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Photogeneration of reactive oxygen species from biochar suspension for diethyl phthalate degradation

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ABSTRACT

In this study, the photogeneration of reactive oxygen species (ROS) from biochar suspension was investigated. The characterizations of biochar particles before and after photochemical reactions were analyzed by using FTIR, Raman, XPS and electron paramagnetic resonance (EPR) techniques. It was found that the model pollutant diethyl phthalate (DEP) was efficiently degraded and partially mineralized under UV and simulated solar lights in biochar suspension, with hydroxyl radicals ($^\bullet$OH) and singlet oxygen ($^1O_2$) as the dominant ROS. EPR coupled with chemical probe methods and free radical quenching studies were used to quantify and elucidate the formation mechanism of $^\bullet$OH and $^1O_2$. The results indicated that biochar carbon matrix (BCM) accounted for 63.6%–74.6% of $^\bullet$OH and 10%–44.7% of $^1O_2$ formation, while dissolved organic matter (DOM) derived from biochar generated 46.7%–86.3% of $^1O_2$ and 3.7%–12.5% of $^\bullet$OH. BCM-bound persistent free radicals (BCM-PFRs) and quinone-like structure of BCM (BCM-Q) were the predominant factors affecting $^\bullet$OH and $^1O_2$ formation from BCM under light. Detailed ROS generation pathways are proposed as: (i) DOM from biochar particles contributes to $^\bullet$OH and $^1O_2$ formation *via* light-induced energy and electron transfer processes; (ii) BCM-Q forms excited triplet states (^{3}[BCM-Q]*) under light irradiation and induces the formation $^1O_2$; (iii) UV promotes the formation of BCM-PFRs, which transfer electrons to oxygen to form superoxide anion radical ($O_2{}^{\bullet -}$), further yielding H_2O_2; and (iv) H_2O_2-dependent pathways including BCM-PFRs activation and photo-Fenton reaction are primarily responsible for $^\bullet$OH production. Furthermore, BCM exhibits the excellent reusability towards DEP degradation during the three cycles under light.

1. Introduction

Heterogeneous photocatalysis based on semiconductors is becoming one of the most promising technologies in the environmental remediation since the pioneering studies in 1977 reporting the ability of titania powders to decompose cyanides under light in aqueous solutions [1]. Besides titania, extensive research has been carried out to develop more efficient photocatalysts such as ZnO, ZrO_2, CeO_2, and sulfides (CdS, ZnS) etc. aiming at fast and complete degradation of various contaminants [2–7]. However, most of these photocatalysts need expensive/scarce metal species that limits their long term and large scale applications. Therefore, it is imperative to develop easily-accessible, metal-free and environmentally friendly photocatalysts for the degradation of contaminants.

Carbon is a strong light absorbing material, and the use of carbon materials, e.g., activated carbon (AC), as supports or modifiers of conventional semiconductor photocatalysts in heterogeneous photocatalysis has attracted much research efforts in recent years [8–10]. AC exhibits a reasonably high efficiency to enhance the photocatalytic ability of TiO_2 [11–13]. Furthermore, under light irradiation, ACs were observed to induce the formation of reactive oxygen species (ROS,) such as $^\bullet$OH, singlet oxygen ($^1O_2$), superoxide radical anion ($O_2{}^{\bullet -}$), and hydrogen peroxide (H_2O_2), in the absence of conventional semiconductors, although the mechanism was unclear [14–16]. A recent study by Velo-Gala et al. found that the surface chemistry of AC plays an important role in its photocatalytic activity under UV or solar light [17]. The photochemical properties of new carbon materials, such as fullerenes (C_{60}), graphene oxide and carbon nanotubes, are also of great interest to environmental scientists due to their photocatalytic performance [18–21]. Although the ability of carbon materials to produce ROS under light has received considerable attention, most previous studies focused on their light induced toxicity effects [22,23]. Meanwhile, little

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attention has been paid to the feasibility of carbon-produced ROS on the transformation of contaminants.

Biochar is an emerging carbon material, mainly produced by biomass pyrolysis, and has received increasing attention due to its extensive uses and benefits as fertilizer, carbon sequestration and soil amendment in agricultural and environmental fields in recent years [24–28]. The practical land application of biochar has led to an increase in biochar particles released into aquatic systems. Wang et al. found that small size biochar particles have a high probability of leaching into groundwater and facilitating the transport of adsorbed contaminants [29]. More importantly, the dissolvable fractions of biochar contribute substantially to the dissolved organic matter (DOM), and thus are readily released into surface water, especially in riparian areas [30,31]. Jaffe et al. found that dissolved black carbon accounts for about 10% of global riverine flux of dissolved organic carbon [32]. Consequently, exploration of the photochemical properties of biochar particles and the related ROS formation mechanism from biochar are crucial to assess its environmental impact, because in general, ROS plays an important role in contaminant transformations by photochemical processes in natural aquatic systems [33–37]. Furthermore, examination of photochemical behavior of biochar could be beneficial for developing new hybrid materials with the conventional metal photocatalysts for the sustainable water remediation and treatment.

Our group and others found the catalytic properties of biochar play an important role in contaminant transformations in aquatic systems [38–40]. Persistent free radicals (PFRs) in biochar can catalyze H_2O_2 and persulfate decomposition in aqueous phase to form free radicals [38–40]. PFRs in biochar and other carbon materials also mediate hydroxyl radical ($^\bullet$OH) formation and degrade contaminants in the presence of dioxygen without additional oxidants [41–44]. Furthermore, biochar can act as an electron shuttle to mediate Fe_2O_3 reduction and promote microbial NH_4^+ oxidation and NO_3^- reduction [45–47]. Recently, the dissolvable portion of biochar was found to exhibit photocatalytic ability and induce the ROS formation under light [48]. By using chemical probe methods, the light-induced ROS formation pathway on dissolved biochar was deduced to be similar to the pathway for natural DOM [33–37,48]. However, the roles of biochar particles (e.g., carbon matrix) in ROS formation, the extent of ROS contribution to contaminant degradation, and the underlying mechanism of ROS formation under light are not fully understood.

We therefore hypothesized that biochar particles exhibit similar photochemical properties to other carbon materials. The main objectives of this study were to investigate the photocatalytic formation of ROS in biochar suspension under light for contaminant degradation, and elucidate the related reaction mechanisms. The characterizations of biochar particles before and after photochemical reactions were analyzed by FTIR, Raman, X-ray photoelectron spectroscopies (XPS) and electron paramagnetic resonance (EPR) techniques. The formation and steady-state concentrations of ROS, such as $^\bullet$OH and $^1O_2$, were determined using EPR and chemical probe methods, respectively. Diethyl phthalate (DEP) was selected as the target pollutant because it is a USEPA priority environmental pollutant and its degradation mechanism by $^\bullet$OH is well established [49].

2. Materials and methods

2.1. Materials

Chemicals used in this study are described in the Supporting Information (SI; Text S1) and the preparation of biochar is described in Text S2 in the SI, following the similar procedure as described in detail in our previous studies [40,41]. Briefly, four different biochars were made and named as P300, P500, W300, and W500, respectively, according to the source materials (P as pine needles and W as wheat straws) and pyrolysis temperatures (300 and 500 °C). The characterizations of biochar were examined by using techniques including elemental analysis, EPR, and FTIR, Raman, and XPS.

2.2. Photochemical experiments

Prior to the light irradiation, the biochar suspensions (200 mg L^{-1}) in borosilicate glass tubes (100 mL) sealed with PTFE screw caps were dispersed by ultrasonication for 30 min, and then DEP stock solution was spiked in to obtain a concentration of 20 mg L^{-1}. The mixture was agitated for 2 h in dark to reach apparent adsorption equilibrium. The aqueous DEP concentrations at equilibrium decreased to 19.2 mg L^{-1}, 18.8 mg L^{-1}, 19.3 mg L^{-1}, and 18.4 mg L^{-1} in P300, P500, W300, and W500 suspensions, respectively, which indicated that adsorption contributed to 4–8% of DEP removal from solution within 2 h. All light irradiation experiments were conducted after 2 h adsorption, and phosphate buffer solution (PBS; 10 mM) was added in the biochar suspensions (200 mg L^{-1}) to fix pH at 7.0 to minimize the effects of pH on the photochemical processes. The borosilicate glass tubes were placed in a photochemical reactor (XPA-7, Nanjing Xujiang Electromechanical Plant, China) and rotated at 500 rpm to ensure uniform light exposure and a well-mixed biochar suspension. A 100-W low pressure mercury lamp (wavelength ranged from 350 to 450 nm and centered at 365 nm) was placed in a quartz cooling pipe positioned vertically in the center of the photochemical reactor. The reaction temperature was controlled at 25 °C and the light intensity at 365 nm in the borosilicate glass tube was 2.3×10^{-5} Einstein cm^{-2} s^{-1}. The schematic diagram of the photochemical reactor was depicted in our previous study [50]. Control experiments without addition of biochar particles were conducted under the same reaction conditions. Dark control experiments were also performed by wrapping the glass tubes with aluminum foil. In addition to UV light, a 500-W xenon lamp was used to simulate solar light, and ROS formation was determined under the simulated solar light at the same reaction conditions. The emission spectra of the xenon lamp are shown in Fig. S1 (provided by Nanjing Xujiang Electromechanical Plant, China).

DOM was extracted from the biochar suspensions to assess the contribution of the dissolved portion of biochar to ROS formation, as follows: biochar particles (0.5 g) were dispersed by ultrasonication in borosilicate glass tubes containing DI water (50 mL), and then agitated on a photochemical reactor at 500 rpm at room temperature (25 °C) without UV light for 2 h. Then, the suspension was passed through a 0.45-μm membrane filter and the photochemical experiments in the filtrate were conducted under UV light. The DOM concentration was determined by a total organic carbon (TOC) analyzer (Multi N/C 3000, Analytik Jena AG, Germany). The fluorescence excitation–emission matrix (EEMs) spectrum of DOM was obtained with a F-7000 fluorescence spectrophotometer (F-7000; Hitachi, Japan).

To examine the contribution of the solid biochar carbon matrix to ROS formation, photochemical experiments were conducted with HCl–HF treated biochar particles under the same conditions as those for untreated biochar. HCl–HF treated biochar particles were prepared by following procedure to fully remove DOM but retain PFRs in biochar particles. Biochar (10 g) was first washed with 1 M HCl solution (500 mL) and then HCl–HF solution (500 mL, 1.0 M, 1:1 *v*/*v*) several times until the DOM concentration was below the detection limit (<0.1 mg L^{-1}). The biochar sample was then washed twice with DI water to remove soluble salts, and freeze-dried prior to use. The process for the determination of reactive oxygen species was presented in the SI (Text S3 and S4). All the experiments were