¹O₂ photosensitizer versus TiO₂ photocatalyst (Degussa P25) capable of OH radical-mediated oxidation based on the kinetics of pharmaceutical degradation in the presence of background dissolved organic matter associated with wastewater treatment plant effluents.

■ MATERIALS AND METHODS

Preparation of ¹O₂ Photosensitizers and Immobilization onto Silica Support. AminoC₆₀/silica was prepared and characterized according to our previously published procedure.²⁹ The aminofullerene content of 0.05 mmol/g was confirmed using thermogravimetric analysis (TGA: SDT Q600, TA Instruments), conducted under air with a heating rate of 10 °C/min. Weight loss of 11.2 ± 1% in temperature range of 200–420 °C was observed, corresponding to decomposition of organic moieties with SiO₂ remaining through the end of the TGA run (at 900 °C). The preparation of *trans*-dihydroxo-[5,10,15,20-tetraphenylporphyrinato]tin(IV) [Sn(OH)₂(TPP)] and the immobilization of Sn(OH)₂(TPP) onto silica support were similarly performed according to the reported procedures.^{23,30} The Sn content in SnP/silica was estimated to be ca. 1.85 atom % from the XPS analysis. The particles of 3-(2-succinic anhydride)propyl functionalized silica (for aminoC₆₀ immobilization) are in the size range of 37 to 75 μm, while the particle size for the bare silica support (for SnP immobilization) ranges between 33 and 75 μm.

Photochemical Experiments. Experiments with variable light sources (fluorescent lamp, black light blue (BLB) lamp, and Xe-arc lamp) were carried out in a magnetically-stirred cylindrical quartz reactor under air-equilibrated conditions at an ambient temperature (22 °C). Detailed descriptions of light irradiation conditions are available in the Supporting Information, SI. The emission spectra of the light sources and transmittance profiles of the cutoff filters are presented in Figures S1 and S2, SI.

Typical reaction suspensions of photosensitizer-derivatized silica, buffered with 10 mM phosphate at pH 7.5, were prepared at a concentration of 50 μM photosensitizing agent (0.5 g/L SnP/silica with a porphyrin content of 0.1 mmol/g and 1 g/L aminoC₆₀/silica with a fullerene content of 0.05 mmol/g) and were dispersed by simultaneous sonication and shaking for 30 s in an ultrasonic cleaning bath. Substrate stock solution (1 mM) was added to the suspension, diluting to the desired concentration (typically 0.1 mM). Sample aliquots of 1 mL were withdrawn at constant time intervals from the photoirradiated reactor using a 1-mL syringe, filtered through a 0.45-μm PTFE filter (Millipore), and injected into a 2-mL amber glass vial for further analysis. More than duplicate photolytic experiments were performed for a given condition. Quantitative analyses of the residual concentrations of target substrates were performed using a HPLC (Shimadzu LC-20AD) equipped with a C-18 column (ZORBAX Eclipse XDB-C18) and a UV-vis detector (SPD-20AV). The mobile phase comprised a binary mixture of 0.1% (v/v) aqueous phosphoric acid solution and acetonitrile (typically 70:30 by volume), while quantification of cimetidine, furfuryl alcohol, and ranitidine was done with a 40% aqueous methanol eluent. The analysis of trimethoprim was performed using a water eluent containing 25 mM ammonium acetate/acetonitrile (70:30 v/v). The HPLC analyses for all target compounds were carried out at the detection wavelength of 230 nm.

Nanosecond Laser Flash Photolysis (LFP). Nanosecond LFP experiments were carried out to monitor transient formation and subsequent decay of triplet state and radical anion in aqueous solutions of SnP and aminoC₆₀. The experimental solutions were saturated with ambient air and buffered at 7.5. The samples were excited using the second harmonic (532 nm, 10 mJ/pulse, 5 ns FWHM) of a Q-switched

Nd³⁺:YAG laser (Continuum, Surelite II-10) operated with temporal control by a delay generator (Stanford Research Systems, DG535). The transmitted probe light was focused on a monochromator (Nikon G250). The output of the monochromator was monitored using a silicon avalanche photodiode detector (Hamamatsu Photonics, S5343). The transient signals were recorded by a digitizer (Tektronix, TDS 580D). Triplet state decay kinetics of SnP and aminoC₆₀ were measured based on the time-resolved data using absorbance at 610 and 650 nm, respectively. Upon laser irradiation, immediate formation of SnP radical anion and subsequent decay were monitored by recording the transient absorption at 680 nm.

Wastewater Characterization. Samples of secondary wastewater effluents were obtained from the municipal wastewater treatment plants located in Pankyo and Uijeongbu, Gyeonggi-do, Korea. The sample of the wastewater effluent from Pankyo contained 9.9 mg/L DOC, 6.2 μM NH₄⁺, 520.5 μM NO₃⁻, 1.1 μM HPO₄²⁻, and 94 mg/L alkalinity (as CaCO₃). The effluent sample from Uijeongbu had a DOC of 8.4 mg/L, 5.5 μM NH₄⁺, 3.4 μM NO₂⁻, 730.0 μM NO₃⁻, 11.3 μM HPO₄²⁻, and 64 mg/L alkalinity (as CaCO₃). The initial pH of each wastewater effluent sample from Pankyo and Uijeongbu was 8.8 and 7.07, respectively.

RESULTS AND DISCUSSION

Rapid Photosensitized Oxidation of Pharmaceutical Compounds. The photochemical activity of SnP/silica was compared to that of hexakis aminoC₆₀/silica under fluorescent light irradiation using photochemical furfuryl alcohol (FFA) degradation as a direct indication of photosensitized ¹O₂ production.¹ FFA degradation was monitored in suspensions containing identical amounts of photosensitizing agents (i.e., [SnP]₀ = [aminoC₆₀]₀ = 50 μM). Whereas sorption or direct photolysis caused negligible FFA reduction, FFA was effectively degraded in the presence of SnP/silica or aminoC₆₀/silica under fluorescent light, confirming their activity for photochemical ¹O₂ production (Figure S3 of the SI). In particular, more rapid FFA degradation (5.4-fold faster based on the comparison of pseudo first-order rate constants (*k* values), with *k* = 2.358 ± 0.163 h⁻¹ (mean ± standard deviation) for SnP/silica (*R*² = 0.998) and *k* = 0.435 ± 0.038 h⁻¹ for aminoC₆₀/silica (*R*² = 0.989)) implies higher efficacy of SnP/silica for ¹O₂ generation relative to aminoC₆₀/silica.

Similar to our earlier work²⁸ showing high photochemical activity of aminoC₆₀/silica toward oxidation of pharmaceuticals, Figure 1 demonstrates efficient degradation of diverse pharmaceutical compounds by SnP/silica photosensitization under fluorescent light illumination. No detectable degradation of pharmaceuticals occurred by light irradiation alone (data not shown), although photochemical reactivity of several compounds (e.g., atorvastatin and propranolol) to produce ROS resulted in self-sensitized degradation has been proposed.^{31,32} No significant adsorption of pharmaceuticals on SnP/silica was observed (Figure S4 of the SI). Efficient production of ¹O₂ and substrate-specific degradation kinetics (reflecting the selective nature of ¹O₂) combined suggest that ¹O₂ was the primary oxidant in the photochemical oxidation with SnP/silica. In particular, the presence of chemical moieties that are very susceptible to singlet oxygenation in the structures of pharmaceuticals (e.g., *k*(furan + ¹O₂ in CH₂Cl₂) = 1.4 × 10⁷ M⁻¹s⁻¹;²¹ *k*(imidazole + ¹O₂ in H₂O) = 3.4 × 10⁷ M⁻¹s⁻¹;²¹ *k*(pyrrole + ¹O₂ in C₆H₅CH₃) = 1.7 × 10⁸ M⁻¹s⁻¹)²¹ resulted

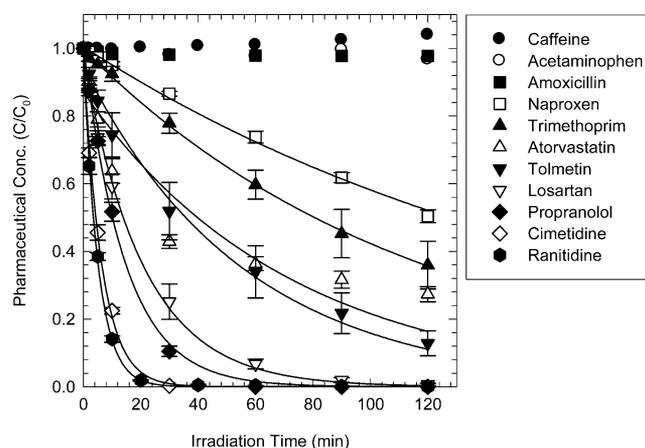


Figure 1. Photochemical degradation of pharmaceutical compounds by tin porphyrin immobilized on silica (SnP/silica) under fluorescent light irradiation. Curves represent nonlinear regression fits to pseudo first-order decay. Error bars indicate ± one standard deviation from the mean of at least three replicate reactors ([SnP/silica]₀ = 0.5 g/L; [pharmaceuticals]₀ = 100 μM ([naproxen]₀ = [losartan]₀ = 40 μM); [phosphate]₀ = 10 mM; pH_i = 7.5).

in faster photochemical decay (e.g., furan in ranitidine; imidazole in cimetidine and losartan, pyrrole in atorvastatin and tolmetin). The vulnerability to electrophilic attack by ¹O₂ seems to change depending on substituents on the aromatic ring. For example, photosensitized degradation kinetics of propranolol (*k* = 4.152 ± 0.090 h⁻¹; *R*² = 0.998) and naproxen (*k* = 0.330 ± 0.006 h⁻¹; *R*² = 0.993) by SnP/silica were significantly different, even though both contain a naphthalene moiety. Despite preferable singlet oxygenation of aminophenols (e.g., *k*(4-aminophenol + ¹O₂ in D₂O) = 1 × 10⁸ M⁻¹s⁻¹)²¹, acetaminophen and amoxicillin were not noticeably degraded in photoirradiated aqueous suspensions of SnP/silica, which may be due to the presence of electron-withdrawing substituents.

Visible-Light-Induced Oxidation. UV-vis reflectance spectra of SnP/silica and aminoC₆₀/silica with similar content of photosensitizing agents show significant visible light absorptions (Figure 2a), implying the possible photoactivation and associated ¹O₂ production under visible light irradiation. While aminoC₆₀/silica exhibits a broad absorption feature in the spectral range of 400 to 550 nm, SnP/silica has an intense absorption band at 420 nm (Soret band), followed by a few moderate to weak absorption peaks at 519, 550, and 590 nm (Q bands). To identify the visible light region to allow the photosensitizers to be photochemically active for ¹O₂ production, the efficacy of SnP/silica and aminoC₆₀/silica for photosensitized FFA degradation was compared under different wavelengths of visible light, which were controlled by using a set of optical filters cutting off below the specific wavelengths (Figure 2b). The photosensitizing activity of aminoC₆₀/silica for ¹O₂ generation was gradually reduced with increasing wavelength and nearly disappeared under illumination by wavelengths longer than 645 nm. In particular, irradiation by visible light above 550 nm caused a ca. 50% decrease in efficacy of the photosensitized FFA degradation (i.e., ¹O₂ production) compared to light irradiation under wavelengths longer than 420 nm. However, high photochemical activity of SnP/silica for ¹O₂ yield was maintained in response to light of wavelengths up to 550 nm, which implies that the macrocyclic conjugated system enables SnP/silica to utilize a broader range of visible light wavelengths for ¹O₂ production. Figure 3 demonstrates

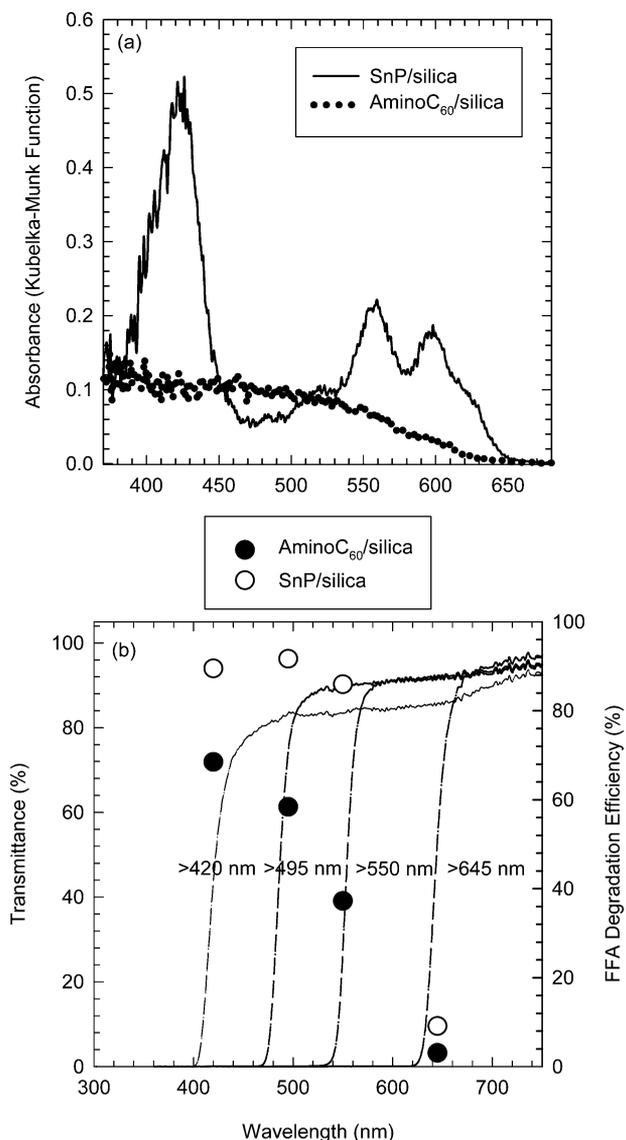


Figure 2. (a) UV-vis diffuse reflectance spectra of SnP/silica and aminoC₆₀/silica; (b) Photosensitized degradation of furfuryl alcohol by SnP/silica and aminoC₆₀/silica under different irradiation wavelengths (controlled by a set of long-pass filters transmitting $\lambda > 420, 495, 550,$ or 645 nm) ([SnP/silica]₀ = 0.5 g/L; [aminoC₆₀/silica]₀ = 1 g/L; [FFA]₀ = 100 μ M; [phosphate]₀ = 10 mM; pH_i = 7.5). The dashed lines indicate the transmittance profiles of the cutoff filters.

that photochemical oxidation of selected pharmaceutical compounds on SnP/silica and aminoC₆₀/silica was significant under visible light irradiation ($\lambda > 400$ nm). Furthermore, there is no marked difference in the rate of photosensitized oxidation of pharmaceuticals by SnP/silica between fluorescent and visible light irradiation, which could be attributed to the negligible loss of photochemical activity under irradiation of long-wavelength visible light.

Alternative Oxidation Pathway Involving Direct Charge Transfer. Figure 4 shows the efficacy of SnP/silica for photosensitized degradation of phenolic compounds including amoxicillin, acetaminophen, bisphenol A, and trichlorophenol after 2 h of UV-A irradiation (4W BLB lamp) as a function of initial pH. Our earlier work²⁸ showed that alkaline pH conditions favored photosensitized oxidation of phenols by tetrakis aminoC₆₀/silica as electrophilic ¹O₂ more

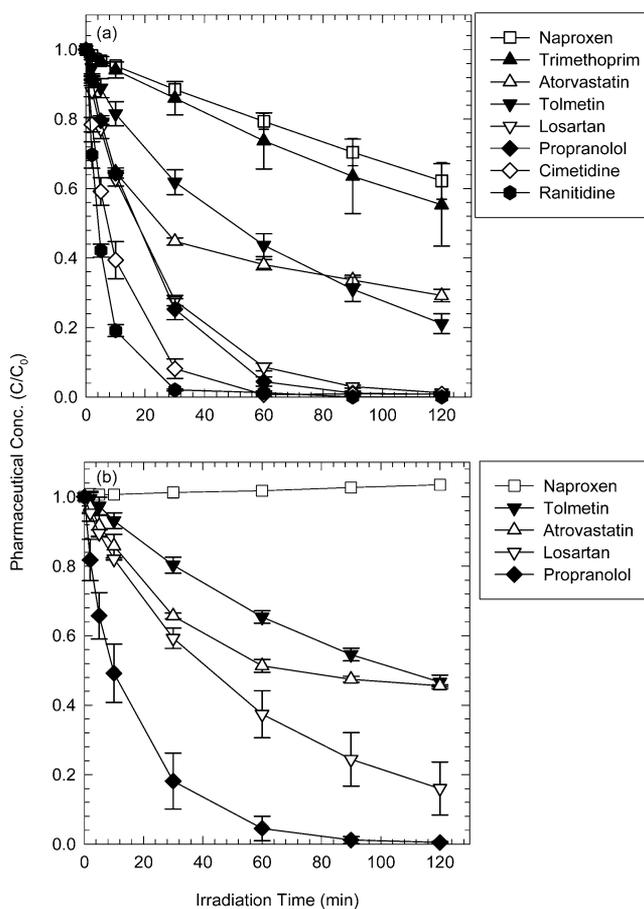


Figure 3. Degradation of pharmaceuticals by (a) SnP/silica and (b) aminoC₆₀/silica in water under visible light irradiation. Error bars indicate \pm one standard deviation from the mean of at least three replicate reactors ($\lambda > 400$ nm) ([SnP/silica]₀ = 0.5 g/L; [aminoC₆₀/silica]₀ = 1 g/L; [pharmaceuticals]₀ = 100 μ M ([naproxen]₀ = [losartan]₀ = 40 μ M); [phosphate]₀ = 10 mM; pH_i = 7.5).

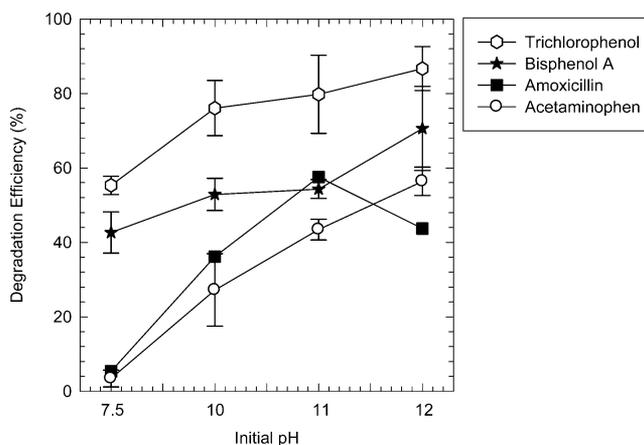


Figure 4. Efficiency (defined as the concentration reduction after 2 h photosensitized reaction) in photochemical degradation of phenolic compounds by SnP/silica as a function of initial pH under UV-A light irradiation. Error bars indicate \pm one standard deviation from the mean of at least three replicate reactors ([SnP/silica]₀ = 0.5 g/L; [phenolics]₀ = 100 μ M).

readily oxidizes phenolate anion than neutral phenol ($k(\text{phenolate anion} + {}^1\text{O}_2 \text{ in H}_2\text{O}) = 1.8 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$;²¹ $k(\text{phenol} + {}^1\text{O}_2 \text{ in H}_2\text{O}) = 3 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$;²¹). Shifting

equilibrium from phenol to phenolate anion under alkaline pH conditions caused the drastic enhancement in the rate of phenol degradation by SnP/silica, which implies that singlet oxygenation provides a crucial reaction pathway in the photosensitized degradation by SnP/silica. However, adsorption of phenolics on SnP/silica decreased with increasing pH (trichlorophenol and bisphenol A) or was insignificant over the applied pH range (amoxicillin and acetaminophen) (Figure S5 of the SI).

Due to the high charge on Sn(IV), the photoexcited triplet state of SnP ($^3\text{SnP}^*$) undergoes facile reduction in the presence of adequate electron donors to form the radical anion ($\text{SnP}^{\bullet-}$), indicating the possible degradation through the direct electron transfer from organic pollutants to $^3\text{SnP}^*$.²³ To identify the alternative reaction route for oxidative degradation, photosensitized degradation of amoxicillin, acetaminophen, and 4-chlorophenol (4-CP) using SnP/silica and aminoC₆₀/silica was initiated at neutral pH under 300W Xe-arc lamp irradiation with a UV cutoff filter ($\lambda > 420$ nm) (Figure 5a). Such high

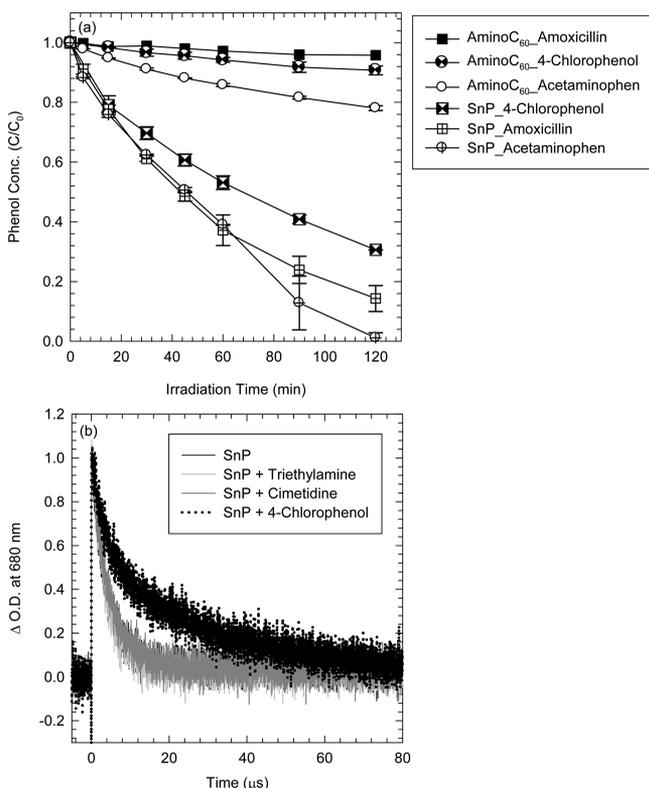


Figure 5. (a) Photosensitized degradation of phenolic compounds by SnP/silica and aminoC₆₀/silica in neutral pH condition ($[\text{SnP}/\text{silica}]_0 = 0.5$ g/L; $[\text{aminoC}_{60}/\text{silica}]_0 = 1$ g/L; $[\text{phenolics}]_0 = 100$ μM; $[\text{phosphate}]_0 = 10$ mM; $\text{pH}_i = 7.5$); (b) Normalized time traces of SnP recorded at 680 nm after the laser flash photolysis (532 nm) in the absence and presence of triethylamine, cimetidine, and 4-chlorophenol ($[\text{SnP}]_0 = 50$ μM; $[\text{triethylamine}]_0 = 10$ mM; $[\text{cimetidine}]_0 = [\text{4-chlorophenol}]_0 = 1$ mM; air-equilibrated). Error bars indicate \pm one standard deviation from the mean of at least three replicate reactors.

power light irradiation can produce triplet state transient at a high concentration to enhance the direct electron transfer. Visible-light-induced oxidation of the selected phenolic compounds negligibly occurred in aqueous suspensions of aminoC₆₀/silica under neutral pH condition, which is compatible with low reactivity of the protonated phenols (as

the predominant form at neutral pH) toward $^1\text{O}_2$.³³ However, SnP/silica initiated significant photochemical degradation of neutral phenolics, suggesting the oxidative degradation pathway not involving singlet oxygenation but through $^3\text{SnP}^*$ -mediated electron transfer.

Triplet state decay of aminoC₆₀ and SnP (suspended in water, not immobilized on silica) was monitored in the absence and presence of oxygen using a laser flash photolysis (Figure S6 of the SI). Rapid quenching of the triplet state by the dissolved oxygen ($k(^3\text{SnP}^* + \text{O}_2) = 9.5 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$, and $k(^3\text{aminoC}_{60}^* + \text{O}_2) = 9.9 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$) indicates effective energy transfer to oxygen, subsequently leading to $^1\text{O}_2$ production. Figure S7 of the SI shows the fate of the triplet state in the presence of cimetidine, 4-chlorophenol, and triethylamine under air-equilibrated conditions. Whereas the presence of cimetidine and triethylamine did not change the decay kinetics of $^3\text{SnP}^*$, the presence of 4-CP decelerated its decay (Figure S7a of the SI), which could be attributed to the appearance of $\text{SnP}^{\bullet-}$ that has an overlapping absorption spectrum with $^3\text{SnP}^*$. The kinetic retardation in the presence of 4-CP was more significant when transient absorption decay was monitored at 680 nm as the detection wavelength of $\text{SnP}^{\bullet-}$ ³⁴ (Figure 5b). Such transient spectroscopic evidence may suggest that the electron transfers from 4-CP to $^3\text{SnP}^*$, which would then result in the oxidation of 4-CP and the formation of $\text{SnP}^{\bullet-}$.

Stability as Catalyst. To explore the possible use of SnP/silica as the photoactive catalyst for oxidative degradation, photochemical FFA oxidation was repeated in aqueous suspensions of SnP/silica over 5 cycles as described in our previous study.²⁹ Figure 6 demonstrates that the rate of

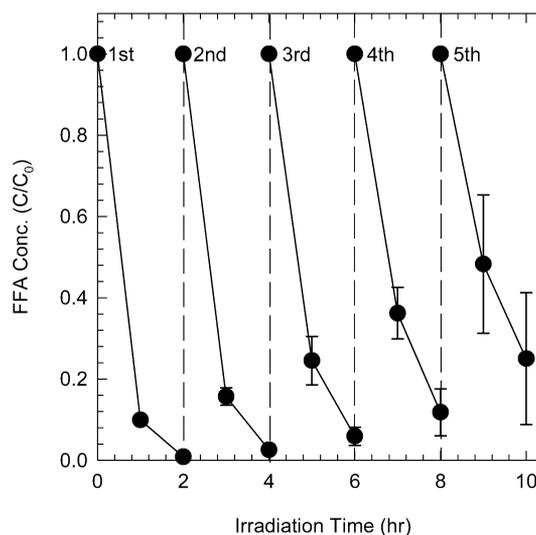


Figure 6. Repeated degradation of furfuryl alcohol by SnP/silica under visible-light illumination ($[\text{SnP}/\text{silica}]_0 = 0.5$ g/L; $[\text{FFA}]_0 = 100$ μM; $[\text{phosphate}]_0 = 10$ mM; $\text{pH}_i = 7.5$). Error bars indicate \pm one standard deviation from the mean of at least three replicate reactors.

photosensitized singlet oxygenation by SnP/silica is gradually retarded during the repeated catalytic cycle, which could be attributed to a self-destructive reaction via $^1\text{O}_2$ -induced oxidation ($k(\text{porphyrin} + ^1\text{O}_2 \text{ in } \text{CHCl}_3) = 4.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ ²¹) or direct electron transfer. In particular, formation of $\text{SnP}^{\bullet-}$, confirmed by the transient absorption spectrum in laser flash photolyzed aqueous solutions of SnP, suggests the possible oxidative degradation through the electron abstraction from the

ground state of SnP by the excited triplet state. Contrary to such a loss of photosensitizing activity of SnP/silica during the multiple uses, our earlier work²⁹ showed that repeated uses through 5 cycles did not cause any decrease in the efficacy of aminoC₆₀/silica for photochemical FFA oxidation, which implies superior catalytic activity of C₆₀ fullerene-based sensitizers based on the high structural stability.

Comparison to OH Radical Oxidation in the Presence of Background Organic Matter in Wastewater Treatment Effluents. As the fate of ROS in complex water matrices involves oxidation reactions with background organic substances, oxidation of high priority micropollutants by OH radical as non-selective oxidant can be kinetically retarded in real water and wastewater treatment. Lee et al.³⁵ demonstrated that selective oxidants such as O₃ and ferrate lead to faster degradation of organic contaminants in the secondary wastewater effluents compared to OH radical-mediated oxidation because the efficacy of oxidant sensitively depends on the competition for oxidant between a target substrate and background organic matter. Considering the selective nature of ¹O₂ in oxidative degradation, it is probable that ¹O₂ photosensitizers could be more efficient in the oxidation of organic pollutants in wastewater matrices than photoactive materials capable of generating OH radical.

Figure 7a and 7b compares the activity of SnP/silica (generating singlet oxygen as a main oxidant) and TiO₂ (generating OH radical as a main oxidant) in terms of

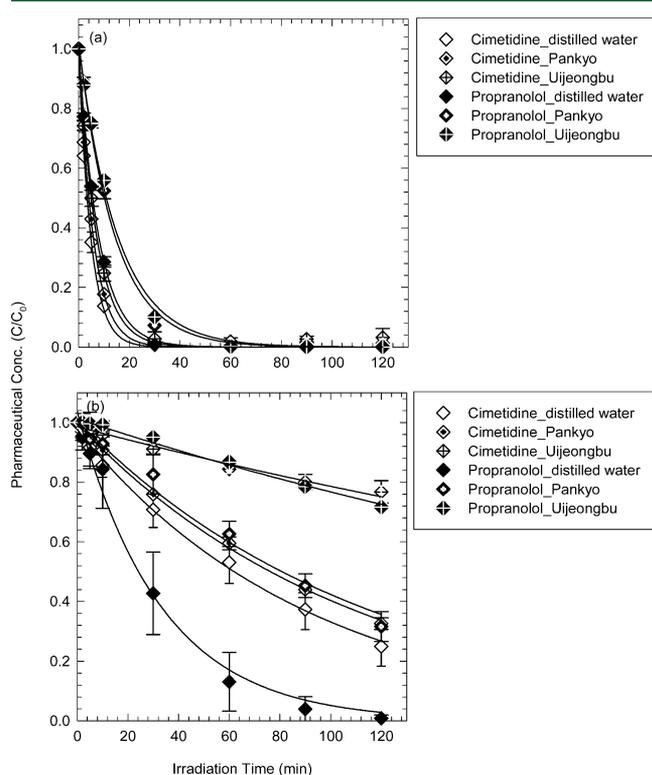


Figure 7. Degradation of cimetidine and propranolol by (a) SnP/silica and by (b) TiO₂ (Degussa P25) in distilled water and secondary wastewater effluents from wastewater treatment plants located in Pankyo and Uijeongbu under UV-A light irradiation. Curves represent nonlinear regression fits to pseudo first-order decay ($[\text{SnP/silica}]_0 = [\text{TiO}_2]_0 = 0.5 \text{ g/L}$; $[\text{pharmaceutical compound}]_0 = 20 \text{ }\mu\text{M}$; pH not adjusted). Error bars indicate \pm one standard deviation from the mean of at least three replicate reactors.

photochemical oxidation of cimetidine and propranolol in the secondary effluents from Pankyo and Uijeongbu wastewater treatment facilities (PSWE and USWE). The selected pharmaceuticals were more rapidly degraded by SnP/silica under UV light irradiation than by TiO₂ photocatalyst, which confirms that photosensitized ¹O₂ generation enables effective destruction of organic pollutants. The comparison of pseudo first-order rate constants for photosensitized degradation of cimetidine and propranolol in the wastewater effluents and distilled water shows moderate loss of photosensitizing activity of SnP to participate in oxidative degradation processes under real world condition (i.e., $k(\text{cimetidine}) = 12.47 \pm 0.28 \text{ h}^{-1}$ for distilled water ($R^2 = 0.998$), versus $k(\text{cimetidine}) = 10.34 \pm 0.28 \text{ h}^{-1}$ for PSWE ($R^2 = 0.999$), versus $k(\text{cimetidine}) = 8.34 \pm 0.27 \text{ h}^{-1}$ for USWE ($R^2 = 0.996$); $k(\text{propranolol}) = 7.53 \pm 0.10 \text{ h}^{-1}$ for distilled water ($R^2 = 0.999$), versus $k(\text{propranolol}) = 4.24 \pm 0.16 \text{ h}^{-1}$ for PSWE ($R^2 = 0.996$), versus $k(\text{propranolol}) = 3.90 \pm 0.13 \text{ h}^{-1}$ for USWE ($R^2 = 0.997$)) (Figure 7a). The results imply that electron-rich background organic substances present in PSWE and USWE scavenge photochemically generated ¹O₂ to a certain degree.

In comparison, the photocatalytic degradation of pharmaceuticals by TiO₂ was drastically retarded when TiO₂ photocatalysis in which OH radical as the primary oxidant initiates oxidative degradation³⁶ was applied into the secondary effluents (Figure 7b). The rate for the photocatalytic oxidation of cimetidine by TiO₂ in USWE decreased by up to 4.6-fold compared to that in distilled water (i.e., $k = 0.65 \pm 0.03 \text{ h}^{-1}$ for distilled water ($R^2 = 0.973$), versus $k = 0.14 \pm 0.01 \text{ h}^{-1}$ for USWE ($R^2 = 0.953$)). The rate retardation was more significant for TiO₂-mediated photodegradation of propranolol in the wastewater effluents, with $k = 1.81 \pm 0.16 \text{ h}^{-1}$ for distilled water ($R^2 = 0.966$), $k = 0.52 \pm 0.03 \text{ h}^{-1}$ for PSWE ($R^2 = 0.944$), and $k = 0.17 \pm 0.01 \text{ h}^{-1}$ for USWE ($R^2 = 0.910$). Such activity reduction is attributed to the competition for OH radicals between the matrix organics and the pharmaceutical compounds. The non-selective reactivity of OH radicals³⁷ continues to hinder the oxidation of target substance as long as the background organic substances remain in the wastewater effluents. Alternatively, ¹O₂, being a selective oxidant, preferably reacts with electron-rich organic substances despite the presence of background organic matters.

Environmental Applications. This study assesses photochemical reactivity of fullerene- and porphyrin-based photosensitizing agents for oxidative degradation of organic pollutants in water. The activity evaluation suggests considerations for further photocatalyst development. In addition to facile physical separation from treated water for subsequent reuse, the ease of functionalization enables chemical linkage of fullerenes and porphyrins to diverse surfaces (e.g., magnetic particles, pH-responsive polymers), to achieve effective sensitizer recovery strategies (using magnetic force or pH adjustment). The photosensitization capability of SnP/silica and aminoC₆₀/silica to yield ¹O₂ resulted in relatively fast degradation of electron-rich organics. In particular, the competitive reactions for ¹O₂ with a complicated water matrix did not cause a significant decrease in pollutant degradation kinetics by ¹O₂ photosensitizers, which is in marked contrast to TiO₂ photocatalyzed oxidation involving OH radical as a primary oxidant. To overcome the applicability limits associated with substrate-specific reactivity of ¹O₂, further studies are required for process integration (e.g., enzymatic hydroxylation of aromatic compounds, followed by ¹O₂-induced oxidation) or

material hybridization (e.g., C₆₀ fullerene-TiO₂ to concurrently enable non-selective oxidation by OH radical in addition to rapid singlet oxygenation). Development of metalloporphyrins with the enhanced activity for direct electron transfer may also provide a complement to the photosensitized singlet oxygenation. In an effort to promote the fullerene and porphyrin derivatives as alternatives to semiconductor photocatalysts for solar-powered water remediation technologies, material modification via incorporation of metal ions or attachment of organic addends to extend the photoresponse of the photosensitizers (to the long-wavelength visible light region) could further enhance the utilization of the solar energy spectrum.

■ ASSOCIATED CONTENT

● Supporting Information

Detailed descriptions of light irradiation conditions (S1), chemical structures of target pharmaceutical compounds and their reactivity toward ¹O₂ (Table S1), and the additional Figures showing the emission spectra of light sources (Figure S1) and transmittance profiles of the cutoff filters (Figure S2), the kinetic comparison of SnP/silica and aminoC₆₀/silica for photochemical FFA degradation (i.e., photosensitized ¹O₂ production) (Figure S3), and adsorption of pharmaceuticals and phenolics on SnP/silica under dark conditions (Figure S4 and Figure S5), and decay kinetics of triplet state in aqueous solutions of tin porphyrin and C₆₀ aminofullerene in the absence and presence of dissolved O₂ (Figure S6) or electron donors including triethylamine, cimetidine, and 4-chlorophenol (Figure S7). This information is available free of charge via the Internet at <http://pubs.acs.org/>.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +82-2-958-6947; fax: +82-2-958-5839; e-mail: lee39@kist.re.kr.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This study was supported by the Korea Ministry of Environment as “Converging Technology Project” (191-101-001). The authors would like to thank Dr. John D. Fortner and Dr. Jaehong Kim for valuable advice and friendly help.

■ REFERENCES

- (1) Haag, W. R.; Hoigne, J. Singlet oxygen in surface waters 3. Photochemical formation and steady state concentrations in various types of waters. *Environ. Sci. Technol.* **1986**, *20* (4), 341–348.
- (2) Nowell, L. H.; Hoigne, J. Photolysis of aqueous chlorine at sunlight and ultraviolet wavelengths 2. Hydroxyl radical production. *Wat. Res.* **1992**, *26* (5), 599–605.
- (3) Zepp, R. G.; Faust, B. C.; Hoigne, J. Hydroxyl radical formation in aqueous reactions (pH 3–8) of Iron(III) with hydrogen peroxide—The photo-fenton reaction. *Environ. Sci. Technol.* **1992**, *26* (2), 313–319.
- (4) Zepp, R. G.; Hoigne, J.; Bader, H. Nitrate-induced photo-oxidation of trace organic chemicals in water. *Environ. Sci. Technol.* **1987**, *21* (5), 443–450.
- (5) Zuo, Y. G.; Hoigne, J. Formation of hydrogen peroxide and depletion of oxalic acid in atmospheric water by photolysis of iron(III) oxalato complexes. *Environ. Sci. Technol.* **1992**, *26* (5), 1014–1022.
- (6) Liu, X. L.; Xu, D.; Wu, F.; Liao, Z. H.; Liu, J. T.; Deng, N. S. Preliminary study on the photoproduction of hydroxyl radicals in aqueous solution with Aldrich humic acid, algae and Fe(III) under

high-pressure mercury lamp irradiation. *Photochem. Photobiol.* **2004**, *79* (3), 259–264.

- (7) Vione, D.; Falletti, G.; Maurino, V.; Minero, C.; Pelizzetti, E.; Malandrino, M.; Ajassa, R.; Olariu, R. I.; Arsene, C. Sources and sinks of hydroxyl radicals upon irradiation of natural water samples. *Environ. Sci. Technol.* **2006**, *40* (12), 3775–3781.

- (8) Grandbois, M.; Latch, D. E.; McNeill, K. Microheterogeneous concentrations of singlet oxygen in natural organic matter isolate solutions. *Environ. Sci. Technol.* **2008**, *42* (24), 9184–9190.

- (9) Jeong, J. S.; Yoon, J. Y. Dual roles of CO₂^{•-} for degrading synthetic organic chemicals in the photo/ferrioxalate system. *Wat. Res.* **2004**, *38* (16), 3531–3540.

- (10) Lei, J.; Liu, C. S.; Li, F. B.; Li, X. M.; Zhou, S. G.; Liu, T. X.; Gu, M. H.; Wu, Q. T. Photodegradation of orange I in the heterogeneous iron oxide-oxalate complex system under UVA irradiation. *J. Hazard. Mater.* **2006**, *137* (2), 1016–1024.

- (11) Han, S. K.; Sik, R. H.; Motten, A. G.; Chignell, C. F.; Bilski, P. J. Photosensitized oxidation of tetrabromobisphenol A by humic acid in aqueous solution. *Photochem. Photobiol.* **2009**, *85* (6), 1299–1305.

- (12) Razavi, B.; Ben Abdelmelek, S.; Song, W. H.; O’Shea, K. E.; Cooper, W. J. Photochemical fate of atorvastatin (lipitor) in simulated natural waters. *Wat. Res.* **2011**, *45* (2), 625–631.

- (13) Kohn, T.; Grandbois, M.; McNeill, K.; Nelson, K. L. Association with natural organic matter enhances the sunlight-mediated inactivation of MS2 coliphage by singlet oxygen. *Environ. Sci. Technol.* **2007**, *41* (13), 4626–4632.

- (14) Kohn, T.; Nelson, K. L. Sunlight-mediated inactivation of MS2 coliphage via exogenous singlet oxygen produced by sensitizers in natural waters. *Environ. Sci. Technol.* **2007**, *41* (1), 192–197.

- (15) Romero, O. C.; Straub, A. P.; Kohn, T.; Nguyen, T. H. Role of temperature and Suwannee River natural organic matter on inactivation kinetics of Rotavirus and Bacteriophage MS2 by solar irradiation. *Environ. Sci. Technol.* **2011**, *45* (24), 10385–10393.

- (16) Kong, L.; Ferry, J. L. Photochemical oxidation of chrysenes at the silica gel-water interface. *J. Photochem. Photobiol. A Chem.* **2004**, *162* (2–3), 415–421.

- (17) Grylik, D.; Miller, J. S.; Ledakowicz, S. Singlet molecular oxygen application for 2-chlorophenol removal. *J. Hazard. Mater.* **2007**, *146* (3), 502–507.

- (18) Escalada, J. P.; Pajares, A.; Gianotti, J.; Biasutti, A.; Criado, S.; Molina, P.; Massad, W.; Amat-Guerri, F.; Garcia, N. A. Photosensitized degradation in water of the phenolic pesticides bromoxynil and dichlorophen in the presence of riboflavin, as a model of their natural photodecomposition in the environment. *J. Hazard. Mater.* **2011**, *186* (1), 466–472.

- (19) Foote, C. S.; Peters, J. W. Chemistry of singlet oxygen 14. Reactive intermediate in sulfide photooxidation. *J. Am. Chem. Soc.* **1971**, *93* (15), 3795–3796.

- (20) Jensen, A. W.; Daniels, C. Fullerene-coated beads as reusable catalysts. *J. Org. Chem.* **2003**, *68* (2), 207–210.

- (21) Wilkinson, F.; Helman, W. P.; Ross, A. B. Rate constants for the decay and reactions of the lowest electronically excited singlet state of molecular oxygen in solution—An expanded and revised compilation. *J. Phys. Chem. Ref. Data* **1995**, *24* (2), 663–1021.

- (22) Chae, S. R.; Hotze, E. M.; Wiesner, M. R. Evaluation of the oxidation of organic compounds by aqueous suspensions of photosensitized hydroxylated-C₆₀ fullerene aggregates. *Environ. Sci. Technol.* **2009**, *43* (16), 6208–6213.

- (23) Kim, W.; Park, J.; Jo, H. J.; Kim, H. J.; Choi, W. Visible light photocatalysts based on homogeneous and heterogenized tin porphyrins. *J. Phys. Chem. C* **2008**, *112* (2), 491–499.

- (24) Badireddy, A. R.; Hotze, E. M.; Chellam, S.; Alvarez, P.; Wiesner, M. R. Inactivation of bacteriophages via photosensitization of fullerol nanoparticles. *Environ. Sci. Technol.* **2007**, *41*, 6627–6632.

- (25) Christoforidis, K. C.; Louloudi, M.; Deligiannakis, Y. Complete dechlorination of pentachlorophenol by a heterogeneous SiO₂-Fe-porphyrin catalyst. *Appl. Catal. B Environ.* **2010**, *95* (3–4), 297–302.

- (26) Gmurek, M.; Kubat, P.; Mosinger, J.; Miller, J. S. Comparison of two photosensitizers Al(III) phthalocyanine chloride tetrasulfonic acid

and meso-tetrakis(4-sulfonatophenyl)porphyrin in the photooxidation of *n*-butylparaben. *J. Photochem. Photobiol. A Chem.* **2011**, *223* (1), 50–56.

(27) Lee, J.; Mackeyev, Y.; Cho, M.; Li, D.; Kim, J.-H.; Wilson, L. J.; Alvarez, P. J. J. Photochemical and antimicrobial properties of novel C₆₀ derivatives in aqueous systems. *Environ. Sci. Technol.* **2009**, *43*, 6604–6610.

(28) Lee, J.; Hong, S.; Mackeyev, Y.; Lee, C.; Chung, E.; Wilson, L. J.; Kim, J. H.; Alvarez, P. J. J. Photosensitized oxidation of emerging organic pollutants by tetrakis C₆₀ aminofullerene-derivatized silica under visible light irradiation. *Environ. Sci. Technol.* **2011**, *45* (24), 10598–10604.

(29) Lee, J.; Mackeyev, Y.; Cho, M.; Wilson, L. J.; Kim, J. H.; Alvarez, P. J. J. C₆₀ aminofullerene immobilized on silica as a visible-light-activated photocatalyst. *Environ. Sci. Technol.* **2010**, *44* (24), 9488–9495.

(30) Crossley, M. J.; Thordarson, P.; Wu, R. A. S. Efficient formation of lipophilic dihydroxotin(IV) porphyrins and bis-porphyrins. *J. Chem. Soc. Perkin Trans.* **2001**, *18*, 2294–2302.

(31) Montanaro, S.; Lhiaubet-Vallet, V.; Iesce, M.; Previtera, L.; Miranda, M. A. A mechanistic study on the phototoxicity of atorvastatin: Singlet oxygen generation by a phenanthrene-like photoproduct. *Chem. Res. Toxicol.* **2009**, *22* (1), 173–178.

(32) Sortino, S.; Petralia, S.; Bosca, F.; Miranda, M. A. Irreversible photo-oxidation of propranolol triggered by self-photogenerated singlet molecular oxygen. *Photochem. Photobiol. Sci.* **2002**, *1* (2), 136–140.

(33) Tratnyek, P. G.; Holgne, J. Oxidation of substituted phenols in the environment—A QSAR analysis of rate constants for reaction with singlet oxygen. *Environ. Sci. Technol.* **1991**, *25* (9), 1596–1604.

(34) Baral, S.; Hambright, P.; Neta, P. One-electron and 2-electron reduction of aluminum and tin pyridylporphyrins—A kinetic spectrophotometric study. *J. Phys. Chem.* **1984**, *88* (8), 1595–1600.

(35) Lee, Y.; von Gunten, U. Oxidative transformation of micropollutants during municipal wastewater treatment: Comparison of kinetic aspects of selective (chlorine, chlorine dioxide, ferrate(VI), and ozone) and non-selective oxidants (hydroxyl radical). *Wat. Res.* **2010**, *44* (2), 555–566.

(36) Hoffmann, M. R.; Martin, S. T.; Choi, W. Y.; Bahnemann, D. W. Environmental applications of semiconductor photocatalysis. *Chem. Rev.* **1995**, *95* (1), 69–96.

(37) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (OH•/O•⁻) in aqueous solution. *J. Phys. Chem. Ref. Data* **1988**, *17* (2), 513–886.