Quantitative analysis the role of reactive oxygen species (ROS) in a Fe/Cu/O₃ process for p-nitrophenol treatment

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Abstract. In this study, a highly efficient catalytic ozonation with Fe/Cu bimetallic catalyst was developed for p-nitrophenol (PNP) aqueous solution treatment. The result shows that the high COD removal (94.1%) was obtained by the Fe/Cu/O₃ process, owing to the strong synergetic effect between Fe/Cu and ozone. In addition, the COD removal (94.1%) obtained by the Fe/Cu/O₃ process after 30 min treatment is twice more than the sum (45.2%) of COD removal efficiencies obtained by sole ozone and sole Fe/Cu. These results confirm that the synergetic effect between Fe/Cu and ozone played a vital role in the degradation of PNP in aqueous solution. Additionally, the formed corrosion products in exhibited high catalytic ability for ozone decomposition, which could generate more •OH to degrade PNP in aqueous solution. Finally, the role of various reactive oxygen species (ROS) was quantitative analyzed by a series of trapping experiments.

1. Introduction
Zero valent iron (ZVI or Fe⁰) is a cost-effective technology for the degradation of toxic and refractory pollutants [1], [2]. Due to the high standard reduction potential difference between Fe⁰ and Cu⁰ (0.777V), Cu⁰ plating on the Fe⁰ surface could noticeably improve the reactivity of Fe⁰ and its reduction efficiency for the pollutants [3], [4]. The reactivity of Fe/Cu bimetallic particles under the anoxic or aerobic condition has been investigated thoroughly [5], [6]. Likewise, ozone as a stronger oxidizing gas than oxygen, it can directly attack the chromophoric groups or indirectly form smaller molecules, and obtain high color removal in wastewater treatment [7]. However, the sole ozonation does not cause the complete oxidation of organic pollutants since some oxidative reactions with ozone are relatively selective and slow [8].

In recent years, there is an increasing interest in the study of catalytic ozonation which utilizes catalysts to accelerate the decomposition of ozone, and its oxidative capacity is much higher than the sole ozonation [7]. Several Fe-based materials were investigated as the catalysts in catalytic ozonation process, which shown satisfactory performance for organic pollutants degradation [9], [10]. In our previous work, we found that the synergistic effects between Fe⁰ and ozone could improve the degradation efficiency for the PNP treatment [11]. Furthermore, ozonation in the present of Fe/Cu bimetallic particles (i.e., Fe/Cu/O₃) process was also developed to degrade the pollutants in automobile coating wastewater, and the satisfactory results indicated that Fe/Cu/O₃ process is a cost-effective technology for the treatment of toxic and refractory automobile coating wastewater [12]. The reaction mechanism of the Fe/Cu/O₃ process consist of four parts: (a) homogeneous catalytic ozonation of Fe²⁺/Fe³⁺, (b) heterogeneous catalytic ozonation of Fe₂O₃, Fe₂O₅ or FeOOH, (c) Fenton-like reaction, and (d) peroxide reaction [11]. The generation of reactive oxygen species (ROS) such as superoxide anion radical (O₂⁻), hydrogen peroxide (H₂O₂), and hydroxyl radical (•OH) would be involved in these reactions. However, the relative contribution of these ROS toward pollutants removal has not been
investigated yet to the best of our knowledge. Therefore, it is of great importance to quantitative analysis the role of the ROS in Fe/Cu/O₃ system. In summary, p-nitrophenol (PNP) as a probe contaminant due to its high toxicity, carcinogenicity. Thus, the original objectives of this study were to (i) confirm the superiority of Fe/Cu/O₃ process toward PNP removal, (ii) characterize the structure and composition of the corrosion products during PNP removal by Fe/Cu/O₃ system, (iii) quantitative analysis the contribution of the ROS in Fe/Cu/O₃ system.

2. Methods

2.1. Materials
Micron-sized zero valent iron powders, CuSO₄·5H₂O (analytical reagent), Na₂SO₄ (analytical reagent), isopropyl alcohol (IPA) and PNP (99%) procured from Chengdu Kelong chemical reagent factory were used in this experiment. Superoxide dismutase (SOD) and catalase (CAT) were purchased from Shanghai Kayon biological technology Co. The zero valent iron powders have mean particle size of approximately 120 µm, and their iron content reaches approximately 99%. Other chemicals used in the experiment were of analytical grade. Deionized water was used throughout whole experiment process.

2.2. Preparation of mFe/Cu bimetallic particles
The mFe/Cu bimetallic particles were prepared through a simple Fe-Cu displacement reaction via adding micron-sized zero valent iron powders into a CuSO₄ aqueous solution. The main prepared process was the same with that in our previous work [3]. In this study, the main prepared conditions including theoretical Cu mass loading (TMLc), temperature, mixing speed and Cu²⁺ concentration (CuSO₄) of planting solution were 0.41 g Cu/g Fe, 40 °C, 250 rpm and 3 g/L, respectively.

2.3. Batch experiments
In this study, 300 mL certain concentration of PNP aqueous solution was placed into a 500 mL beaker. Meanwhile the desired dosage of prepared Fe/Cu particles was added, and ozone was continuously dispersed into the reacting solution through a gas diffuser. Ozone was generated onsite from pure compressed dry oxygen (99.9%, v/v) by a laboratory model ozone generator (the maximum generation capacity is 3 g/h, Chengdu Yifeng, China), and the inlet concentration of ozone ([O₃]i) was 5.42 mg/L. In addition, to ensure the complete fluidization of Fe/Cu particles in reaction solution, the slurry was stirred by a mechanical stirrer (300 rpm). The whole experiment process was performed at a running temperature of 25±1 °C by heating in thermostatic bath for 30 min.

In order to affirm the superiority of Fe/Cu/O₃ process, three control experiments including (a) O₃, (b) Fe/Cu, and (c) Fe/Cu/air were set up. Meanwhile, the operating conditions of these control experiments were in accordance with the optimal conditions of the Fe/Cu/O₃ process. During the reaction process, the samples were withdrawn at pre-determined time intervals, and diluted by deionized water and filtered through a PTFE syringe filter disc (0.45 µm). And then, the COD concentrations of PNP in the samples were measured by COD rapid analyzer.

2.4. Analytical methods
COD of the effluents were measured by COD rapid analyzer (Lianhua, China). Ozone concentrations were measured by the iodometric and indigo method. The compound composition of particles before and after Fe/Cu/O₃ system treatment were analyzed by XRD (Xpert Pro, Phillips, Netherlands). The concentrations of dissolved Fe²⁺, Fe³⁺ and total iron were measured by using the 1,10-phenanthroline colorimetric method at 510 nm with a UV–vis spectrophotometer (UV-2550, Shimadzu, Japan).

3. Results and discussion

3.1. Superiority of the Fe/Cu/O₃ process
In order to evaluate the superiority of the Fe/Cu/O₃ process and synergetic effect between Fe/Cu and ozone, three control experiments including (a) O₃, (b) Fe/Cu, (c) Fe/Cu/air were setup to treat the PNP
aqueous solution under the same conditions (i.e., initial PNP concentration of 500 mg/L, initial pH of 5.4, gas flow rate of 200 mL/min, Fe/Cu dosage of 20 g/L, and treatment time of 30 min). In particular, the two control experiments of O3 and Fe/Cu were used to confirm the synergetic effect between ozone and Fe/Cu in Fe/Cu/O3 process. In addition, dissolved oxygen (DO) could cause Fenton-like reaction in Fe/Cu bimetallic system, which could enhance the yield of •OH and improve its treatment efficiency [5]. Therefore, it is necessary to compare the treatment efficiencies of Fe/Cu/air and Fe/Cu/O3 process.

Figure 1 shows the COD removal obtained by the Fe/Cu/O3 process was higher than those of three control experiments. In addition, the COD removal (94.1%) obtained by the Fe/Cu/O3 process after 30 min treatment is twice more than the sum (45.2%) of COD removal efficiencies obtained by sole ozone and sole Fe/Cu. These results confirm that the synergetic effect between Fe/Cu and ozone played a vital role in the degradation of PNP in aqueous solution. Furthermore, the COD removal obtained by the Fe/Cu/O3 process (94.1%) was 9 times higher than that of the Fe/Cu/air process (9.7%). The present of DO could facilitate the direct reduction on the catalytic activity site of the iron surface and formed the Fenton-like reaction in Fe/Cu/air system [5], [6]. However, the corrosion products generated in Fe/Cu/O3 process could be used as catalyst for the decomposition of ozone, which could generate more •OH to degrade PNP in aqueous solution [9], [13]. Besides, the generated organic acids in the decomposition of catalytic ozonation could promote the corrosion rate of Fe/Cu, which could enhance the catalytic rate of ozone decomposition in return [7]. Therefore, there is strong synergetic effect between Fe/Cu and ozone, and the Fe/Cu/O3 process is much superior to the existing Fe/Cu/air process.

3.2. Characterization of mFe/Cu particles

In order to confirm the corrosion products, the Fe/Cu bimetallic particles were further analyzed by XRD. The XRD pattern in Figure 2(a) indicates that the chemical composition of the fresh Fe/Cu bimetallic particles were mainly iron and copper. The same chemical composition was obtained in our previous work even if their preparation conditions were different [3]. Figure 2(b) indicated Fe0 was transformed to lepidocrocite (γ-FeOOH) and goethite (α-FeOOH) after 30 min of Fe/Cu/O3 treatment. It can be observed that γ-FeOOH was the predominant corrosion product in Fe/Cu/O3 system, which could generate by the continuous supply of oxygen (equation (1)) [14]:

$$4Fe^0 + 3O_2 + 2H_2O \rightarrow 4\gamma-FeOOH$$  \hspace{1cm} (1)

Additionally, the transformation of γ-FeOOH into α-FeOOH is important in the process of iron corrosion, because the initial corrosion product of γ-FeOOH is gradually transformed to the more stable α-FeOOH [15]. Thus, a slight quantity of α-FeOOH could be formed in Fe/Cu/O3 system. The formed α-FeOOH and γ-FeOOH exhibit high catalytic ability for ozone decomposition [16], [17], which could generate more •OH to degrade PNP in aqueous solution.
In order to evaluate the corrosion products released into the solution, dissolved iron ions and total iron ions (i.e., Fe^{2+} and Fe^{3+}) concentrations were detected during 30 min of Fe/Cu/O_{3} treatment. As shown in Figure 3, it can be observed that the total iron ions concentration continuously increased and eventually achieved to about 1277 mg/L after 30 min of Fe/Cu/O_{3} treatment, which was much higher than the concentration of dissolved iron ions. Furthermore, the generated Fe^{2+}/Fe^{3+} also could catalyze the decomposition of ozone and generate the •OH, which result in the formation of homogeneous catalytic ozonation in solution.

![Figure 2. XRD patterns of (a) fresh Fe/Cu bimetallic particles, (b) Fe/Cu bimetallic particles after mFe/Cu/O_{3} treatment (G: goethite (α-FeOOH), L: lepidocrocite (γ-FeOOH)).](image)

![Figure 3. The total iron ions and dissolved iron ions concentration during 30 min of Fe/Cu/O_{3} treatment.](image)

### 3.3. The role of ROS on PNP degradation

In order to clarify the roles of ROS on PNP degradation in Fe/Cu/O_{3} system, we therefore carried out a series of trapping experiments to compare the contribution of ROS in Fe/Cu/O_{3} system by adding excess isopropyl alcohol (IPA) (•OH scavenger), catalase (CAT, H_{2}O_{2} scavenger), and superoxide dismutase (SOD, O_{2}•^{−} scavenger) as scavengers. Herein, CAT and SOD were selected as scavengers for H_{2}O_{2} and O_{2}•^{−} rather than p-benzoquinone and p-nitro-blue tetrazolium chloride due to their better stability and selectivity [18]. As shown in Figure 4(a), The PNP degradation was largely depressed by the addition of IPA, revealing the leading role of •OH on the degradation of PNP. Interestingly, the degradation rates of PNP also decreased after adding CAT and SOD, indicating that H_{2}O_{2} and O_{2}•^{−} were also involved in Fe/Cu/O_{3} system. It can be observed from Figure 4(b) that \( k_{\text{obs}} \) for PNP degradation was 0.0917 min^{-1} in the absence of scavengers, while the addition of IPA, CAT, and SOD decreased \( k_{\text{obs}} \) to 0.0078, 0.0463, and 0.0682 min^{-1}, respectively. To preferably manifest the contribution of different ROS for PNP degradation, we thus estimated the inhibitory efficiency (\( \eta \)) of different scavengers through equation (2).

\[
\eta = \left( \frac{k_{0} - k_{s}}{k_{0}} \right) \times 100\%
\]

(2)
Figure 4. (a) Degradation of PNP with the addition of different scavengers and (b) $k_{obs}$ for PNP treatment with the addition of different scavengers in ECP system (IPA = 30 mM, CAT ≥ 500 U/mL, SOD ≥ 500 U/mL).

Where $k_0$ and $k_s$ were the degradation rate constant in the absence or presence of scavengers, respectively. The inhibitory efficiencies of IPA, CAT, and SOD were found to be 91.5%, 49.5%, and 25.6%, respectively, as shown in Figure 4(b). Besides, the residual degradation rate in the presence of IPA was calculated about 8.5%, which mainly was attribute to direct molecular ozone reaction. Consequently, the contribution of various ROS could be analyzed by the inhibitory efficiencies of different scavengers. It can be calculated that the role of •OH, H$_2$O$_2$, O$_2$•$^-$ and sole ozone were 91.5%, 49.5%, 25.6%, and 8.5%.

3.4. Reuse of Fe/Cu in the reaction system

To evaluate the reusability of the Fe/Cu in Fe/Cu/O$_3$ process, the reuse of Fe/Cu particles were investigated by running five successive catalytic ozonation experiments under the same optimal conditions (i.e., $[\text{Fe/Cu}]_0 = 20 \text{ g/L}$, TML$_{\text{Cu}} = 0.41 \text{ g Cu/g Fe}$, $[\text{Na}_2\text{SO}_4] = 50 \text{ mM}$, initial pH = 5.4, gas flow rate = 200 mL/min, stirring speed = 300 rpm, reaction time = 30 min). At the end of each cycle, Fe/Cu particles were separated from the reaction solution and collected, and then were gently rinsed three times with deionized water and dried at 25 °C in the vacuum drying oven. As shown in Figure 5, the COD removal efficiencies were all above 87% in each cycle, and no evident decline was observed after five successive Fe/Cu/O$_3$ experiments, which indicate the approving recyclability of the Fe/Cu particles.

Figure 5. The COD removal for five successive Fe/Cu/O$_3$ experiments.

4. Conclusion

The high efficient catalytic ozonation of Fe/Cu/O$_3$ process was developed to degrade PNP in aqueous solution. The result shows that the COD removal obtained by the Fe/Cu/O$_3$ process was much higher than those of sole ozone, sole Fe/Cu and Fe/Cu/air processes, owing to the strong synergetic effect between Fe/Cu and ozone. Additionally, Fe$^0$ was transformed to $\gamma$-FeOOH and $\alpha$-FeOOH after 30 min of Fe/Cu/O$_3$ treatment, and corrosion products (i.e., Fe$^{2+}$ and Fe$^{3+}$) could release into the solution.
These corrosion products exhibited high catalytic ability for ozone decomposition, which could generate more •OH to degrade PNP in aqueous solution. Finally, the contribution of •OH, H₂O₂, O₂⁻ and sole ozone were analyzed to about 91.5%, 49.5%, 25.6%, and 8.5% in Fe/Cu/O₃ system for PNP treatment.

5. References

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