GENERAL INFORMATION

**Data Article**

**Title**:[*Enhanced mineralization of dimethyl phthalate by heterogeneous ozonation over nanostructured Cu-Fe-O surfaces: Synergistic effect and radical chain reactions*]

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**Abstract**

Cu-Fe-O nanoparticles (CFO NPs), synthesized with zero-valent iron (ZVI) and Cu(NO3)2 as the metal precursors, were used to enhance ozonation to degrade dimethyl phthalate (DMP). Great DMP degradation and mineralization rates were achieved in a wide range of the initial pH values (3–9); the amount of ·OH in catalytic ozonation was much higher than that of O3 alone at the initial pH of 5.70. The dissolved O3 concentrations were directly determined on a UV-vis (TU-1810) spectrophotometer at 610 nm using the indigo method [[1](#_ENREF_1)]. The concentration of DMP was determined using a high-performance liquid chromatography (HPLC, Agilent 1260, USA) equipped with an ultraviolet detector at 274 nm. Samples of 10 μL were injected into the chromatograph, and a 50/50 (v/v) methanol/water mixture passed at a flow rate of 1.2 mL/min as the mobile phase. The separation was performed using an Agilent Zorbax Eclipse XDB C18 (150 mm × 4.6 mm, 5 μm) column at 40°C. The low-molecular-weight organic acids were quantified using an Ion Chromatograph (IC, Dionex ICS-900) equipped with an IonPAC®AS11-HC (0.4 × 250 mm). The mobile phase was 25 mM KOH at a flow rate of 1.0 mL/min. Dissolved Fe and Cu ions were determined using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, Agilent 720ES) with a detection limit of 0.03 mg/L. The pH was measured using a pH meter (pH-2s, Hach), and the pH of the medium was maintained via the addition of appropriate amounts of HCl (0.1 M) or NaOH (0.1 M). Zeta potential was measured by an acid-base titration method using Zetasizer (Nauo Z) [[2](#_ENREF_2)].

**Specifications Table** [*Please fill in right-hand column of the table below.*]

|  |  |
| --- | --- |
| Subject area | *E.g., chemistry, environment* |
| More specific subject area | *Heterogeneous ozonation* |
| Type of data | *Table, image (SEM, XRD), figure* |
| How data was acquired | *SEM, XRD, UV spectrometry, HPLC, IC etc.; if an instrument was used, please give the model and make.* |
| Data format | *Raw, filtered, analyzed, etc.* |
| Experimental factors | *Water samples were withdrawn at specific time intervals and filtered with cellulose acetate filters (0.22 μm); The residual oxidation reaction was immediately quenched with a diluted NaS2O3 solution.* |
| Experimental features | *Very brief experimental description* |
| Data source location | *Shanghai, China* |
| Data accessibility | *State if data is with this article or in public repository; if public repository, please explicitly name repository and data identification number, and provide a direct URL to data.* |
| Related research article | *The most relevant research article.* |

**Value of the Data**

1 Knowing the specific structure of Cu-Fe-O catalysts by SEM, XRD

2. Comparing the catalytic effect of different catalsts by DMP removal

3. Detecting oxygen species such ·OH by ESR and p-HBA generation and make clear the reaction mechanism

4. Detecting intermediates of DMP

**Data**



**(b)**

**(d)**

Figure 1. SEM images (a), XRD patterns of CFO NPs (b) and CuxO-Fe3O4 (c), and XPS spectra of Cu(2p) (d).



Figure 2. Comparison of the efficiencies of DMP and TOC transformation by O3, O3/CuO, O3/Fe2O3, O3/CFO NPsand O3/CuO + Fe2O3 processes, DMP removal efficiency (a) and TOC removal efficiency (b). Conditions: [DMP]0 = 50 mg/L, t = 2 h, [O3]0 = 1.8 mg/min, pH = 5.7.



**(b)**

**(a)**

Figure 3. Effect of different initial solution pH values on DMP removal rate (a) and E (the ratio of the TOC removal rate in catalytic ozonation to that in single ozonation) (b) by catalytic ozonation. Reaction conditions: [DMP]0 = 50 mg/L, t = 2 h, [O3]0 = 1.8 mg/min, catalyst dosage = 0.10 g/L.



Fig. 4 Stability of CFONPs in the mineralization of DMP by ozonation (a) and XRD pattern of CFO and recycled CFO (b). Reaction conditions: [DMP]0 = 50 mg/L, t = 2 h, [O3]0 = 1.8 mg/min, pH0 = 5.7, catalyst dosage = 0.10 g/L.



**(b)**

**(a)**

Figure 5. Influence of the NaHCO3 (a) and TBA (b) concentration on the degradation of DMP in the ozonation alone and O3/CFO NPsystem. Conditions: [DMP]0 = 50 mg/L, t = 2 h, [O3]0 = 1.8 mg/min, pH = 5.7, catalyst dosage = 0.1 g/L.



Figure 6. DMPO spin-trapping EPR spectrum recorded in aqueous dispersions with O3, O3/CuO, O3/Fe2O3, O3/CFO NPs, O3/CuO + Fe2O3 and blank water for DMPO-·OH.





Figure 7. XPS spectra of Cu(2p) (a), Fe(2p) (b). Conditions: [DMP]0 = 50 mg/L, t = 2 h, [O3]0 = 1.8 mg/min, pH = 5.7, and catalyst dosage = 0.1 g/L.



Figure 8. DMPO spin-trapping EPR spectra recorded in methanol dispersion with blank (a), O3 (b), O3/CFO NPs (c) and in a DMP solution dispersion with O3/CFO NPs (d), DMPO-·OH, ♦; DMPO-·O2-, ♣; DMPO-·CH3, \*.



Figure 9. Generation of p-HBA, which is indicative of trapped ·OH. Conditions: [BA]0 = 2 g/L, t = 2 h, [O3]0 = 1.8 mg/min, pH = 5.7, catalyst dosage = 0.1 g/L.





Figure 10. UV absorption changes for solutions with ozonation alone (a), O3/CFO (b); variation of the low-weight organic acids in catalytic ozonation (c).

**Tab. 1.** The TOC removal rate and leaching metal ion in the heterogeneous ozonation process.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Catalyst  (mg/L) | TOC removal rate (%) | Leaching Fe (mg/L) | Leaching Cu (mg/L) | Time range  (min) |
| CFO NPs | 50.1 | <0.03 mg/L | 0.49 mg/L | 120 |
| CuO | 39.6 | / | / | 120 |
| Fe2O3 | 40.0 | / | / | 120 |
| CuO+Fe2O3  (1:1 mole ratio) | 40.3 | / | / | 120 |
| CuxO-Fe3O4 | 48 | 1.25 mg/L | 2.30 mg/L | 120 |

**Tab. 2.** Reaction mechanisms proposed for O3/CFO NPscatalytic ozonation

|  |  |
| --- | --- |
| Reaction | No. |
| ≡Cu(I)2O–OH- + O3 → ≡Cu(I)2O-OH-O3 | 1 |
| O2 + 4e → 2O2- | 2 |
| O2- + ≡Cu(I)2O-OH-O3 → 2≡Cu(II)O + HO2·- + O2·- | 3 |
| O3 + HO2·- → ·OH + O2·- + O2 | 4 |
| ≡Cu(II) + O2·- → ≡Cu(I) + O2 | 5 |
| ≡Fe(III) + O2·- → ≡Fe(II) + O2(K = 1.5\*108) | 6 |
| ≡Cu(I) + ≡Fe(III) → ≡Cu(II) + ≡Fe(II) | 7 |
| ≡Fe(II)O–OH- + O3 → ≡Fe(II)O-OH-O3 | 8 |
| O2- + 2≡Fe(II)O-OH-O3→≡Fe(III)2O3 + HO2·- + O2·- | 9 |
| ·OH + CH3-R→·CH3 + R-OH | 10 |

**Experimental Design, Materials, and Methods**

The single ozonation (O3 alone without catalysts) and catalytic ozonation experiments were conducted in semi-batch mode in the same column reactors (internal diameter of 10 cm and working height of 50 cm) made of borosilicate glass equipped with agitation at room temperature (298±1 K) as a set of parallel controlled tests. O3 was generated from pure oxygen using a laboratory O3 generator (CF-3-10 g, Guolin, Qingdao, China). After the generator reached steady state, O3 gas was bubbled into the DMP solution in the reactor with a silica dispenser under ambient conditions. A certain amount of catalyst was added into the reactor and followed by the input of a steady O3 flow at 1.8 mg/min detected by iodometry method [[3](#_ENREF_3)]. The excess O3 in the outlet gas was trapped in a series of gas-washing bottles filled with iodide potassium solution. The experimental setup is listed in Fig. S1. Water samples were withdrawn at specific time intervals and filtered with cellulose acetate filters (0.22 μm). The residual oxidation reaction was immediately quenched with a diluted Na2SO3 solution. For evaluation of the stability of the catalyst, the CFO NPs were magnetically separated, washed three times with 500 mL of ultrapure water and then dried at 105°C. Experiments under the same conditions were repeated three times, and the data reported were the averages of triplicate experiments.

**Materials and reagents**

DMP, 5,5-dimethyl-1-pyrroline N-oxide (DMPO), tert-butyl alcohol (TBA), and benzoic acid (BA) were supplied by Aladdin Chemistry Co., China. Other reagents such as NaHCO3, Cu(NO3)2·3H2O were at least of analytical grade and used without further purification. Ultrapure water (18 MΩ·cm-1, Millipore) was used throughout the experiments.

**Acknowledgments**

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