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Simultaneous removal of Cu^{2+} and bisphenol A by a novel biochar-supported zero valent iron from aqueous solution: Synthesis, reactivity and mechanism☆

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ABSTRACT

In this study, a novel biochar-supported zero valent iron (BC-nZVI) was synthesized through a green method. A high performance on the simultaneous removal of Cu^{2+} and bisphenol A (BPA) by a combination of BC-nZVI with persulfate (BC-nZVI/PS) system was successfully achieved. The simultaneous efficiencies of Cu^{2+} and BPA could reach 96 and 98% within 60 min, respectively. Both HO• and $SO_4^{\bullet-}$ were two major reactive species in BC-nZVI/PS system, and $SO_4^{\bullet-}$ was primary radical responsible for the degradation of BPA. Four kinds of Cu species, such as $Cu(OH)_2$, CuO, Cu_2O and Cu^0 were generated via the adsorption and reduction of the BC-nZVI, whereas six kinds of products of BPA including p-isopropenyl phenol and 4-isopropylphenol were generated via the combined oxidation of $SO_4^{\bullet-}$ and HO•. The possible reaction mechanism for the simultaneous removal of Cu^{2+} and BPA by BC-nZVI/PS system contained a synergistic effect between the reduction of Cu^{2+} and the oxidation of BPA. This is the first report on the feasibility of the remediation of coexistence of heavy metal and organic compound in aquatic environment using the BC-nZVI/PS system.

1. Introduction

In the past decades, nanoscale zero-valent iron (nZVI) has been widely used in environmental applications, and regarded as one of the most promising materials for the elimination of pollutants including nitrate, heavy metal ions and organic compounds (Song and Carraway, 2005, 2013; Shi et al., 2011; Guan et al., 2015; Diao et al., 2016a, 2016b; Stefaniuk et al., 2016; Wang et al., 2017). However, nZVI easily tends to aggregate, thus its reactivity will be significantly decreased (Shi et al., 2011; Stefaniuk et al., 2016; Oh et al., 2016). To overcome this disadvantage, several materials have been used to stabilize nZVI, such as zeolite (Kim et al., 2013), kaolinite (Zhang et al., 2011), activated carbon (Chang et al., 2011) and bentonite (Shi et al., 2011; Diao et al., 2016a, 2016b). In the last few years, biochar (BC), a solid material produced from the carbonization of biomass in an oxygen-limited environment, has been extensively used as a low-cost material for the remediation of pollutants (Ahmad et al., 2012, 2014, 2016a, 2016b, 2017; Rajapaksha et al., 2014, 2015, 2016, 2018; Xiong et al., 2017). Many recent studies have demonstrated the potential of biochar in removing heavy metals and organic compounds in water and sediment (Ahmad et al., 2016a, 2016b, 2017; Rajapaksha et al., 2014, 2015, 2016, 2018; Xiong et al., 2017). Interestingly, BC has also been caught increasing interest as a support to stabilize and disperse nZVI (Tan et al., 2016; Dong et al., 2017; Li et al., 2017; Wang et al., 2017). Many studies have shown that the BC could be not only used as a supporter of nZVI but also effectively enhance the removal efficiencies of pollutants (Tan et al., 2016; Su et al., 2016; Li et al., 2017; Wang et al., 2017).

To date, $NaBH_4$ based reduction has been regarded as one of the most common method for the nZVI synthesis, in which iron ions are reduced by $NaBH_4$ (Shi et al., 2011; Stefaniuk et al., 2016). However, the utilization of $NaBH_4$ might bring about the secondary pollution

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(Machado et al., 2013; Devatha et al., 2016). More recently, a green synthesis method of the nZVI has been developed (Machado et al., 2013; Wu et al., 2015; Devatha et al., 2016), in which green tea extract is widely used as a reductive (Machado et al., 2013; Wu et al., 2015). Numerous reports have demonstrated that the nZVI synthesized by the green method also showed a high reactivity (Machado et al., 2013; Wu et al., 2015). However, to date, little reference has been published on the feasible of the biochar-supported zero valent iron (BC-nZVI) synthesized by the in situ growth of nZVI on the BC surface using green tea extract and iron salt. Furthermore, the occurrence of heavy metals and organic compounds could be frequently found in the most of real wastewaters (Diao et al., 2016a; Stawiński et al., 2017; Deng et al., 2017). Thus, it would be interesting to couple the BC-nZVI with persulfate (PS) for the simultaneous removal of heavy metals and organic compounds from aqueous solution.

In this study, Cu^{2+} and bisphenol A (BPA) were selected as the targets. Cu^{2+} is widely used in feedstuff, whereas BPA is identified as an endocrine disrupting chemical in cultivation industry (Doong et al., 2012; Molkenthin et al., 2013). The main objectives of this study were to (1) evaluate the feasibility of the BC-nZVI synthesized by the kenaf bar and green tea extract; (2) investigate the removal of Cu^{2+} and/or BPA by the BC-nZVI/PS system under different conditions; (3) evaluate the reusability of the BC-nZVI; (4) identify the reactive oxygen species in the BC-nZVI/PS system; (5) determine the transformation products of Cu^{2+} and BPA during the reaction; and (6) explore the possible reaction mechanism for the simultaneous removal of Cu^{2+} and BPA.

2. Materials and methods

2.1. Materials

Bisphenol A (BPA, >99.0%) and 5, 5-dimethyl-1-pyrroline N-oxide (DMPO, >99%) were purchased from Sigma-Aldrich (USA) and stored at 4 °C. $FeSO_4 \cdot 7H_2O$, $Cu(NO_3)_2$ and $K_2S_2O_8$ were purchased from the Tianjin Fuchen Chemical Reagent Factory, China. All chemicals were of analytical reagent grade without further treatment. The double distilled water was used in the whole experiment. Stock standard solutions of BPA (1000 mg L^{-1}) were prepared in ethanol and then diluted with the double distilled water.

2.2. Synthesis of the biochar-supported zero valent iron nanoparticles (BC-nZVI)

BC was produced by the pyrolysis of kenaf bar. The kenaf bar used in this study was obtained locally in ShaoGuan, Guangdong Province, China. The kenaf bar was washed with water for removing dirt and then dried in electric dry oven at 100 °C. The dried kenaf bar was broken into granule and then loosely placed in a tube furnace for 2 h at 600 °C under N_2 atmosphere. After cooling, as-obtained black solid was ground into a size of 150 mesh and then washed with water. Finally, the above black solid was dried and sealed. This solid was designated as the BC. The synthesis of the BC-nZVI was similar to the following method reported previously (Diao et al., 2016b, 2017a). Briefly, the BC (2.0 g) was mixed with $FeSO_4 \cdot 7H_2O$ (0.1 M) to a final volume of 50 mL in a three-necked flask. The 50 mL mixture was mechanically stirred to form a mixture of the BC and iron for 30 min. Subsequently excess amount of green tea extract was added to produce a solid under N_2 atmosphere. Then, the obtained solid was separated and quickly washed with ethanol. Finally, the above solid was dried and sealed. This as-obtained solid was designated as BC-nZVI. The green tea extract was obtained following method reported previously (Machado et al., 2013; Wu et al., 2015), and the preparation procedure of the green tea extract was provided in the Supporting Information.

2.3. Experimental procedures

Batch experiments were conducted in a 100-mL conical flask containing 50 mL of reaction solution (5 mg L^{-1} Cu^{2+} and/or 10 mg L^{-1} BPA) at atmospheric pressure, which were carried out by putting the flask in a shaker bath with a rotation speed of 150 rpm at room temperature. The initial reaction time was defined at the moment when persulfate (PS) and BC-nZVI were added. Unless stated otherwise, the concentrations of Cu^{2+}, BPA, PS and the BC-nZVI were 5 mg L^{-1}, 10 mg L^{-1}, 0.75 mM and 1.0 g L^{-1}, respectively. The initial solution pH was kept at 3.0 ± 0.03. At the given time intervals, aliquot samples were withdrawn and quenched immediately by the same volume of ethanol. Then samples were centrifuged and filtered before analysis. All experiments were conducted three times, and the relatively standard deviations were usually within 3% unless otherwise stated.

To investigate the catalytic activity of the BC-nZVI for the heterogeneous Fenton degradation of BPA, a series of control experiments were carried out. The concentrations of BPA, PS, the BC and BC-nZVI were set at 10 mg L^{-1}, 0.75 mM, 1.0 g L^{-1} and 1.0 g L^{-1}, respectively. To study the effect of Cu^{2+} on the removal of BPA by the BC-nZVI/PS system, Cu^{2+} concentrations varied from 0 to 10 mg L^{-1}. To examine the effect of solution pH on the simultaneous removal of Cu^{2+} and BPA by the BC-nZVI/PS system, the solution pH values varied from 3.0 to 9.0. Various concentrations of PS (0.25, 0.75 and 1.25 mM) were used to study the effect of PS. To evaluate the recyclability of the BC-nZVI, reusability experiments were repeated by three runs with the same BC-nZVI sample. Upon the completion of each run, the BC-nZVI was separated from the suspension by centrifugation, washed by double distilled water and recycled for the next run. Then all the processes were carried out in the same operation conditions as before. To identify the role of the generated reactive oxygen species including HO•, $SO_4^{\bullet-}$ and $O_2^{\bullet-}$, *tert*-butanol, ethanol and chloroform were employed as the scavenger, respectively. In view of their different kinetic rate constants, *tert*-butanol was used as the $SO_4^{\bullet-}$ scavenger following method reported previously (Hazime et al., 2014; Diao et al., 2017b). Ethanol and chloroform were used as the HO• and $O_2^{\bullet-}$ scavenger, respectively (Bae et al., 2013; Diao et al., 2017b). Additionally, the •OH and $SO_4^{\bullet-}$ radicals were also trapped with DMPO and measured using electron spin resonance.

2.4. Analytical methods

The morphologies and elemental compositions of the BC-nZVI samples were investigated by a field emission scanning electron microscopy (SEM, Jeol, JSM-7500F) equipped with an energy-dispersive X-ray spectrometer (EDX, Oxford X-Max). The corresponding X—ray diffraction patterns were collected on a D/Max-IIIA Powder X—ray Diffractometer (XRD). The chemical states of surface elements were measured by an X—ray photoelectron spectrometry (XPS). The concentration of BPA was analyzed by an Agilent 1100LC system equipped with a UV detector. The separation was performed on a C18 column (5 μm, 150 × 4.6 mm, Phenomenex) with a flow rate of 1.0 mL min^{-1} at 45 °C. A mobile phase contains water and acetonitrile with a volume ratio at 60:40. The sample injection volume was 20 μL, and the detection wavelength was set at 280 nm. The degradation products of BPA were identified by a GC/MS-QP2010 system equipped with a DB-5 column (30 m × 0.25 mm, 0.25 μm) at splitless injection mode. Helium gas was used as the carrier gas at a flow rate of 1.5 mL min^{-1}. The final sample (1 μL) was injected from the injection port. The temperature program