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Heterogeneous photocatalytic treatment of pharmaceutical micropollutants: Effects of wastewater effluent matrix and catalyst modifications

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ABSTRACT

This study evaluates the applicability of TiO_2-based photocatalysts for the treatment of pharmaceutical micropollutants in secondary wastewater effluent (SWE). Photolytic experiments using SWEs with different compositions demonstrated that the rates of photocatalytic degradation of acetaminophen and carbamazepine inversely correlated with the concentration of dissolved organic carbon (DOC), regardless of the type of applied light source and initial pharmaceutical concentration. The critical relevance of organic matter to the scavenging behavior of SWE was further verified by assessing the photocatalytic performance as a function of the concentrations of potential effluent-derived quenchers (i.e., NO_3^-, Cl^-, alkalinity, and humic acid). Kinetic comparison of the degradation of trace levels of pharmaceuticals (i.e., caffeine, cimetidine, propranolol, and sulfamethoxazole) using TiO_2/UV-A, TiO_2/UV-C, and H_2O_2/UV-C systems revealed that heterogeneous processes showed more significant performance reduction with increasing DOC concentration; this result indicates that organic matter plays dual roles in the scavenging activity of an effluent matrix: (1) OH radical (•OH) quenching and (2) active-site coverage. TiO_2 surface modifications (i.e., Pt and SiO_x loading) accelerated the degradation of all the tested pharmaceuticals in SWEs to a certain degree. Particularly, the relevant altered surface affinity preferentially increased the susceptibility of specific pharmaceuticals to photocatalytic treatment. The presence of the effluent matrix substantially impaired the performance of visible-light-active photocatalysts in most cases. However, photocatalytic pharmaceutical degradation on Pt-doped TiO_2, which occurs via direct charge transfer, was much less hindered in SWEs than that on Pt-deposited WO_3, which occurs via •OH-mediated oxidation.

1. Introduction

Advanced oxidation processes (AOPs), which involve the *in-situ* production of highly reactive oxygen species (e.g., hydroxyl radical (•OH)) in contaminated environmental media, constitute a promising strategy for the remediation of municipal and industrial wastewater that contains recalcitrant organic substances [1–3]. In contrast to the substrate-dependent activities of chemical oxidants (e.g., chlorine and ozone) and microbial communities used in conventional water treatment infrastructures, the indiscriminate nature of •OH-induced oxidation [4] enables the application of AOPs to the degradation and mineralization of a wide range of organic compounds. As a result, •OH effectively mediates the chemical transformation of bio-refractory organics into intermediates that are highly vulnerable to microbial degradation, which indicates the potential suitability of AOPs as a pre-treatment for biological processes [5,6]. AOPs are also considered to be a post-treatment option for the oxidative destruction of emerging organic contaminants (e.g., endocrine disruptors, pharmaceuticals, and personal care products) that survive secondary biological treatment [7,8].

Pharmaceutical compounds are biologically active in trace quantities and conserve their behavior after being discharged into

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aquatic environments, raising concerns regarding the potential risks to the environment and human health [9,10]. Treatability studies have reported significant substrate-specific variation in the removal efficacy of physicochemical and biological processes [11,12]; this implies that select groups of pharmaceuticals could pass intact through conventional water treatment facilities. On the other hand, recent performance assessments have shown that AOPs based on the non-selective reactivity of •OH rapidly degraded a broad spectrum of pharmaceuticals [1,8,13]. For instance, hydrogen peroxide (H_2O_2) in conjunction with UV light (H_2O_2/UV) is highly efficient for the treatment of most of the pharmaceutical substances (e.g., analgesics, antiarrhythmic agents, and antibiotics) that are present in secondary wastewater effluent, while UV photolysis alone degrades only a limited number of pharmaceuticals [8]. Fenton treatment of secondary effluent also leads to complete removal of various trace-level pharmaceuticals including caffeine, carbamazepine, ibuprofen, naproxen, sulfamethoxazole, and trimethoprim [14]. The combination of H_2O_2 and alkaline pH conditions, which facilitate the decomposition of ozone into •OH, kinetically enhances the ozonation of pharmaceuticals and their metabolites in biologically pre-treated municipal wastewater [15].

Titanium dioxide (TiO_2) that requires a relatively low photon energy for charge separation can photosensitize oxidative degradation of organic compounds via production of powerful oxidizing species under artificial UV and solar light irradiation [16,17]. Similar to AOPs, a multi-activity assessment using a diverse range of pharmaceuticals suggested that heterogeneous TiO_2 photocatalysis as an effective approach for the high-yield generation of •OH is applicable for the remediation of pharmaceutical-polluted water bodies [18,19]. On the other hand, most investigations into the treatability of pharmaceuticals by TiO_2 photocatalytic systems [18–22] have been conducted using relatively high concentrations of pharmaceuticals (typically ranging from 10 to 500 μM) in deionized or distilled water; this is in contrast to the applicability assessments of homogeneous AOPs (e.g., O_3/UV and H_2O_2/UV), which have been tested on trace levels of pharmaceuticals in secondary effluent matrices [18,19]. There is a high likelihood that effluent-derived inorganic ions (e.g., NH_4^+, NO_3^-, and HCO_3^-) modify the surface charge of TiO_2 and, consequently, its adsorption affinity toward organic substances. Background organic matter, which acts as a •OH sink in wastewater effluent and surface waters probably causes a competition with organic micropollutants for •OH-mediated oxidation on photoirradiated TiO_2. Therefore, characterization of the TiO_2 photocatalytic oxidation of pharmaceutical micropollutants under experimental conditions that include realistic water compositions needs to be prioritized for the rational evaluation of the activity of TiO_2-based photocatalysis as a viable tertiary treatment option.

This study demonstrates the potential application of heterogeneous TiO_2 photocatalysts for the removal of trace-level (typically 1 μM) pharmaceuticals, including acetaminophen, caffeine, carbamazepine, cimetidine, propranolol, and sulfamethoxazole, in secondary wastewater effluents (SWEs). The effect of the water quality on photocatalytic oxidation kinetics is investigated using effluents from four municipal wastewater treatment plants and distilled water suspensions containing background constituents at varying concentrations that have been spiked with pharmaceuticals. We evaluate the impact of the background water matrix on the performance of TiO_2 photocatalysts for the treatment of pharmaceuticals relative to direct UV photolysis and H_2O_2/UV. Various photocatalyst modifications, i.e., surface platinization, silica loading, and transition metal and non-metal doping, are examined in order to improve the heterogeneous photocatalytic systems by kinetically enhancing pharmaceutical oxidation and reducing the energy required for catalyst activation.

2. Materials and methods

2.1. Reagents

The chemicals that were used in this study include tungsten oxide (WO_3, nanopowder), chloroplatinic acid hydrate(H_2PtCl_6), tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$), titanium tetraisopropoxide (TTIP, $Ti(OCH(CH_3)_2)_4$), acetaminophen, acetic acid, phosphoric acid, and ethanol, which were purchased from Aldrich. Caffeine, carbamazepine, hydrogen peroxide solution, methanol, and perchloric acid were sourced from Sigma–Aldrich, while cimetidine and propranolol were purchased from Sigma. Titanium dioxide (TiO_2, Degussa P25), sulfamethoxazole (Fluka), acetonitrile (J.T. Baker), Ti(IV) sulfate solution (Kanto chemical), and sodium hydroxide solution (Fluka) were also used. Ultrapure deionized water (18 MΩ cm) prepared with a Millipore system was used. All chemicals were of reagent grade and used without further purification.

2.2. Photochemical experiments

Photolytic experiments using various light sources, i.e., a germicidal lamp, black light blue lamp, and fluorescent lamp (output power: 4 W; Philips Co.), were performed in a magnetically stirred 60 mL cylindrical quartz reactor at ambient temperature (22 ± 1 °C). The emission spectra of the three types of lamps were recorded using a Spectropro-500 spectrophotometer (Acton Research Co.) (Supplementary Data, Fig. S1). The UV intensities of the germicidal and black light blue lamps were 1.8 and 0.7 mW/cm^2, respectively, as measured using a UVX radiometer (Ultraviolet Products Ltd.) equipped with a UVX-25 or UVX-36 sensor. The experiments that used visible-light-active photocatalysts were performed with a UV cut-off filter, which blocks the irradiation of the UV fractions of fluorescent lamp emission ($\lambda > 400$ nm).

The photocatalytic reactions proceeded in un-buffered aqueous suspensions containing 0.5 g/L photocatalyst and the target pharmaceutical compounds (typically 1 μM) under air-equilibrated conditions. The photocatalytic oxidation of the pharmaceuticals spiked in SWEs was performed without initial pH adjustment, while the initial pH of the distilled water suspensions was tuned to around 8.0 (i.e., close to the original pH level of the secondary effluent) using 1 M $HClO_4$ or NaOH solutions. Aliquots (1 mL) were withdrawn from the photoirradiated reactor at predetermined time intervals using 1 mL syringes, filtered through 0.45 μm PTFE filters (Whatman), and injected into 2 mL amber glass vials for further analysis for target substrates. More than duplicate photolytic experiments were performed for each given condition. The residual concentrations of pharmaceutical compounds were quantitatively analyzed via high-performance liquid chromatography (HPLC) using a Shimadzu LC-20AD instrument equipped with a C-18 column (ZORBAX Eclipse XDB-C18, Agilent) and a UV/vis detector (SPD-20AV, Shimadzu). The mobile phase comprised a binary mixture of 0.1% (v/v) aqueous phosphoric acid solution and acetonitrile.

2.3. Evaluation of oxidizing capacity

Methanol and benzoic acid were used as chemical probes for detecting photogenerated •OH. The photolytic experiments were performed in aqueous suspensions of photocatalysts containing excess amounts of probe compounds (200 mM methanol and 10 mM benzoic acid) to make sure that the photoproduced •OH was completely scavenged by the chemical indicators. Formaldehyde and *p*-hydroxybenzoic acid as the primary oxidation products were quantitatively analyzed using the HPLC. Chemical derivatization