Catalysis of CuSO₄ for total organic carbon detection based on supercritical water oxidation

Zhang Hui, Han Dongdong, Chen Yi and Lin Chunmian

ABSTRACT

The catalytic effects of CuSO₄ in total organic carbon (TOC) detecting processes based on supercritical water oxidation have been investigated. Using benzoic acid as a model pollutant, the presence of a CuSO₄ catalyst can significantly decrease the reaction temperature and H₂O₂ multiple during the TOC detection processes. A better TOC conversion efficiency was obtained at a much lower temperature in the catalytic system compared with the non-catalytic condition. The use of the catalyst effectively lowered the necessary H₂O₂ multiple from 20.0 without catalyst to 3.0 in the catalytic system. The established device could detect the TOC concentration precisely in model wastewater without inorganic carbon (IC). Moreover, the detection of the practical wastewater was studied. Detection results were total carbon of wastewater rather than TOC of practical wastewater. A detection or removal unit of IC is necessary before it can be practically utilized.

Key words | benzoic acid, catalytic supercritical water oxidation, continuous detection, total organic carbon

INTRODUCTION

Supercritical water oxidation (SCWO) has been developed to treat aqueous waste streams by Modell since the 1980s (Modell 1982) and became one of the most environmentally friendly advanced oxidation processes. Organic materials can be completely oxidized in supercritical water. When the temperature and pressure exceed its critical point \( T_C = 374 \, ^\circ C, \quad P_C = 22.1 \, MPa \), water becomes an excellent solvent and is miscible with gases and organic substances in any proportion (Aki & Abraham 1999). The interphase mass resistance can be eliminated in supercritical water (Yu & Savage 2000). As a result, the reaction can occur faster. During the SCWO process, the organic compounds can be oxidized completely forming CO₂ and H₂O. The hetero-atoms in the organic wastes are transformed into the mineral acids (chlorine, sulfur and phosphorus forms HCl, H₂SO₄ and H₃PO₄, respectively). Organic nitrogen predominately forms N₂ and small amounts of N₂O. Undesired by-products known from incineration (dioxines, NOₓ) are normally not formed (Kritzer & Dinjus 2001). The commonly used method to detect the total organic carbon (TOC) is to oxidize the organic carbon to CO₂, and the TOC can be obtained by detecting the amount of CO₂. So the SCWO can be used as a TOC detecting method replacing other methods, such as high temperature catalytic oxidation, wet oxidation, etc.

Studies on the technology of SCWO have been mainly focused on the environmentally friendly treatment of organic wastewater, especially wastewater with high concentration of organics and high toxicity which is difficult to dispose of (Veriansyah et al. 2005). These studies can be mainly divided into two categories: one is the study of degradation of model pollutants, including N,N-dimethylformamide (García-Jaranaa et al. 2015), polyvinyl alcohol (Zhang et al. 2013), acetonitrile (Youngprasert et al. 2010), fulvic acid (Gong et al. 2014) and disperse orange 25 (Sögüt & Akgün 2007; Wang et al. 2013), etc.; the other is the utilization of the technology in the treatment of actual wastewater, including oily wastewater (Ma et al. 2015), olive mill wastewater (Erkonak et al. 2008), leachate (Zou et al. 2013a, 2013b; Gong et al. 2014) and laboratory wastewater (Dong et al. 2014), etc. Besides, utilization of SCWO in tannery sludge (Zou et al. 2013a, 2013b) is also reported. Different from the above studies, a device that can detect the TOC in water continuously has been developed by using SCWO as the oxidation method in our earlier research (Zhang et al. 2011, 2012). TOC is widely
used in water quality control as an important parameter to evaluate the organic pollution of water, especially in many developed countries such as the USA and Germany. The device can detect TOC in water accurately (Zhang et al. 2011, 2012). However, the operating condition of the device is still much too severe, especially the temperature and H$_2$O$_2$ multiple. The severe reaction conditions will go against the long-time steady running of the device. It is necessary to develop a novel SCWO process which can be operated in milder conditions.

Catalytic supercritical water oxidation (CSCWO) was the improvement of SCWO by introducing the catalyst into the reaction system. Catalysts used in CSCWO can be divided into two kinds: heterogeneous (Shin et al. 2009; Jing et al. 2012) and homogeneous (Perez et al. 2011). Homogeneous catalysts are active and stable, but they are difficult to be separated from wastewater. As SCWO is mainly used in the decontamination of wastewater in previous research, homogeneous catalyst will result in the secondary pollution inevitably. Heterogeneous catalysts can be separated from wastewater easily. However, the poor stability and activity in supercritical water (Arslan-Alaton & Ferry 2002) and the diffusion of the reactants in the pores of the catalyst limit the reaction rate (Aki & Abraham 1999). The catalysts are mainly used to improve the detection performance of instruments in environmental monitoring. The activity and stability of catalysts are more crucial than the separating ability; therefore, our study focused on homogeneous catalysts. Homogeneous catalysts used in catalytic SCWO are mainly KMnO$_4$ and the transition metal salts of copper, manganese, and zinc (Ding et al. 1996; Gizir et al. 2005; Perez et al. 2011).

In this study, a solution of Cu$^{2+}$ was chosen as a homogeneous catalyst in the TOC detection for stimulant wastewater containing benzoic acid. The relationships between temperature, H$_2$O$_2$ multiple, flow rate and conversion efficiency were studied in the system with and without Cu$^{2+}$ catalyst.

**EXPERIMENTAL**

**Preparation of materials**

Model wastewater was prepared with chemicals benzoic acid (Chinasun Specialty Products Co., Ltd, AR) and potassium hydrogen phthalate (Yonghua Chemical Technology (Jiangsu) Co., Ltd, AR). A solution of CuSO$_4$ was prepared with CuSO$_4$·5H$_2$O (Sinopharm Chemical Reagent Co., Ltd, AR). High purity nitrogen (99.999% (v/v)) was used to blow off the CO$_2$ dissolved in the effluent. Oxidant was prepared by diluting commercially available H$_2$O$_2$ (30% (m/m)) into different concentrations. H$_2$O$_2$ multiple ($m$) was used as an index to describe the amount of oxidant used in the experiment. H$_2$O$_2$ multiple is the ratio of practical oxidant dosage and the theoretical value calculated from the chemical equation.

**Experimental device and conditions**

Figure 1 is the schematic diagram of the experimental device. Water sample, oxidant, catalyst and pure water flowed into the low-pressure gradient mixer, through the four flow lines numbered 1, 2, 3, and 4, respectively, to get mixed proportionally. The mixed reactants were then pumped into the SCWO reactor with a certain flow rate to oxidize the organics into CO$_2$ under experimental pressure and temperature. The reactor, made by winding stainless steel tubes (with 0.125” o.d., 0.060” i.d. and 50 m in length) into spiral shape, was placed in the chamber of electric furnace. A proportional-integral-derivative controller was used to regulate the temperature of the furnace. The pressure of the reaction was controlled by a back pressure valve. The effluent from the reactor firstly ran through a cooling tank and was cooled to lower than 100 °C. Then the cooled effluent was depressurized and became suitable for gas–liquid separation. The gas–liquid separator was a sealed glass tube with two outlets on the top and two outlets on the bottom. The effluent flowed into the separator from one outlet on the top. High purity nitrogen flowed through the effluent in the separator and blew off the CO$_2$ dissolved in the effluent. Mixture of nitrogen and CO$_2$ flowed out from the other outlet on the top and was dried by an electronic dehumidifier. As carbon dioxide can absorb specific light with a wavelength of 4.26 μm, a commercially available
non-dispersive infrared (NDIR) detector (AIDE GmbH NDIR Optics Bench) which was produced by Analytische Instrumente Dessau GmbH was used to detect the dried gas mixture. The flow rate of N₂ was regulated by a mass flow meter and the NDIR signal was recorded by the computer in real time. The concentration of TOC in the water sample was calculated by the calibration curve according to the NDIR signal. Table 1 shows the experimental conditions.

**Evaluation of results**

Performance of the device for TOC detection was investigated under different conditions. As the device was a continuous running system in the detecting process, analytical frequency was no longer suitable for the characterization of the device, and performance of the device were mainly evaluated by an index named conversion efficiency \( X \).

\[
X = \frac{\text{TOC}_m}{\text{TOC}_t} \times 100\%,
\]

where \( \text{TOC}_m \) was the concentration of TOC obtained from the experimental device, while \( \text{TOC}_t \) was the theoretical value.

**RESULTS AND DISCUSSION**

**Correlation between TOC concentration and NDIR signal**

Experiments were performed to study the correlation between the concentration of benzoic acid in the range of 10 to 250 mg/L and the NDIR signal. The experimental condition of temperature was 460 °C, pressure was 24.0 MPa, \( \text{H}_2\text{O}_2 \) multiple was 10.0, and flow rate was 2.0 mL/min. Earlier research had proven that organic compounds could be oxidized completely (Zhang et al. 2011, 2012) under such conditions. The NDIR signal is directly proportional to the TOC concentration of the water sample because the NDIR signal reflects the concentration of \( \text{CO}_2 \) which was in direct proportion with the \( \text{CO}_2 \) generated during the oxidative process. A perfect linear correlation, as shown in Figure 2, was observed between the NDIR signal and theoretical TOC concentration. As a matter of fact, a good linearity was obtained with \( R^2 \) being more than 0.999. The line proves that it is viable to detect TOC by the experimental device and methods.

**Effect of temperature on TOC conversion efficiency**

A relatively milder experimental condition was used to highlight the effect of temperature with catalyst. The reaction temperatures were in the range of 380 to 460 °C, reaction pressure was 23.2 MPa, \( \text{H}_2\text{O}_2 \) multiple was 1.0, flow rate was 2.5 mL/min and TOC concentration \( ([\text{TOC}]) \) was 180.0 mg/L. The concentration of \( \text{Cu}^{2+} \) in the mixed reactants was 1.0 mg/L. The results of the experiments are shown in Figure 3.

Controlling experiments without catalyst were also conducted to illustrate the catalytic effect of \( \text{CuSO}_4 \). The increase of conversion efficiency can be mainly divided into three stages in the temperature range of 380–460 °C. Firstly the conversion efficiency only increased slowly from 35.47 to 41.03% when the temperature increased from 380 to 420 °C. Then the conversion efficiency increased quicker from 41.03 to 65.26%, although the temperature only increased from 420 to 440 °C. Lastly when the temperature exceeded 440 °C, the increase rate of conversion efficiency tended to be slow again. This

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Experimental conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Items</td>
<td>Benzoic acid ( ^a ) (mg/L)</td>
</tr>
<tr>
<td><strong>Concentration range</strong></td>
<td>10–250</td>
</tr>
<tr>
<td><strong>Items</strong></td>
<td><strong>Temperature (°C)</strong></td>
</tr>
<tr>
<td><strong>Range</strong></td>
<td>300–500</td>
</tr>
</tbody>
</table>

\( ^a \) Count with \( \text{TOC} \).  
\( ^b \) Count with \( \text{Cu} \).
shows similar results with other research (Thornton & Savage 1992).

An obviously different trend can be seen between the temperature and conversion efficiency when the catalyst was introduced into the system. Conversion efficiency increases slowly at a high level with the rising of temperature in the whole range of experimental temperature. When the temperature was 380 °C, TOC conversion efficiency reached a value of 86.00% in the catalytic system, obviously higher than the value of 35.47% obtained for the non-catalytic condition. In general, the conversion efficiency in the CuSO4 catalytic system are higher than the non-catalytic system under lower temperature. It is feasible to decrease the operation temperature by using CuSO4 as the catalyst. This shows similar results as relevant research (Zhou et al. 2011; Jing et al. 2012; Wang 2014). The principle is that the outer electrons of the metal ions combined with the electrons of organic and molecular oxygen which increased their activity by electron transfer. This forms living radicals as a Fenton-like system (Nichela et al. 2013). The high activity reactants need low activation energy, so the reaction can be carried out at low temperature with catalyst when other conditions are unchanged.

**Effects of H2O2 multiple on TOC conversion efficiency**

Two group experiments were performed at 420 °C and 23.2 MPa to study the catalytic effect of CuSO4 on improving the utilizing efficiency of oxidant. H2O2 multiple adopted in the experiments were in the range of 0.5 to 20. The flow rate chosen in the experiments was 2.5 mL/min and TOC concentration was 180.0 mg/L. Figure 4 shows the different trends between the two group experiments vividly. When CuSO4 was introduced into the reaction system, TOC conversion efficiency increased rapidly when H2O2 multiple increased from 0.5 to 2.0 and nearly reached the maximum value at 3.0. H2O2 multiple has little or no effect on the conversion efficiency when it was higher than 3.0. As to the group without catalyst, TOC conversion efficiency increased continuously in the whole range of H2O2 multiple from 0.5 to 20.0. When H2O2 multiple was 20.0, conversion efficiency tended to be the same level as the catalytic system at 3.0. The use of CuSO4 catalyst can greatly decrease the H2O2 multiple necessary. This is because the catalyst can increase the activity of the molecular oxygen which comes from H2O2, therefore increasing the utilization of H2O2. So the reaction can be carried out at lower H2O2 with catalyst when other conditions are unchanged.

**Effect of flow rate on TOC conversion efficiency**

The flow rate could affect the retention time of reactants in the reactor, and then affect the TOC conversion efficiency. Experiments were performed under conditions at $T = 420$ °C, $p = 23.2$ MPa, $m = 2.0$, $[\text{Cu}^{2+}] = 1.0$ mg/L and $[\text{TOC}] = 180.0$ mg/L. The flow rates used in the experiments were in the range of 1.0 to 3.0 mL/min. Relationship between flow rate and TOC conversion efficiency is shown in Figure 5.

No significant change could be seen when the flow rate increased from 1.0 to 2.5 mL/min. Non-linear curve fit of the experimental data can be regarded as the prediction value under experimental conditions. It can be seen from the fit curve that the conversion efficiency could be maintained at 100% on the whole when the flow rate varied from 1.5 to 2.0 mL/min. But a distinct decrease appeared
when the flow rate increased from 2.5 to 3.0 mL/min. A much shorter retention time will lead to the incomplete oxidation of benzoic acid and decrease the amount of CO2 generated in the oxidative process, which will result in the decrease of conversion efficiency. This indicates that the retention time was long enough when the flow rate was lower than a certain value (2.5 mL/min) and will no longer be the major limitation in oxidation of organics. Besides retention time of the oxidative reaction, flow rate will also affect the response time of the instrument, which is defined as the total amount of time the NDIR detector takes to respond to a water sample.

As the instrument was designed to monitor water environment quality, shorter response time can better satisfy the requirements of real-time, online and continuous detection of TOC. In the consideration of the complete oxidation of organics, the optimized flow rate was 2.0 mL/min.

### TOC detection of model and practical wastewater samples

Two kinds of model wastewaters and two kinds of practical wastewaters were used to verify the performance of the established device under optimized conditions. One of the practical wastewater were generated in the process of synthetic drug production, and the other was generated in the production of dye. They were provided, respectively, by a pharmaceutical industry producing medicine and a fine chemicals industry producing dye in Zhejiang Province, China. Both of the detections were taken at 420°C, 23.2 MPa. Concentration of Cu²⁺ was 1.0 mg/L and flow rate was 2.0 mL/min.

Table 2 shows the results of the model wastewater detected by experimental device. The accuracy of the results was assessed by the relative errors between the theoretical and experimental values of TOC concentration. Both of the relative errors were less than 5.00% and the detection value can be considered to be in great accordance with the real value. The experimental device can accurately detect the TOC concentration of model wastewater.

Table 3 lists the detection results of the two practical wastewaters detected by Shimadzu TOC analyzer (TOC-VCPN) and experimental device. It can be seen from the detection results of the TOC-VCPN that a large proportion of inorganic carbon (IC) existed in the practical wastewater. The results of the experimental device were nearly the same as TC detected by TOC-VCPN. It is more appropriate to say that the device detected the TC of wastewater with IC in it.

<table>
<thead>
<tr>
<th>Type</th>
<th>TOC&lt;sub&gt;t&lt;/sub&gt; (mg/L)</th>
<th>TOC&lt;sub&gt;m&lt;/sub&gt; (mg/L)</th>
<th>Std Dev (RSD)</th>
<th>Repeatability</th>
<th>Relative error, E (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium hydrogen phthalate</td>
<td>200</td>
<td>204.87</td>
<td>3</td>
<td>1.23</td>
<td>0.60%</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>200</td>
<td>205.27</td>
<td>3</td>
<td>2.60</td>
<td>1.27%</td>
</tr>
</tbody>
</table>

*Experimental TOC concentration was tested at T = 420°C, p = 23.2 MPa, [Cu²⁺] = 1.0 mg/L, and flow rate = 2.0 mL/min. TOC<sub>t</sub>– Theoretical value of total organic carbon. TOC<sub>m</sub>– Experimental value of total organic carbon. N– Number of replicates. Std Dev – Standard deviation. E – Relative error, E = (TOC<sub>m</sub>−TOC<sub>t</sub>)/TOC<sub>t</sub> × 100%.

<table>
<thead>
<tr>
<th>Type</th>
<th>pH</th>
<th>TC (mg/L)</th>
<th>IC (mg/L)</th>
<th>TOC (mg/L)</th>
<th>Experimental device (mg/L)</th>
<th>n</th>
<th>Relative error, E (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pharmaceutical</td>
<td>2</td>
<td>321.79</td>
<td>0.65</td>
<td>321.08</td>
<td>319.6</td>
<td>3</td>
<td>−0.68</td>
</tr>
<tr>
<td>Dipdye industry</td>
<td>8</td>
<td>874.24</td>
<td>0.1</td>
<td>874.14</td>
<td>889.4</td>
<td>3</td>
<td>1.7</td>
</tr>
</tbody>
</table>

*TOC detected by experimental device were tested at T = 420°C, p = 23.2 MPa, [Cu²⁺] = 1.0 mg/L, and flow rate = 2.0 mL/min. TC – Total carbon. IC – Inorganic carbon. TOC – Total organic carbon. N– Number of replicates. Std Dev – Standard deviation.
and the results are also highly accurate. Adding of detection or removal unit of IC to the device is necessary before it can be practically utilized in the monitoring of practical wastewater.

**CONCLUSIONS**

The excellent catalytic performances of Cu$^{2+}$ were observed in this study. Compared with the non-catalytic system, milder operation conditions could be adopted to detect TOC concentration of wastewater in Cu-catalytic system. The optimized temperature and H$_2$O$_2$ multiple were decreased to 420°C and 3.0, respectively. A flow rate of 2 mL/min can both satisfy the high TOC conversion efficiency and short response time of the device. The device can precisely detect the concentration of TOC in practical wastewater, during which ICs were also transferred into wastewater without IC. When it was used to detect practical wastewater, during which ICs were also transferred into CO$_2$, detection results were TC of the wastewater rather than TOC. The precise detection of TOC in practical wastewater will be investigated in our future studies.

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