Removal of 1,4-Dioxane from Wastewater by Copper Oxide Catalyzed WAO with Mild Condition

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Abstract. 1,4-Dioxane is a contaminant of emerging concern that is classified by the U.S. Environmental Protection Agency as a likely human carcinogen. Moreover, 1,4-dioxane easily migrates to groundwater due to its high solubility in water and hard to be biodegraded or removed by traditional water treatment technology. Therefore, it is indispensable to develop new methods and technologies to dispose of 1,4-dioxane in the wastewater. Herein, this study presented catalytic wet air oxidation (CWAO) with CuO as a catalyst and O_2 as an oxidant to treat 1,4-dioxane and investigated the influence of reaction conditions, including temperature, reaction time, oxygen content, catalyst addition and pH, on the degradation of 1,4-dioxane. The highest degradation rate (*R*) of 1,4-dioxane was 95.8 % when the optimal reaction conditions were at 200 °C and 1 MPa O_2 for 60 min with 5 mmol CuO added. If the effect of Cu^{2+} dissolution was not considered, the *R* of 1,4-dioxane is up to 99.8 % was achieved at an acidic condition (pH=3) with 2 mmol CuO added.

1 INTRODUCTION

1,4-Dioxane is miscible in water, essentially nonvolatile when dissolved in water, not well adsorbed by activated carbon, not readily biodegraded and not well eliminated by reverse osmosis at concentrations relevant to drinking water standard[1]. Whereas an effective method to dispose of 1,4-dioxane is advanced oxidation processes (AOPs), which produces free radicals that reacts with organic pollutants quickly. Among all kinds of AOPs, O_3/ H_2O_2 system [2], ultra-violet (UV) based AOP, such as UV/H_2O_2 [3-5], UV/$S_2O_8^{2-}$ [3, 6], UV/HOCl [7, 8], UV/NH_2Cl [8, 9], UV/Fe(II)/H_2O_2 [10], UV-vis/ferrioxalate/H_2O_2 [11], and the photoelectro-peroxone process [12] have been widely studied [13]. Although these AOPs has a good efficacy on degrading 1,4-dioxane, some obstacles still exist including expensive oxidants, metal salts as secondary pollutants, highly ecotoxic by-products and low efficiency [14]. In addition, almost all methods removing 1,4-dioxane from wastewater are hard to reach the standard of 1,4-dioxane-concentration <0.5 ppm.

Catalytic wet air oxidation (CWAO) has been applied as one of the AOPs to treat bio-toxic organic wastewater treatment for many years [15-17]. In this process, organic pollutants are almost oxidized into carbon dioxide and water at high temperature (150-375 °C) and pressure (0.5-20 MPa) with oxygen as an oxidant. It is known to all that oxygen is cheap and easily available, which could replace the expensive and unstable oxidant. Furthermore, CWAO process is extremely clean without any harmful and toxic by-products. Since, the catalyst is the heart of CWAO process, the selection of the catalyst is important for the feasibility of CWAO. Although, homogenous catalysts and noble metals have very good activity towards oxidation of 1,4-dioxane, they are very expensive and easily poisoned by halogens and sulphur group containing compounds.

In recent years, metal-oxide catalysts such as copper, iron, manganese, and nickel oxides have been widely used for the treatment of various organic compounds. Santos et al. studied CWAO of phenol using copper-oxide catalyst at 127–160 °C and 8–16 bar pressure, and phenol mineralization of 77 % was obtained. The leaching of copper was minimized using sodium bicarbonate and the intermediates formed in CWAO effluent were found to be less toxic than phenol. Kim and Ihm reported optimum copper loading of 20 wt% for CuO_x/TiO_2 catalyst for CWAO of phenol [18]. However, few researches reported the CWAO process used on degradation of 1,4-dioxane. Hence, in this work, we present a new method using CWAO process to decompose 1,4-dioxane from wastewater with copper oxide catalyst and O_2 as an oxidant.

2 MATERIAL AND METHODS

2.1 Materials

MnO2, Ag2O, MoO3, SiO2 and 1,4-dioxane (99.99 %) were obtained from Sinopharm Chemical Reagent Co. Ltd.; CuO (99.99 %, 10 µm), CeO2, CoO3, TiO2 were

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brought from Shanghai Macklin Biochemical Co., Ltd; formic acid (for mass spectrometry, 98 %) from Sigma-Aldrich (Shanghai) Trading Co., Ltd.; gaseous O2 (>99.99 %) and N2 (>99.99 %) both from Shanghai Poly-Gas Technology Co. Ltd. All of the raw materials used in the experiment were in analytical grade without further purification. The solvent used in the experiment is distilled water.

2.2 Experimental facilities

In this experiment, a six-linked high-temperature parallel reactor with an effective volume of 7 ml was used as the reactor. It is convenient for the reaction system to add oxygen at different partial pressures and ensure the stability of reaction temperature and time. The reactor can carry out up to 6 experiments at the same time, with the uniform temperature and pressure. It can also control stirring speed, air intake and air bleed.

2.3 Analytical methods

The crystalline phases in the solid samples were detected by X-Ray Diffraction (XRD) (Shimadzu, LabXRD-6100, scanning speed: 2° min−1, 2θ ranges: 5−80°). The morphology of the CuO particles was observed by scanning electron microscope (SEM). The X-ray photoelectron spectroscopy (XPS) spectra were obtained with incA-Max 80 type energy dispersive X-ray spectrometer of Oxford Company, which was used to analyze the changes of the valence states of elements before and after the reaction of CuO. The Fourier Transform Infrared Spectra (FTIR) of CuO before and after reaction of 1,4-dioxane were observed. The concentrations of 1,4-dioxane and by-products were measured by High Performance Liquid Chromatograph (HPLC) and Gas Chromatography- Flame Ionization Detector (GC-FID) equipped with a HP- INNOWAX polyethylene glycol capillary column. The by-products were detected by GC-MS (Agilent7890A GC system, 5975C inert MSD with Triple-Axis Detector) equipped with the same column as the GC-FID. The degradation rate of 1,4-dioxane (R) was calculated according to the following equation:

$$R=\frac{C}{C_0}\times 100\% \quad (1)$$

where C and C0 are the molar concentrations after and before the reaction, respectively.

2.4 Experimental procedure

All reactions were conducted in a 316L high-pressure hydrothermal reactor with magnetic stirring and a charge valve, and the internal volume of reactor is 7 mL. The certain amount of 1,4-dioxane (1000 ppm) solution (3 mL e.g.) and catalyst (1 mmol e.g.) were added into the reactor first, and then the reactor was purged with O2 for 1 min. After the reactor filled with a certain pressure (1 MPa e.g.) of oxygen, it was placed at a heater instrument at the desired reaction temperature (200 oC e.g.) and time (60 min e.g.) with continuous stirring. Finally, after reaction, the reactor was cooled down to the room temperature. Liquid samples were collected and filtered with 0.22 µm Syringe Filter and transferred to a vial for subsequent analysis. The solid samples were washed by deionized water several times and dried in vacuum for subsequent analysis.

3 RESULTS AND DISCUSSION

3.1 Screening of metal oxides

To investigate the degradation performance of 1,4-dioxane by CWAO with different metal oxides, 100 mg/L of 1,4-dioxane solution and 1 mmol of metal oxide were added into the reactor, and the filling amount was 40 %. The reaction was carried out at 200 oC, 1 MPa O2 for 60 min, and the results were shown in the Figure 1. Without any metal oxide addition, hydrothermal environment had a weak effect on removal of 1,4-dioxane that the R was only 7.78 %. The R increased by 10-30 % after adding different metal oxides. Particularly, CuO showed a good improvement effect on R reaching 34.68 %. Because of its good catalytic performance, copper oxide was chosen as the catalyst for this experiment.

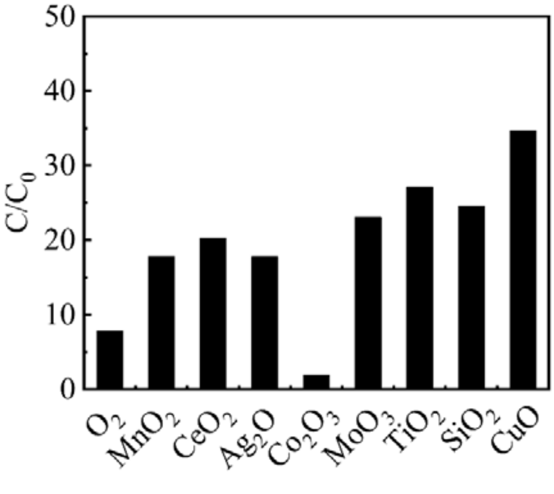

Figure 1. Effects of different metal oxides on the degradation of 1,4-dioxane by wet air oxygen oxidation. (1,4-dioxane: 100 mg/L; temperature: 200 °C; time: 1 h; O_2: 1 MPa; oxides: 1 mmol)

3.2 Catalyst characterization

In the SEM analysis, the CuO powder showed the typical particle morphology with a spherical shape in Figure 2. There are small particles appearing on the surface after the reaction.

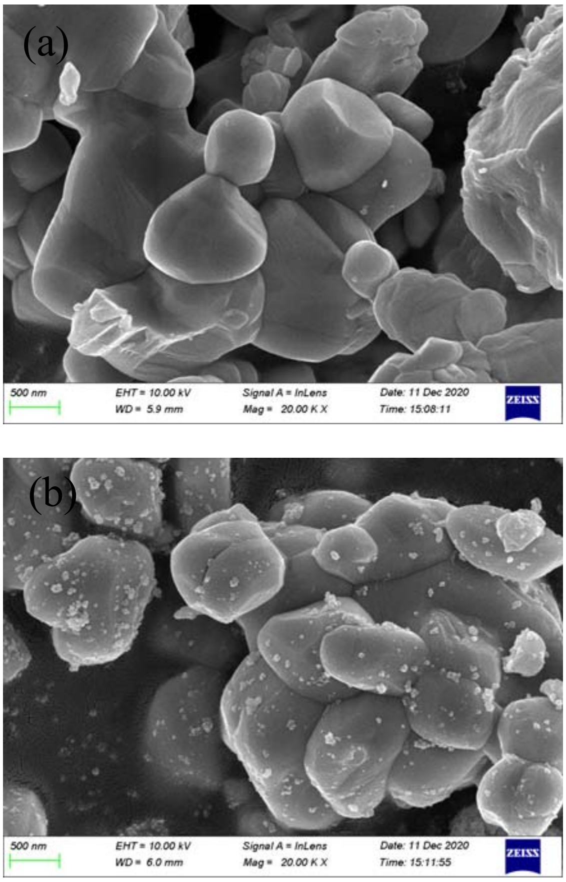

Figure 2. SEM images of CuO (a) before and (b) after the reaction. (temperature: 200 ^{o}C; time: 1 h; O_2: 1 MPa; CuO: 1 mmol)

The XRD patterns of CuO samples before and after the reaction are given in Figure 3. Prominent peaks at the diffraction angle (2θ) 35.4°, 38.5°and 48.8°refer to (0,0,2), (2,0,0) and (2,0, -2) lattice planes of monoclinic CuO (JCPDS No. 48-154), respectively [19]. The two samples exhibited a similar diffraction pattern and the half-peak width, which means the structure and crystallinity of the CuO did not change after reaction.

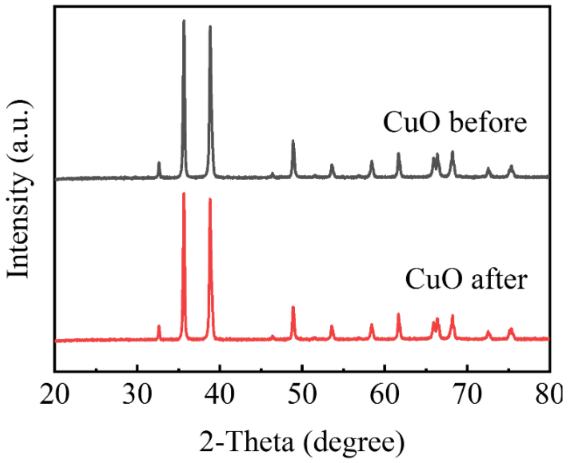

Figure 3. XRD patterns of CuO before and after the reaction. (temperature: 200 ^{o}C; time: 1 h; O_2:1 MPa; CuO: 1 mmol)

The oxidation states of Cu in the CuO before and after the catalytic oxidation of 1,4-dioxane was investigated by XPS, which is shown in Figure 4. The peaks located at 933.4 and 953.2 eV can be attributed to Cu 2p 3/2 and Cu 2p 1/2 of CuO, respectively. In addition, shake-up satellite peaks located at 940.6, 943.2 and 961.8eV may be due to the open 3d9 shell of Cu2+ [20]. The XPS peaks located at 932.6eV and 952.4eV are the characteristic signals of Cu(I) for Cu 2p3/2 and Cu 2p1/2, respectively [21]. Since no diffraction peaks belonging to Cu2O were detected in the XRD pattern (Figure 3 (b)), the Cu2O species is probably restricted to the surface. For the CuO sample after catalytic oxygen oxidation the peaks at 934.2 and 954.2 eV shifted to lower binding energy when compared to the sample before the reaction, which means that more Cu+ was presented on the CuO surface after oxygen oxidation[22].

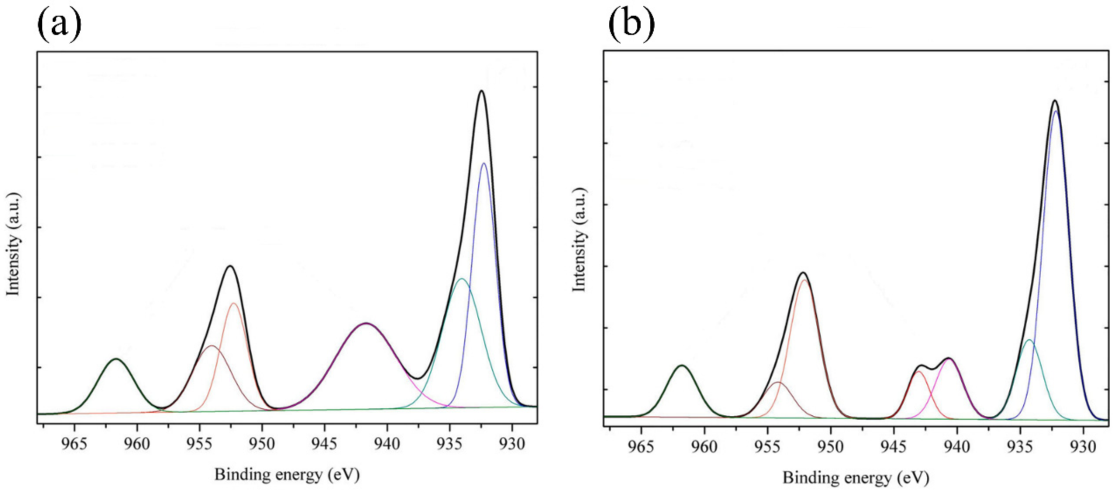

Figure 4. XPS spectra of CuO (a) before and (b) after the reaction; (temperature: 200 ^{o}C; time: 1 h; O_2:1 MPa; CuO: 1 mmol)

The chemical functional group analysis for CuO were carried out by using FTIR spectrometer. As shown in Figure 5, the spectra indicated similar chemical identities of CuO samples before and after the oxidation reaction, as the peaks at 520 cm-1 are both assigned to the Cu-O stretching vibration. However, a high-intensity peak observed at 3300-3500 cm-1 in the spectrum of the CuO after the reaction refers to the vibration of O-H bonds[19], demonstrating that hydroxyl radicals could be produced in the reaction system.

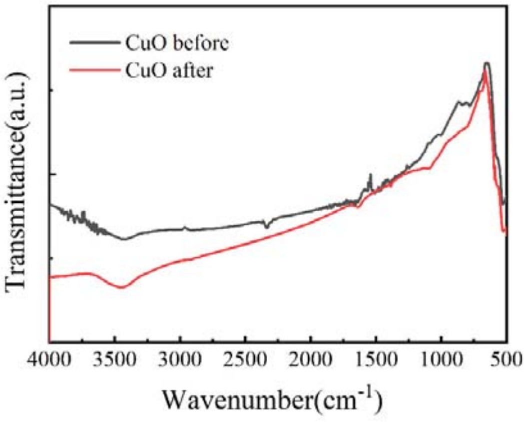

Figure 5. FTIR spectra of CuO before and after the reaction

3.3 Catalytic wet air oxidation of 1,4-dioxane with CuO

In general, temperature is a key factor in the application of catalytic wet air oxidation technology. Especially when oxygen used as an oxidant, the temperature dominates the overall reaction efficiency. In order to explore the appropriate reaction temperature, setting the temperature range was from 125 to 225 oC, and the results were shown in Figure 6. The increase of temperature has an obvious promoting effect in the reaction. The R of 1,4-dioxane increased by only 10 % from 125 oC to 150 oC. When the temperature rose from 150 to 200 oC, the R rapidly increased from 20 to 95.8 %, and the degradation reached 100 % if the temperature continued to rise. However, from the perspective of energy utilization, it is not recommended to use excessive temperature for reaction, so 200 oC is chosen as the appropriate reaction temperature. From the temperature range of the catalytic wet air oxidation technology (150 - 375 oC), the degradation of 1,4-dioxane by CuO is a medium-temperature reaction and has an application prospect.

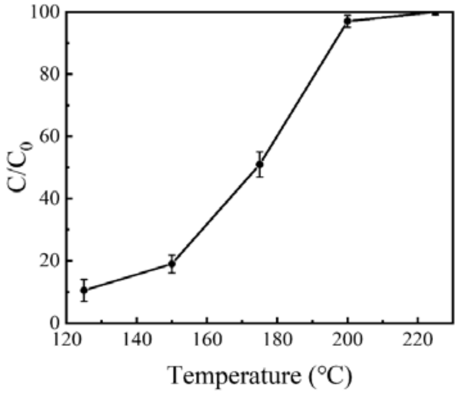

Figure 6. Effects of the reaction temperature on the degradation of 1,4-dioxane; (1,4-dioxane: 100 mg/L; time: 1 h; O_2: 1 MPa; CuO: 4 mmol)

Oxygen, as an oxidant, is also a crucial factor affecting the oxidation capacity of the reaction system and the removal rate of 1,4-dioxane. As shown in Figure 7, although the degradation of 1,4-dioxane can occur without the addition of O2, it could be greatly improved when a certain amount of O2 was added. When the oxygen pressure was 1 MPa, the removal rate got the best result, and there was no significant improvement effect when the oxygen pressure continued to increase. This indicates that 1 MPa of oxygen will provide sufficient oxidation dose for the reaction system.

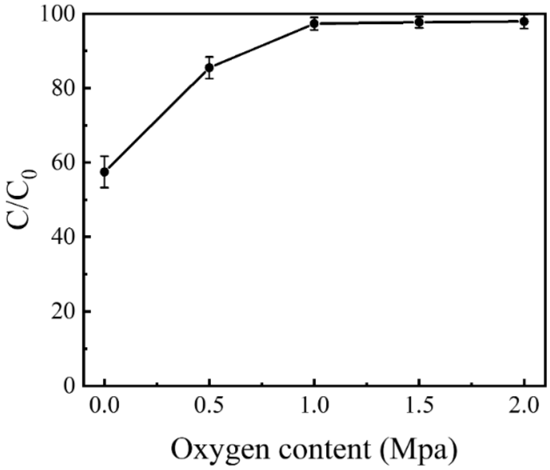

Figure 7. Effects of oxygen content on the degradation of 1,4-dioxane; (1,4-dioxane: 100 mg/L; temperature: 200 °C; time: 60 min; CuO: 5 mmol)

The influence of the CuO amount toward the degradation of 1,4-dioxane can be seen in Figure 8. The addition of CuO promoted the reaction within a certain range. When the added amount was at the range of 4-6 mmol, the enhancement of R was not significant. However, when the added amount was more than 6 mmol, the continued addition of CuO resulted in a decrease of R. The reason may be that the active sites increased and hence the reaction rates enhanced with the increasing CuO addition. However, exceeding CuO leaded to accumulation of catalysts, incurring the decrease of catalyst dispersion which resulting in the decrease of exposure of active sites, ultimately affecting the reaction efficiency.

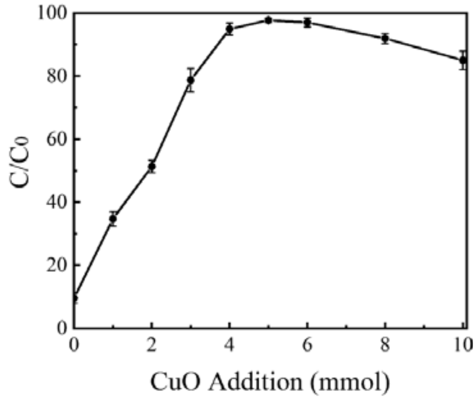

Figure 8. Effects of different CuO addition on the degradation of 1,4-dioxane; (1,4-dioxane: 100 mg/L; temperature: 200 °C; time: 60 min; O_2: 1 MPa)

With the increase of reaction time, the R of 1,4-dioxane was also continuously improved, as shown in Figure 9. The reaction rate rose slowly in the first 20 min, then increased rapidly, and reached a high R of 95.8 % at 60 min. The removal efficiency of 1,4-dioxane was still increased for a long time, but the improvement effect was not obvious. Considering the removal effect and energy utilization, the optimal reaction time was selected to be 60 min.

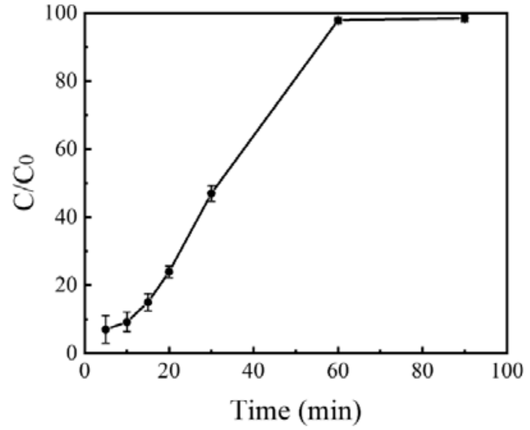

Figure 9. Effects of reaction time on the degradation of 1,4-dioxane; (1,4-dioxane: 100 mg/L; temperature: 200 °C; O_2: 1 MPa; CuO: 5 mmol)

In heterogeneous catalytic wet air oxidation, the role of the pH involves multiple aspects, including the decomposition of the oxygen molecules, the surface properties of the catalyst and the charge of ionizable organic molecules, which in turn affects the production of reactive oxygen species (ROS) and the degradation rate of water contaminants [23, 24]. The effect of the initial pH on 1,4-dioxane degradation and mineralization under catalytic oxidation was investigated using 2 mmol of CuO. The results in Figure 10 show that the rate of 1,4-dioxane removal decreased rapidly as the pH increased and the rate of degradation was the highest at pH 3, up to 99.8 %. The removal rate of 1,4-dioxane reached to 98.5% at pH 5, but only 51 % at pH 7. Under alkaline conditions, the rate of 1,4-dioxane removal is less than 30 %. This indicates that acidic conditions are suitable for the reaction system, and the more H+ in the solution, the easier it is for the ring-opening degradation of 1,4-dioxane.

Then, the dissolution of Cu2+ in solution after different pH reactions was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). The results are shown in Table 1, at pH=7 and 9, only trace amount of Cu2+ was dissolved into the solution. However, under acidic conditions, there was a large amount of Cu2+ in the solution, especially under a strong acid condition at pH=3, the dissolution of Cu2+ was as high as 7.231 mg/L. It also reached 3.084 mg/L at pH=5, which was hundreds of times of the amount of Cu2+ dissolved under neutral conditions. Although the dissolution of Cu2+ decreased slightly under the weakly alkaline condition of pH=9, with the increase of alkalinity, the dissolution of Cu2+ in solution also increased continuously. Although strong acid conditions were conducive to the reaction, it might cause secondary pollution of water bodies.

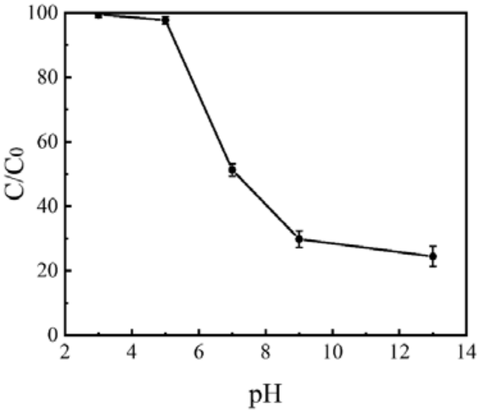

Figure 10. Effects of pH on the degradation of 1,4-dioxane; (1,4-dioxane: 100 mg/L; temperature: 200 °C; time: 60 min; O_2: 1 MPa; CuO: 2 mmol)

Table 1. The amount of Cu^{2+} dissolved in different pH

sample	dissolution of Cu^{2+}（mg/L）
pH=3	7.2310
pH=5	3.0840
pH=7	0.0183
pH=9	0.0158
pH=11	0.6497

The recyclability and stability of the catalyst are critical factors for the large-scale application of heterogeneous catalytic oxygen systems for water and wastewater treatment. In this study, the recyclability and stability of the CuO used in the treatment of 1,4-dioxane by catalyst oxygen were assessed during three consecutive reuse cycles. The catalytic activity of CuO during each cycle decreased slightly (Figure 11) but remained at acceptable values. The 1,4-dioxane removal efficiencies decreased from 95.8 to 76 %. The apparent loss of activity could result from the poisoning of the active sites, fouling of the catalyst surface by the reaction products, the loss of catalyst mass during each reusing cycle and copper leaching [25, 26].

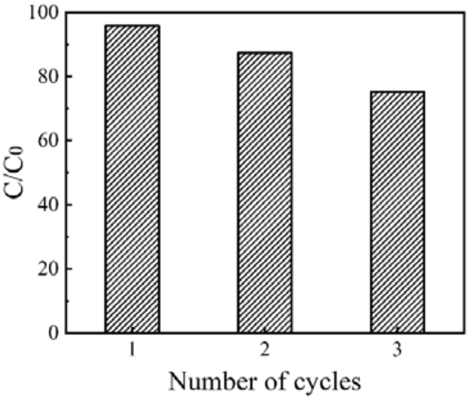

Figure 11. Effect of catalyst cycle times on removal rate of 1,4-dioxane; (1,4-dioxane: 100 mg/L; temperature: 200 °C; time: 60 min; O_2: 1 Mpa; CuO: 5 mmol)

4 CONCLUSIONS

In summary, a CWAO process was introduced to degrade

1,4-dioxane catalysed by CuO in this work. The highest removal rate of 1,4-dioxane was 95.8 % when the optimal reaction conditions were 200 oC and 1 MPa O2 for 60 min with 5 mmol CuO added. If the effect of Cu2+ dissolution was not considered, acidic conditions were suitable for pH=3 with 2 mmol CuO added, the removal rate of 1,4-dioxane was up to 99.8 %. Results indicated that CWAO with CuO showed promising performances on degradation 1,4-dioxane and it could be a potential way on disposition of all kinds of non-biodegradable organic wastewater.

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