Heterogeneous catalytic ozonation of hydroquinone using sewage sludge-derived carbonaceous catalysts

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ABSTRACT
This study converted sewage sludge into a carbonaceous catalyst via pyrolysis and employed it in the ozonation of hydroquinone. The catalyst was characterized by Mössbauer spectroscopy, X-ray photoelectron spectroscopy, temperature programmed desorption, scanning electron microscopy, transmission electron microscopy, Fourier transform infrared spectroscopy and X-ray diffraction. Intermediate products were detected by gas chromatography–mass spectrometry, and a pathway for hydroquinone degradation was proposed. The results showed that sludge pyrolyzed at 700 °C promoted hydroquinone degradation, compared with commercial activated carbon derived from coal. When the catalyst dose was 0.5 g/L, the hydroquinone (200 mg/L) removal rate reached 97.86% after exposure to ozone (the ozone concentration was 17 mg/L and the flow rate was 50 mL/min) for 60 min. The results indicated that basic groups contributed to the catalysis.

INTRODUCTION
The increasing amount of sewage sludge has become a large challenge. In China, 2.6–5.2 × 10^7 t of sewage sludge is produced from wastewater treatment plants every year (Kroiss 2004). Anaerobic digestion, agriculture application, biotechnology, novel oxidation and thermal treatment are the main processes in sludge management. Sewage sludge contains biodegradable organic matter as well as contaminants (Siebielska 2014). Due to the widespread use of combined drainage systems in China, commonly used sludge treatments, such as anaerobic digestion and aerobic composting, are not applicable (Feng et al. 2015).

Sewage sludge-derived carbon (SC) has attracted interest as a catalyst or catalyst support because of its environmentally friendly and catalytically active characteristics. Surface-modified or metal-loaded SC catalysts have been employed in advanced oxidation processes (AOPs), such as catalytic wet peroxide oxidation (Yu et al. 2013), wet air oxidation (Marques et al. 2011), photo-Fenton oxidation (Yuan et al. 2016) and heterogeneous catalytic ozonation (Tu et al. 2014), and showed good catalytic efficiency.

Phenolic compounds, commonly used in the chemical industry, are considered as priority pollutants in wastewater treatment because of their high chemical oxygen demand, low biodegradability and high toxicity. Among them, hydroquinone (HQ, 1,4-dihydroxybenzene) is widely used as a raw material for stabilizers, developers, antioxidants and dyes. Furthermore, among the three dihydric phenols, HQ is the least biodegradable (Latkar et al. 2005). Although the biodegradability of HQ has been reported (Pramparo et al. 2012; Samolada & Zabaniotou 2014), the analysis utilized pre-adapted microorganisms or acclimated microorganisms in dynamic tests, which requires a long time and cannot be compared with natural inoculation. AOPs might be effective for the degradation of HQ.

In this work, the effect of non-surface-modified SC on the degradation of HQ via heterogeneous catalytic ozonation was studied. The characteristics of the catalysts were examined, and the pathway of HQ degradation was investigated.

MATERIALS AND METHODS
The HQ (99.0%) was purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. All other chemical reagents were of analytic grade and obtained from Sinopharm Chemical Reagent Co., Ltd. All glassware was soaked in ethyl alcohol, ultrasonically cleaned, thoroughly flushed
with tap water and then washed with deionized water (18.2 MΩ cm) three times.

**Preparation of SC**

Sewage sludge, the raw material of SC, was obtained from a municipal wastewater treatment plant (Malanhe sewage treatment plant, Dalian, China) and dried at 105 °C to a constant weight (dry sludge) before further treatment. Then, the dried sludge was carbonized at 500 °C (SC-500), 600 °C (SC-600), 700 °C (SC-700), and 800 °C (SC-800) for 4 h at a heating rate of 3 °C/min in a high-purity nitrogen (99.999 wt%, 500 mL/min) atmosphere. When the furnace was cooled to room temperature, the SCs were obtained. SC-HNO3 was obtained by modifying the surface of SC-700. For this, 38 g SC-700 was immersed in 50 mL HNO3 (40.5 wt%) for 24 h. The recovered solid was washed with deionized water until the pH of the effluent reached 6–7 and then dried at room temperature.

**Structural characterization**

A Topologic 500A spectrometer with a proportional counter was used to obtain the 57Fe Mössbauer spectra at room temperature. The radioactive source was 57Co(Rh) moving at a constant acceleration. The isomer shift (IS), the electric quadrupole splitting (QS), the full width at half maximum (line width), and the relative resonance areas of the different components in the absorption patterns were determined.

A scanning electron microscope (Quanta 200F, FEI Company) with an accelerating voltage of 20 kV was used to perform the scanning electron microscopy (SEM) experiments. The elemental compositions and compositional maps of the catalysts were determined by energy dispersive X-ray spectroscopy (EDX) detected by an EDX silicon-drift detector (EDX’s Sapphire Si (Li) Detector, USA). To analyze the composition and chemical state of the surface elements of the SC catalysts, X-ray photoelectron spectroscopy (XPS) was performed on a Thermo ESCALAB 250Xi instrument using an Al Kα X-ray (1486.6 eV) source at a pressure of 6.5 × 10⁻⁵ Pa and binding energy of 284.6 eV.

The functional groups on the surface of SC were measured by temperature programmed desorption (TPD). The SC powder sample was pretreated in pure He (99.999%) flow for 2 h. Then, the temperature was ramped up to 900 °C at a heating rate of 6 °C/min. The released CO and CO2 were detected with a mass spectrometer (Pfeiffer Vacuum, Ominstar GSD 301 O2). Transmission electron microscopy (TEM) images were obtained on a JEOL JEM-2100 microscope. The functional groups on the SC catalysts were analyzed by Fourier transform infrared spectroscopy (FTIR, IRAffinity-1, Shimadzu). Powder X-ray diffraction (XRD) was recorded on an X-ray polycrystal diffractometer (XD6, Beijing Purkinje General Instrument Co., Ltd).

**Hydroquinone degradation experiment**

The experimental set-up was shown in Figure 1. The degradation experiments were performed in a glass cylindrical reactor (250 mL) with 200 mL of model wastewater containing a certain concentration of HQ (200 mg/L) and a catalyst dose of 0.5 g/L. A mixture of ozone and oxygen gas was dosed into the reactor through a porous nozzle settled at the bottom. Ozone was produced from oxygen using a laboratory ozone generator (CF-G-3-010 g, Qingdao Guolin Environmental Technology Co., Ltd). The pH of the HQ solution was the original pH of 6 without adjustment. The experiments were carried out with a constant flow and concentration of ozone, which were maintained at 50 mL/min and 17 mg/L using a flowmeter and an ozone concentration detector, respectively. The water solubility content of HQ was 84.78 g/L (26.5 °C). In this study, the solution contained 200 mg/L HQ.

Samples were taken at specific reaction times and filtered through 0.45 μm pore size membranes. Then, 0.01 mL Na2S2O3 (0.01 mol/L) was immediately added into each sample as a radical inhibitor. At the end of the reaction, the solution was filtered and collected for high-performance liquid chromatography (HPLC), total organic carbon (TOC), chemical oxygen demand (COD) and biochemical oxygen demand (BOD) analysis.

Figure 1 | Experimental set-up: 1. ozone generator; 2. ozone concentration detector; 3. cylindrical reactor; 4. water inlet; 5. thermometer; 6. sample connection; 7. porous nozzle; 8. water outlet; 9. flowmeter; 10. gas absorption.
Analytical methods

The HQ concentration was determined by HPLC (Shimadzu LC-20A). The analysis was performed with a C18 column (Inertsil ODS-HL 4.6 mm × 150 mm, 5 μm) using a mobile phase of methanol and water in a 50:50 (v/v) proportion at a flow rate of 0.8 mL/min. The wavelength was set to 277 nm. A TOC analyzer (TOC-LCPH, Shimadzu, Japan) was employed to determine the residual amount of organic substances in the effluent. The pH of the HQ solution was measured with a pH meter (PHB-4, INESA). The COD was analyzed according to the dichromate method (HJ 828–2017). A Hach BODTrak II analyzer was employed to detect the BOD of the treated liquid. The samples were neutralized with NaOH (10%, v/v) before analyses.

To identify the intermediates in the treated solutions, a gas chromatography–mass spectrometer (GC-MS, 7890A, Agilent) equipped with a capillary column (HP-5MS, 30 m × 0.25 mm × 0.25 μm, Agilent) was utilized. Acids of low molecular weight were detected by GC-MS through the esterification reaction. After concentration by a rotary evaporator, the sample was esterified at 70 °C for 16 h with 10% H2SO4–methanol (1:5, v:v). After the liquid was cooled, saturated NaCO3 was added for neutralization. Fatty acids were extracted with dichloromethane. Then, the dichloromethane layer was dried with anhydrous Na2SO4 and filtered for GC-MS analysis. The column temperature was first held at 50 °C for 10 min and then ramped up to 250 °C for 10 min at an increased temperature rate of 15 °C/min. The He (99.999%) flow rate was 1 mL/min.

RESULTS AND DISCUSSION

Characterization of catalysts

The EDX analysis (Table 1) indicated that the proportions of C, O, Si, Ca, Al and Fe in SC-700 were 30.63%, 43.29%, 12.8%, 3.49%, 4.49% and 2.16%, respectively.

The 57Fe Mössbauer spectrum of SC-700 is shown in Figure 2. The IS of 0.44 mm/s with a QS of 0.96 mm/s could be attributed to Fe2+ (Elewa & Cadogan 2017) and accounted for 49.2% of the total spectral area. The IS of 1.03 mm/s with a QS of 2.18 mm/s could be attributed to Fe3+ (Zhang et al. 2015) and accounted for 50.8% of the total spectral area. Fe2+ and Fe3+ may act as active sites to promote the catalytic activity (Marques et al. 2011). SEM and TEM images (Figure 3) showed that SC-700 had a stacked structure with little pore structure.

The CO and CO2 TPD spectra of SC-700 are shown in Figure 4(a). The CO2 spectrum contained one peak (at 680–750 °C), which was attributed to lactones. The other peaks observed in the CO TPD spectrum of SC-700 were attributed to quinones (peak at 750–800 °C), carbonyls (peak at 820–870 °C) and phenols (peak at 690 °C) (Figueiredo & Pereira 2010; Shafeeyan et al. 2010; Li et al. 2016). Therefore, the surface of SC-700 contained quite a few basic groups. The XPS peaks of SC-700 are presented in Figure 4(b). The peaks at 284.6, 285.1 and 286.3 eV were assigned to C-C (64.3%), C-O (23.4%) and C = O (12.3%), respectively.

The XRD patterns and FTIR spectra of the catalysts are shown in Figure 5. The XRD patterns indicated that SiO2 was the main inorganic component in the catalysts. The FTIR spectra of all the catalysts exhibited a broad peak at approximately 3,400 cm⁻¹, which was related to hydroxyl groups, corresponding to alcohols or carboxylic acids. The peaks at 1,481, 1,070, 1,028, 877 and 796 cm⁻¹ represent the stretching or flexural vibrations of CO2⁻. The peak at approximately 1,630 cm⁻¹ is commonly assigned to C = O. The 1000–1100 cm⁻¹ region was attributed to Si-O-C or Si-O-Si structures (Marques et al. 2011), which was consistent with the XRD results. Peaks between 830 and 650 cm⁻¹ were associated with aromatic structures and amide groups. The peaks corresponding to C = O and CO2⁻ on SC-700 were stronger than those on the other bio-chars, which indicated more basic groups on SC-700 than the others.

Table 1 | Element content of SC-700

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>O</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>K</th>
<th>Ca</th>
<th>Fe</th>
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</thead>
<tbody>
<tr>
<td>Content (%)</td>
<td>30.63</td>
<td>43.29</td>
<td>0.49</td>
<td>0.81</td>
<td>4.49</td>
<td>12.8</td>
<td>0.5</td>
<td>0.26</td>
<td>1.08</td>
<td>3.49</td>
<td>2.16</td>
</tr>
</tbody>
</table>

Preliminary study of HQ degradation using different catalysts

Figure 6(a) indicates that SC-700 had the highest HQ removal rate, followed by commercial activated carbon derived from coal (CAC), the blank, SC-HNO3 and dry sludge. As
shown in previous studies (Sánchez-Polo et al. 2005; Faria et al. 2006; Chen et al. 2015), HQ was easily oxidized in alkaline solution, and basic groups were favorable for catalytic ozonation. A significant number of basic sites presented on the surface of SC-700, which may promote HQ ozonation.

SCs pyrolysed with higher temperature had higher HQ removal rates (Figure 6(b)). This might be because, with the rising temperature, acidic functional groups on the sludge were easily decomposed and caused the basic property. The increasing amount of alkali organic along with the higher temperature was also responsible for the alkalinity (Yuan et al. 2011). However, after 30 min of ozonation, the HQ removal rate was slightly raised from 89.95% (SC-700) to 91.65% (SC-800), smaller than that from 79.87% (SC-600) to 89.95% (SC-700). In other words, the removal rate gap between SC-800 and SC-700 was smaller than that between SC-700 and SC-600. Besides, higher temperature brings higher cost. For those reasons, 700 °C was considered the ideal temperature for the catalyst in this study.

When the initial HQ concentration was increased, the amount of ozone catalyzed by SC was not sufficient to reach the target objective, leading to a decrease in the removal (Figure 6(c)). The TOC removal rates (60 min) are shown in Figure 6(d). There was no removal for dry sludge, obtaining a TOC value higher than the initial. It was assumed that HQ degraded into low molecular weight organic matter, such as oxalic acid, which was not easily decomposed by ozone (Liao et al. 2014), and
therefore the TOC removal rates were not significantly different.

After catalytic treatment, the COD of the solution decreased from 382 mg/L to 238 mg/L, and the BOD₅ increased from 0 mg/L to 83 mg/L (Figure 7), which caused the BOD₅/COD of the solution to increase from 0 to 0.35, indicating improved biodegradability and reduced toxicity.

Figure 4 | TPD spectrum (a) and XPS spectrum (b) of SC-700.

Figure 5 | FTIR spectra ((a) and (b)) and XRD patterns ((c) and (d)) of the catalysts.
HQ oxidation mechanism

The proposed mechanism (Figure 8) implies that HQ was first oxidized into \( p \)-benzoquinone (BQ). In solution, HQ appeared colorless, and BQ appeared yellow. However, when HQ and BQ were mixed, the solution appeared brown because of the formation of quinhydrone (Mijangos et al. 2014). During ozonation, the color of the solution changed from colorless to yellow, brown, light brown and light yellow. To investigate the HQ degradation pathway, GC-MS was applied to identify the intermediates. After oxidation to BQ, a semiquinone (A in Figure 8) and an intermediate radical (B) were formed through a hydroxyquinone adduct. Then, 2-hydroxy-1, 4-benzoquinone (D) was formed from the intermediate radical through the secondary radical 2-hydroxy-1, 4-benzosemi-quinone (C) (Pedersen 1973). Then 2-hydroxy-1, 4-benzoquinone (D) was oxidized to 4-ketopentenic acid (E) and \( \alpha \)-ketoglutaric acid (F), which were oxidized to maleic acid and proceeded to succinic acid, malonic acid and oxalic acid. Although previous studies (Marques et al. 2011; Li et al. 2015) indicated that HQ was eventually degraded to acetic acid and formic acid by AOPs, this experiment did not detect acetic acid or formic acid. It was because the ozone molecule had a slight potential...
to oxidize oxalic acid (Hoigné & Bader 1985; Wen et al. 2012).

CONCLUSIONS

In this study, SC-700 promoted HQ ozonation due to the sufficient presence of basic groups and catalytically active metals (Fe) on the surface. When the catalyst dose was 0.5 g/L, the HQ (200 mg/L) removal rate reached 97.86% after exposure to ozone (the ozone concentration was 17 mg/L and the flow rate was 50 mL/min) for 60 min. GC-MS detection showed that HQ was first oxidized to BQ, and then the aromatic ring was attacked by O$_3$ and degraded to small molecular weight acids. This study demonstrated a simple resource utilization of sewage sludge and proved the activity of a sewage sludge-derived carbonaceous catalyst in the ozonation of HQ.

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