



Research article

Ozonation of aqueous phenol catalyzed by biochar produced from sludge obtained in the treatment of coking wastewater



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ABSTRACT

Sludge collected from industrial wastewater treatment possesses a threatening effect on environment, and changing it into functional material provides an alternative for its disposal. Biochar synthesized by pyrolysis of sludge obtained from coking wastewater treatment was evaluated for the catalytic ozonation of phenol in aqueous solution. The present work focused on testing the catalytic performance of biochar, deducing the kinetics of phenol removal in various reaction conditions, and finally elucidating the mechanism of biochar-enhanced phenol removal. The results demonstrated that biochars produced at pyrolysis temperatures of 700 and 900 °C revealed highly comparable catalytic activity in phenol ozonation, leading to around 95% phenol removal within 30 min reaction, due to the abundant carbonyl groups on biochar surface. The biochar, however, was suffered from poor stability, which was attributed to biochar loss and changes in surface chemistry. On the basis of examining reaction variables, an empirical kinetic model was developed well matching experimental results. It was found that ozone concentration adsorbed on biochar surface was first increased with a peak (3.8 mg/L for biochar obtained at 700 °C) at reaction time 10 min, after which it decreased along with proceeding reaction. In light of radical scavenging test, superoxide radical ($\cdot\text{O}_2^-$) was identified as main radical species produced from the interaction of ozone with biochar surface, while hydroxyl radical ($\cdot\text{OH}$) played negligible role in biochar catalytic ozonation. The promoting mechanism of bicarbonate on phenol ozonation was verified to be the generation of $\cdot\text{O}_2^-$ via series reactions of HCO_3^- with $\cdot\text{OH}$ and ozone, apart from increase in solution pH. These results provide important implications for future recycling of coking wastewater treatment sludge in environmental remediation.

1. Introduction

Coking wastewater produced from coal processing technologies including high temperature carbonation, coal gas purification and by-product recovery processes generally contains substantial amount of phenols, cyanide, sulphide, polycyclic aromatic hydrocarbons (PAHs), heterocyclic and acyclic compounds (Zhang et al., 2012). In order to control and minimize the adverse effect of coking wastewater on environment, activated sludge treatment is normally used as pre-treatment process before the employment of advanced treatment techniques, such as catalytic ozonation. In the process of pre-treatment, however, huge amount of sludge will be generated, with average amount of dewatered sludge estimated at $1.4 \times 10^5 \text{ m}^3$ per year (Lei et al., 2017). Owing to the hydrophobic and lipophilic properties of some organic

compounds (e.g., PAHs, log K_{ow} of 3.37–6.84), considerable quantity of these substances could be accumulated by the sludge (Zhang et al., 2012, 2015a). The severe problems of sludge also originate from compositional pathogens (e.g., bacteria, viruses, helminths eggs) and inorganic pollutants (Bratina et al., 2016). Therefore, sludge resulted from activated sludge treatment of coking wastewater possesses a threatening influence on the environment without proper disposal.

A large spectrum of technologies, including landfill (Lou et al., 2015), incineration (You et al., 2016), mechanical treatment (Nazif et al., 2016) and advanced oxidation processes (Praspaliauskas and Pedišius, 2017; Zhang et al., 2016), have been developed to reduce or immobilize the toxicity of waste sludge. Alternatively, increasing efforts have been paid to waste sludge recycling, producing applicable biochar or syngas from initial sludge. Biochar is generally defined as a carbon-

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rich and porous solid produced by bio-mass pyrolysis with nitrogen protection and at moderate temperatures (Mettler et al., 2012; Song et al., 2014). Biochar derived from wastewater treatment sludge and bio-mass has been extensively employed as catalyst support or direct active catalyst in assisting ozone reaction with pollutants. According to Huang et al. (2017), for example, the activated carbon produced from sewage sludge was used to support MnO_x in ozonation of aqueous oxalic acid. Similarly, sewage sludge-derived activated carbon was used as metal oxides support, accelerating the catalytic ozonation of biologically treated Lurgi coal gasification wastewater (Zhuang et al., 2014). The authors attributed the excellent stability and superior catalytic performance of catalysts to the increasingly available radicals generated by the catalytic effect of evenly dispersed metal oxides on activated carbon surface. In addition, pistachio hull biochar was prepared as catalyst in catalysing ozonation of reactive red 198 dye (Moussavi and Khosravi, 2012). Results indicated that a strong basic surface property of biochar originated from its surface hydroxyl group and phenolic functional groups was responsible for enhanced ozone decomposition. Kumar et al. (2017) reported the activity of pinus needle based biochar in photocatalytic ozonation of pollutants, confirming that superior hydroxyl radical ($\cdot\text{OH}$) generation was resulted from the photo-induced ozone decomposition. By contrast, $\cdot\text{OH}$ had a minor role in oxalic acid ozonation catalyzed by sewage sludge derived activated carbon, on the basis of *tert*-butanol scavenging test (Wen et al., 2012). This discrepancy may be ascribed to the distinct surface acidic-basic properties of biochars, which would show different affinities towards dissociated pollutant molecule and dissolved ozone.

In light of the reported works, biochar used as ozonation catalyst is mostly produced from agricultural bio-mass or municipal wastewater treatment sludge, focusing on the identification of surface active sites and catalytic performance in terms of radical generation and pollutants degradation. To the best of authors' knowledge, there has been little researches concentrating on the application of biochar derived from coking wastewater treatment sludge in catalytic ozonation, especially on the adsorption-decomposition behaviour of ozone on solid-liquid interface. This typical industrial sludge contains plentiful hydrophobic phenolic compounds and PAHs, characterized by substituted aromatic structures that are typically the precursors (or intermediate components) for graphitic or polyaromatic carbon generation during sludge pyrolysis (Liu et al., 2015). Moreover, the extremely abundant element compositions in coking wastewater should bring a large spectrum of elemental contents in coking wastewater treatment sludge, which might give rise to desirable physicochemical properties of sludge originated biochar.

The objectives of present study were to analyse the effectiveness and activation mechanism of biochar in catalytic ozonation of phenol. The biochar in this work was produced using raw sludge collected from coking wastewater treatment by one-step simple pyrolysis. The physicochemical properties of biochar closely related to its catalytic activity were characterized and its catalytic performance in ozonation of phenol was evaluated. The effects of reaction variables on phenol removal were elucidated and an empirical model was developed accordingly. Besides, the oxidizing species both on biochar surface and in bulk solution were identified. Finally, the influences of inorganic anions, especially bicarbonate, on catalytic ozonation of phenol were explored. On the basis of above observations, the activation mechanism of biochar for phenol ozonation was proposed.

2. Materials and methods

2.1. Materials and reagents

Coking wastewater treatment sludge was collected from coking wastewater treatment plant, Shaoguan Steel Company in Guangdong province, China. Sludge samples were taken in the aerobic activated sludge reactor, and dewatering procedure was described in Text S1.

Phenol and indigo blue were purchased from Aladdin Chemistry Co. Ltd. Ammonia solution, 4-aminoantipyrine and potassium ferricyanide were obtained from Sinopharm Chemical Reagent Co. Ltd. *p*-benzoquinone and *tert*-butanol were provided by Guangzhou Chemical Reagent Factory. All chemical reagents were analytic grade, and used in experiments without any purification. Milli-Q water in 18.2 M Ω cm resistivity was used to prepare all solutions.

2.2. Preparation of biochar

The pre-dried sludge was employed as raw material for direct carbonization following the pyrolysis procedures described previously with proper modification (Zhou et al., 2014). The ground sludge was subjected to pyrolysis in a tubular furnace at four temperatures (300, 500, 700, 900 °C) maintaining for 2 h with a heating rate of 5 °C/min, under nitrogen atmosphere. The gases produced during heating program were released into fume hood. Then, the resulting biochar was crushed into fine powder by agate mortar, and stored in desiccator before usage. The biochars obtained at 300, 500, 700, 900 °C pyrolysis temperatures were denoted as BC300, BC500, BC700, BC900, respectively.

2.3. Characterization and analytical methods

Specific surface area and pore size distribution of samples were determined by nitrogen adsorption at 77 K and the Barrett-Joyner-Halenda (BJH) method, respectively, using a surface area analyser (ASAP 2020 V3.00 E, Micromeritics, United States). Prior to measurement, samples were degassed at 200 °C for 4 h. Surface functional groups were qualitatively identified on Fourier Transform Infrared Spectrometer (FT-IR, Nicolet-6700, Thermo, United States) in the range of 400–4000 cm^{-1} . Micro-surface morphologies of biochar were obtained from Field Emission Scanning Electron Microscopy (FE-SEM, Merlin, Zeiss, Germany). Prior to SEM analysis, samples were subjected to vacuum coating with platinum to prevent charging. Insights into thermal-decomposition behaviours of raw sludge and calcined biochar were analysed on a thermogravimetric-differential scanning calorimetry (TG-DSC, STA449 F3, Netzsch, Germany). The heating program was operated under nitrogen protection, with a heating rate of 5 °C/min in a temperature range of 25–900 °C. The ash contents of biochar or raw sludge were obtained as the mass residual percentages of samples, which were calcinated to constant weight within 120 min at 650 °C. Surface species containing carbon and oxygen elements were evaluated by X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD, Kratos, United Kingdom). Mass percentages of compositional elements including carbon, hydrogen, nitrogen, oxygen and sulfur were examined by Elemental Analyser (Vario EL cube, Elementar, Germany) with sensitivity no larger than 0.1%. Moreover, graphite structure of biochar was characterized by Raman spectroscopy (LabRAM Aramis, H.J.Y, France).

Colorimetric 4-aminoantipyrine method was employed for the measurement of aqueous phenol concentration (Shi et al., 2011; Zhang et al., 2015b). Total organic carbon (TOC) dissolved from biochar suspension (suspended in Milli-Q water) was obtained from a Total Organic Carbon analyser (TOC-V_{CPH}, Shimadzu, Japan). Concentrations of metal ions leached from biochar after catalytic ozonation were analysed by atomic absorption spectrometer (Z-2000, Hitachi, Japan). Variation of solution pH value was monitored with a pH meter (PHS-3C) provided from Shanghai Precision & Scientific Instrument Co. Ltd. China. Gaseous ozone concentration was measured online with an ozone analyser (PGD3-H, Xins Technology, China), whereas aqueous ozone concentration was determined by indigo blue reagent at 600 nm ($\epsilon = 20000/(\text{M cm})$) (Bader and Hoigné, 1981). During the catalytic ozonation process, ozone concentration adsorbed on biochar surface was attained according to the procedures described in Text S2 (Bing et al., 2015). Surface hydroxyl group density of biochar was obtained

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