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A novel solid digestate-derived biochar-Cu NP composite activating H_2O_2 system for simultaneous adsorption and degradation of tetracycline☆

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ABSTRACT

Solid digestate, a by-product of anaerobic digestion systems, has led to a range of environmental issues. In the present study, a novel composite based on a solid digestate-biochar-Cu NP composite was synthesized for tetracycline removal from an aqueous medium. The removal efficiency values for tetracycline (200 mg L^{-1}) were 31.5% and 97.8%, respectively, by the biochar-Cu NP composite (0.5 g L^{-1}) in the absence and presence of hydrogen peroxide (H_2O_2, 20 mM) within 6 h of reaction time. The possible degradation pathway of tetracycline was investigated using liquid chromatography-mass spectrometry. The desorption experiment results suggested that no significant concentration of tetracycline was detected on the composite after the reaction, but a small amount of intermediates in terms of total organic carbon (TOC) accounting for 3.1%, and 23.3% of the end-product NH_4^+ was adsorbed onto the biochar sheets. The dispersive Cu NPs on the biochar resulted in an increase in the surface area and pore volume of the biochar-Cu NP composite, which enhanced tetracycline adsorption as well as the degradation efficiency. Relative tetracycline removal mechanisms were dominantly ascribed to $\cdot OH$ generation from the Cu(II)/Cu(I) redox reaction with H_2O_2 and the electron-transfer process of free radicals (FRs) in biochar. The proposed approach serves dual purposes of waste digestate reuse and treatment of antibiotic pollutants.

This study highlights the activation of H_2O_2 by the dispersive Cu NPs coupling with biochar derived from a waste solid digestate for tetracycline treatment.

1. Introduction

Solid digestate, produced from the explosive growth of biogas plants which are established to sustain positive growth throughout China, is normally used as a fertilizer for crops without any further processing (Svoboda et al., 2013). Such an inappropriate application has led to a serious threat to the soil matrix and crop qualities and indirectly to human beings. Therefore, being a renewable resource and due to its environmental benefits, research is required to develop suitable solid digestate products for other purposes; for example, fabrication of biochars through fast pyrolysis has become an increasingly attractive option for solid digestate management.

The specific properties of biochars, including abundant surface functional groups, large specific surface areas, porous structures, and mineral compounds, make it possible to employ them as proper adsorbents to remove pollutants from aqueous solutions (Huggins et al., 2016; Kearns et al., 2014; Shimabuku et al., 2016; Xie et al., 2014; Zhang et al., 2011). More importantly, compared to biochar produced from undigested biomass, biochar from anaerobically digested biomass seems to exhibit superior adsorption capacity because the latter possesses higher surface area, porous volume, hydrophobicity and a more suitable surface charge (Inyang et al., 2010). Although biochars themselves exhibited excellent performance for contaminant removal, biochar-based composites

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were recognized as more efficient and eco-friendly remediation materials, especially with metal or metal oxide nanoparticles (NPs, *e.g.*, Fe, Zn, FeO, MgO, MnOx) introduced into the biochar surfaces (Su et al., 2016; Usman et al., 2016; Van Vinh et al., 2015; Yu et al., 2015). Biochar coupled with metal or metal oxide NPs, which favor strong aggregation into macroscale particles and greatly weaken their affinities and activation, enhanced their performance in contaminant treatment due to either the increased surface area or the improvement of pore structure by supplying more active sites (Peng et al., 2014).

More importantly, biochar with metal or metal oxide NPs could be coupled with free radicals (FRs, *e.g.*, cyclopentadienyl, phenoxy and semiquinone), which was successfully certified in connection with organic pollutant degradation by mediating oxidants (*e.g.*, O_2, persulfate) to produce $\cdot OH$ (Dellinger et al., 2007; Fang et al., 2014; Yang et al., 2015). Although Fe, Mn or the corresponding oxide NPs with FRs play an important role in organic reactions because of their high surface to volume ratio that can significantly enhance the interaction of active sites per unit area, Cu NPs seem more likely to be dispersed on the biochar surface rather than incorporated into the pores or clogging the pore opening (Yu et al., 2015). This method could vastly improve the adsorption and degradation performance of organic pollutants. In addition, studies have emphasized the strongly oxidative ability of the Cu-based oxidative system, Cu(II)/H_2O_2, as an effective oxidative system for a wide range of contaminant degradation and microorganism inactivation, ascribed to hydroxyl radical ($\cdot OH$) generation from the Cu(II)/Cu(I) redox reaction collaborating with H_2O_2 (Lyu et al., 2015; Nguyen et al., 2013). These studies have been carried out mostly on the utilization of Cu^{2+} combined with H_2O_2. However, limited information is available on the oxidative degradation of organic pollutants with the coupled Cu NPs with H_2O_2, as well as the Cu NP-based composite cooperating with the H_2O_2 systems. Additionally, little is known about the activation ability of H_2O_2 by FRs in solid digestate-derived biochar. Hence, it is expected that a novel composite, biochar-Cu NP composite, will be applied to the further treatment of organic pollutants.

Therefore, the potential performance for organic pollutant treatment when applying the biochar-Cu NP composite through the activation of H_2O_2 was investigated. For this purpose, tetracycline was selected as a model contaminant in this study. This was chosen not only because tetracycline is an important group of antibiotics, but also because it widely exists in the environment, especially biogas plants. The main objectives of the present work were to i) prepare and characterize a novel biochar-Cu NP composite, ii) evaluate the adsorption and degradation ability of the composite in the absence and presence of H_2O_2 for tetracycline, and iii) investigate the removal mechanisms of tetracycline by the composite.

2. Materials and methods

2.1. Reagents

Tetracycline (AR Grade, 98%) and Nessler's reagents (AR Grade, 99%) were purchased from Shanghai Aladdin Industrial Corporation (China). The former's molecular structure and relevant properties are presented in Table S1. Hydrogen peroxide (AR Grade, 30%, v/v) was obtained from Shanghai Yuanda Peroxide Co., Ltd. (China). 2,9-Dimethyl-1,10-phenanthroline (AR Grade, 99%) was provided by Chengdu Xiya Reagent Co., Ltd. (China). Potassium sodium tartrate tetrahydrate (AR Grade, 99%), potassium borohydride (AR Grade, 97%), and other conventional reagents were supplied by Shanghai Sinopharm Chemical Regent Co., Ltd. (China). All chemicals were used as received without further purification. Ultrapure water used in this study with a resistivity of 18.2 MΩ cm was prepared by using a Milli-Q apparatus (Merck Millipore, China). The tetracycline solution (200 mg L^{-1}) was freshly prepared prior to its use.

2.2. Preparation of the materials

Biochar was prepared from solid digestate, which was initially generated from the anaerobic digestion of rice straw. The fresh digestate was collected from the Chengdou Institute of Biology, Chinese Academy of Sciences (China), centrifuged at 8000 rpm for 5 min to separate the solid phase from the digestate using a Universal 320, centrifuge (Hettich, Germany), and subsequently air-dried for one week. The dried solid digestate was crushed in a mechanical grinder (FW 100, Jingsen, China) to particles less than 5 mm and loosely placed in a tube furnace (MTI, Richmond, USA) at 500 °C for 2 h of pyrolysis under N_2. After cooling, the charred digestate was treated with 0.1 M HCl for 6 h, followed by washing with ultrapure water several times. Cu NPs were synthesized by the reduction of $CuCl_2 \cdot 2H_2O$ using $NaBH_4$.

The biochar-Cu NP composite was produced as follows: biochar (2.16 g) was first dissolved in 250 mL of 27 mmol L^{-1} $CuCl_2 \cdot 2H_2O$ solution, and then the solution was purged with a N_2 stream for 1 h to exclude dissolved O_2 during the preparation. After stirring, Cu NPs were produced and deposited on the biochar matrix in situ by the addition of 250 mL of 54 mmol L^{-1} $NaBH_4$ solution, and the suspension was stirred for another 30 min. The remaining solid settled and separated from the liquid phase and then was washed with ethanol and ultra-pure water several times and finally vacuum dried. The final product was labeled as the biochar-Cu NP composite. Biochar-Fe and biochar-FeCu NP composites with the same metal molar ratio were also prepared through the same process.

2.3. Characterizations

Zeta potentials of the biochar and biochar-Cu NP composite suspensions (0.5 g L^{-1}) were measured using a Zetasizer Nano (ZS90, UK). The C, O, H and N contents were determined by element analysis (Elementar, Germany). The specific surface area and porosity measurements were carried out on a Nova 1200e instrument using the BET nitrogen adsorption isotherm method. X-ray diffraction (XRD) measurements were performed on an Ultima IV X-ray diffractometer (Rigaku, Japan) using Cu $K\alpha$ radiation ($\lambda = 0.154$ nm) at 40 kV, 30 mA, at a rate of 10°/min. Fourier transform infrared (FTIR) spectra were collected on a Nicolet Avatar 660 (Thermo, USA) in the range of 400–4000 cm^{-1} using KBr pellet techniques. Scanning electron microscope (SEM, Zeiss Sigma, Germany) images along with a Bruker Quantax 400 EDS detector were recorded by spraying samples over the carbon tape to detect the surface morphology and composition of the samples. The inner structure of film was determined by high-resolution transmission electron microscopy (HRTEM, Tecnai F30, Netherlands). X-ray photoelectron spectroscopy (XPS) data were collected using a Quantum 2000 ESCA spectrometer (Physical Electronics) equipped with a hemispherical electron energy analyzer using monochromatic Al $K\alpha$ X-ray (1486.60 eV) operating at 15 kV and 25 W.

2.4. Batch experiments

The experiments to determine tetracycline removal efficiency for the obtained composites (*e.g.*, biochar-Cu, biochar-CuFe and biochar-Fe NP composites) were first performed to evaluate and select the most effective activator in the presence of H_2O_2 (20 mM). Thirty-milliliter serum bottles sealed with Teflon Mininert containing 24 mL of reaction solutions were placed in a rotary shaker