

Degradation of 2-MIB in aqueous solution by ZnOOH catalyzed ozonation

Jimin Shen, Lin Dong and Zhonglin Chen

ABSTRACT

In this study, ZnOOH was used as a catalyst and its efficiency in removing trace organic matter, 2-methylisoborneol (2-MIB), in conjunction with ozone was investigated. The catalyst was characterized by X-ray diffraction (XRD), the Brunauer-Emmet-Teller (BET) method and Fourier transform infrared spectrometry (FT-IR). The performance of the ozone oxidation process alone and the O₃/ZnOOH system were both studied. Factors such as ozone dose, catalyst dosage, radical inhibitor and water qualities were analyzed to investigate their effects on catalysis activity and 2-MIB removal efficiency. Results showed that the removal of 2-MIB was better in O₃/ZnOOH system. The removal efficiency increased with the increase of catalyst dosage. However, the increase became inconspicuous when the dose was higher than 400 mg. Tert-butanol inhibits the removal of 2-MIB, and this effect was even more obvious in O₃/ZnOOH system. This indicates that O₃/ZnOOH system promotes the hydroxyl radical production, and removal reaction process in this system follows the mechanism of hydroxyl radical reaction. The water qualities also affected the removal of 2-MIB. Tap water was better than distilled water in the degradation of 2-MIB, while the effect of Songhua River was the weakest.

Key words | 2-MIB, catalyzed oxidation, hydroxyl radical, ozone, ZnOOH

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INTRODUCTION

Odor-producing trace organic compounds produced by actinomyces and cyanobacterial blooms have been detected in many waterbodies in China. The odor detection threshold in humans for 2-methylisoborneol (2-MIB) is low, and the compound is ubiquitous and occurs at a wide range of concentrations (Peter *et al.* 2009; Lin *et al.* 2002; Srinivasan & Sorial 2011). In this study, 2-MIB was used as the representative of odor-producing trace organic compounds to explore removal and control technologies.

The molecular structure of 2-MIB is stable, and routine technology is inefficient in its removal. Conventional O₃ oxidation does not achieve good removal of 2-MIB from aqueous solution. Degradation of 2-MIB mainly depends on the hydroxyl radical produced by ozone (Qi *et al.* 2008);

therefore, its removal can be enhanced by increasing hydroxyl radical production.

Metal oxides, supported metals or carbon catalysts are promising technologies in 2-MIB removal (Beltrán 2004). Previous studies mainly focused on TiO₂, MnO₂, ZnO and Al₂O₃ (Beltrán *et al.* 2002, 2005; Rivas *et al.* 2008; Pocostales *et al.* 2011). However, little research on catalytic ozonation by ZnOOH has been reported (Xu *et al.* 2009). This study aimed to use an O₃/ZnOOH system to examine the removal of 2-MIB.

The objectives of this study are: (1) to evaluate the efficiency and the stability of ordinary ZnOOH powder in catalytic ozonation; (2) to investigate the factors influencing 2-MIB removal in the O₃/ZnOOH system; and (3) to explore the elementary mechanism of catalysis.

MATERIALS AND METHODS

Materials and ozonation equipment

A stock solution of 2-MIB at a concentration of 25 mg/L was prepared by dissolving 2-MIB in distilled water. The ozonation apparatus in the laboratory consisted of an ozone generator and ozonation reactor (1 L flat-bottomed flask). The gaseous ozone entered the reactor and changed into small bubbles as it passed through the distributing plate at the bottom of the column. Residual ozone in the off-gas was absorbed by 2% KI solution.

Analytical methods

The concentration of aqueous ozone was measured by the indigo method (Bader & Hoigné 1981; von Gunten 2003) at 612 nm with a UV-visible spectrophotometer (T6, Beijing Burkinje General Instrument Co. Ltd, China). Analysis of 2-MIB was by gas chromatography (6890N, Agilent Technologies, USA). The catalyst detection methods included X-ray diffraction (XRD), the Brunauer-Emmet-Teller (BET) method, Fourier transforms infrared spectrometry (FT-IR) and atomic force microscopy (Bio-scope™, Veeco, USA).

Preparation and properties of ZnOOH catalyst

Preparation of ZnOOH

The basic sluggish precipitation method was used to prepare ZnOOH. NaOH solution (0.5 mol/L) was added drop-wise to 0.2 mol/L Zn(NO₃)₂ in a glass beaker, and the mixture was stirred evenly. After the precipitation was complete, the pH of the mixture was adjusted within the range 10–12. The crucial step for increasing the yield of catalyst was to keep the reaction system under alkaline conditions.

The mixture was allowed to stand for a while, then the beaker was placed in an insulated container and the catalyst activated for 10–15 h at 25 °C. The precipitate was removed and washed with deionized water until the effluent was neutral and its conductivity was almost constant.

Finally, the precipitate was dried at 50 °C, ground into powder, sieved to collect the small particles (<0.35 mm) and stored for future use.

Point of zero charge and isoelectric point

The point of zero charge (pH_{PZC}) of ZnOOH is obtained by stripping protons fully from the hydrogen bonds (by the addition of excess alkali) and measuring the density of surface hydroxyl groups. The isoelectric point (pH_{IEP}) is determined by the powder addition method.

Experimental procedure

The experimental apparatus is shown in Figure 1. A corona ozone generator (DHX-IIB model, Harbin Jiujiu ECE&T Co.) was used to generate ozone at a maximum rate of 9 g/h. The feed gas O₂ was dried and purified with silica gel prior to entering the generator. The O₂/O₃ mixture was delivered into the reactor through a medium porosity glass frit. The O₃ concentration was changed by varying the voltage and O₂ flow rate. The gas flow rate was monitored by a gas flow meter. The desired O₃ concentration in the O₃-O₂ mixture was introduced into the reactor first. The experiment then began after 2-MIB and other substances (the catalyst or other substances for examining the influences on the removal) were introduced into the reactor. To ensure the uniformity of the 2-MIB solution, a magnetic stirrer was used during the reaction. The reaction was quenched by adding 0.1 mL of 0.1 mol/L Na₂S₂O₃ solution (supplemented with 0.1 g Na₂CO₃ to prevent

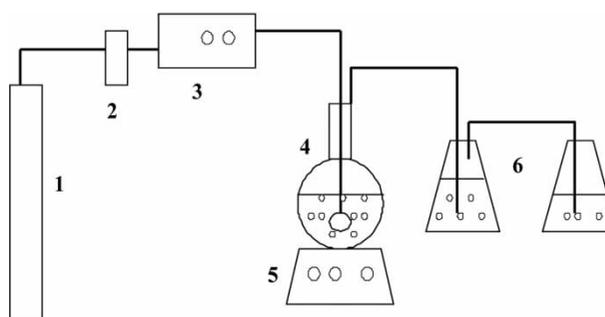


Figure 1 | Schematic diagram of ZnOOH catalyzed system. 1: oxygen cylinder; 2: meter; 3: ozone generator; 4: reactor; 5: magnetic stirring apparatus; 6: aqueous KI.

decomposition), after sampling at various intervals. The treated samples were then analyzed.

RESULTS AND DISCUSSION

Characterization of ZnOOH

Figure 2 shows the XRD pattern of ZnOOH. The ZnOOH catalyst contains a large proportion of ZnO and a small proportion of Zn(OH)₂ crystals.

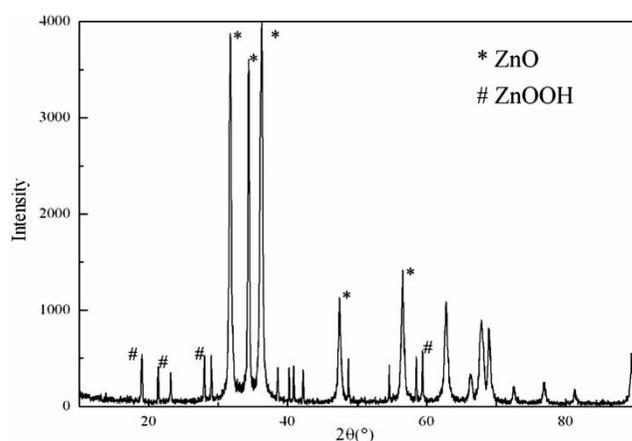


Figure 2 | The XRD pattern ZnOOH.

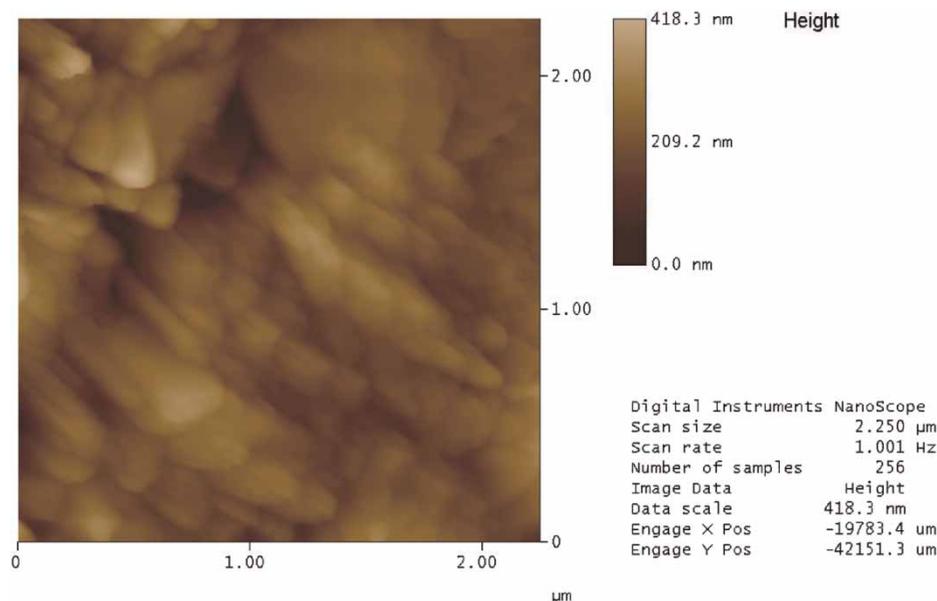


Figure 3 | Nanostructure of ZnOOH by atomic force microscopy.

ZnOOH has a grainy nanostructure, as shown in Figure 3. Diameter of the particles ranges from 50 to 80 nm, and the length of particles is no more than 1 μm. Porosimetry and the BET method were used to determine the ZnOOH catalyst's specific surface, pore volume and pore diameter. The results and other surface characteristics are shown in Table 1.

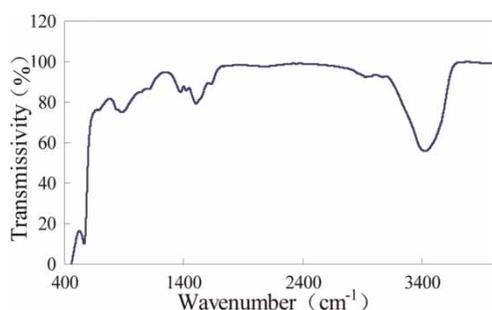
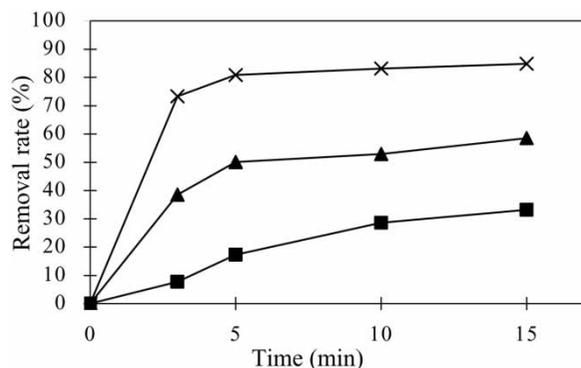
Figure 4 shows the FTIR spectrum of ZnOOH catalyst. The characteristic absorption peak of ZnO is at 450 cm⁻¹, and the strong absorption peak at 3,392 cm⁻¹ is the stretching vibration of the hydrogen bond of surface-combined water. There is a relatively weaker peak at 1,489 cm⁻¹, which is the absorption peak of surface coordination hydroxyl in metallic hydroxylate. This peak demonstrates that there are many hydroxyl groups on the surface of the catalyst. The absorption peak at 850 cm⁻¹ is generated by CO₂ absorbed on the surface of ZnOOH.

Effectiveness analysis of O₃/ZnOOH system in removing 2-MIB

Figure 5 shows the effect of initial concentration of ozone on the 2-MIB degradation rate. It can be seen that the ozone concentration has a positive effect on 2-MIB degradation. The 2-MIB removal rate reached 33 and 80% when the

Table 1 | Pore volume, pore diameter, surface area and other surface characteristics of ZnOOH

Parameters	Value
Pore volume (cm ³ /g)	0.041
Pore diameter (nm)	12
BET surface area (m ² /g)	12.7
pH _{pzc}	7.05
pH _{iep}	8.61
Surface hydroxyl density (mmol/g)	3.16

**Figure 4** | FT-IR spectrum of ZnOOH.**Figure 5** | Effect of ozone concentration on 2-MIB removal. $C_0(2\text{-MIB}) = 25 \mu\text{g/L}$, $\text{pH} = 7$, $T = 18 \pm 2^\circ\text{C}$. The concentration of ozone: \times : 1.8 mg/L; \blacktriangle : 1.3 mg/L; \blacksquare : 0.7 mg/L.

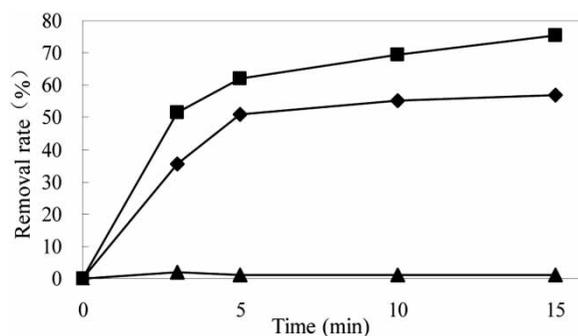
concentration of O_3 was 0.7 and 1.8 mg/L respectively. When the concentration of ozone was 0.7 mg/L, the removal rate of 2-MIB was 17% at 5 min, and then increased to 26% after 10 min. When the concentration of ozone was 1.8 mg/L, the removal rate of 2-MIB increased to 80% after 5 min, and the removal rate in the following 10 min scarcely changed.

von Gunten (2003), Liu *et al.* (2011) and Shen *et al.* (2008) reported that the reaction rate of hydroxyl with target compounds is much greater than that of O_3 . So in the early stages of the reaction, the removal rate increased rapidly due to hydroxyl; this was the quick reaction stage. Later the removal rate increased slowly, possibly because molecular O_3 began to play a significant role in oxidizing 2-MIB. The higher the concentration of O_3 , the quicker the reaction reached the set removal rate. We suggest that plenty of hydroxyl was generated from ozone decomposition and quickly engaged in oxidizing 2-MIB. When the concentration of ozone was low, O_3 would slowly oxidize 2-MIB, and the removal rate of 2-MIB would still increase obviously over time.

As observed in Figure 6, although the sorption of 2-MIB on ZnOOH catalyst was low, the removal rate by catalyzed ozonation was higher than that of ozonation only.

Effect of different dosage of ZnOOH catalyst

Figure 7 shows the effect of different doses of ZnOOH catalyst on the removal rate of 2-MIB. When the dose of ZnOOH catalyst was 500 and 0 mg/L, the removal rate at 15 min was 88 and 58%, respectively; thus ZnOOH catalyst had a positive effect on 2-MIB degradation. As sorption of 2-MIB by ZnOOH catalyst is so small that it can be neglected (Figure 6), it can be deduced that as the ZnOOH dose increased, the intermediates' strong oxidant capacity was upgraded correspondingly, and the chance of generating hydroxyl increased. Increasing ZnOOH dosage from 0 to 200 mg/L leads to a significant improvement in 2-MIB

**Figure 6** | Effect of catalyzed sorption of ZnOOH. $C_0(2\text{-MIB}) = 25 \mu\text{g/L}$, $C_0(\text{O}_3) = 1.3 \text{ mg/L}$, catalyst 200 mg, $T = 18 \pm 2^\circ\text{C}$, $\text{pH} = 7$. \blacklozenge : ozonation only; \blacksquare : catalytic ozonation; \blacktriangle : catalyst only.

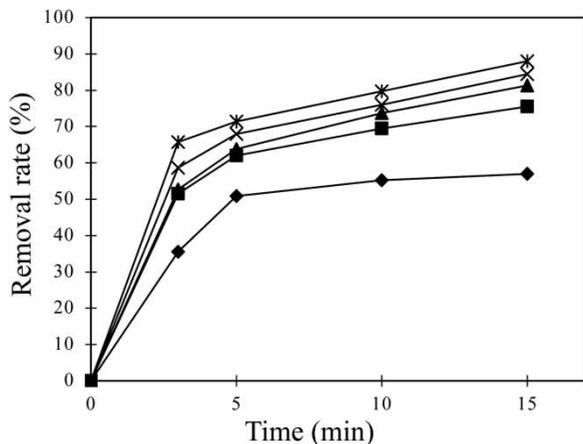


Figure 7 | Effect of different dosage of ZnOOH. $C_0(2\text{-MIB}) = 25 \mu\text{g/L}$, $C_0(\text{O}_3) = 1.4 \text{ mg/L}$, $T = 18 \pm 2 \text{ }^\circ\text{C}$, $\text{pH} = 7$. Dosage of ZnOOH catalyst: ◆: 0 mg, ■: 200 mg, ▲: 300 mg, ×: 400 mg, *: 500 mg.

removal rate, but only a slight enhancement is observed when ZnOOH dosage is further increased (Figure 7).

Effect of tert-butanol on the ozonation of 2-MIB

It is well known that tert-butanol (*t*-BuOH) is a strong radical scavenger due to its high rate constant with hydroxyl radicals ($K_{\text{OH}}^{t\text{-BuOH}} = 5 \times 10^8 \text{ mol/L s}$). Tert-butanol reacts with the hydroxyl radical and generates inert intermediates and, thus, can cause termination of the radical chain reaction. Therefore, Qi *et al.* (2008) argued that *t*-BuOH is a suitable indicator for a radical type reaction. Figure 8 shows that removal rate of 2-MIB decreased by 17.4% after adding 0.5 mg/L *t*-BuOH to the system, indicating

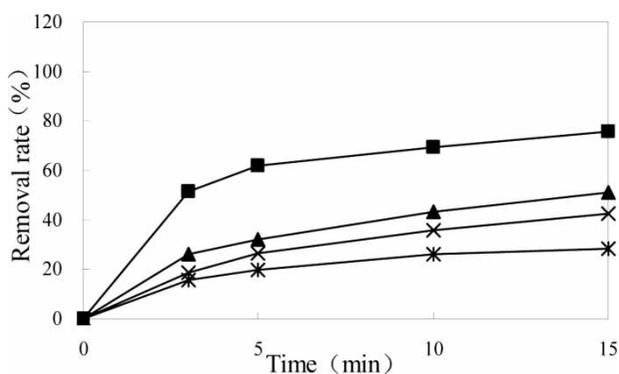
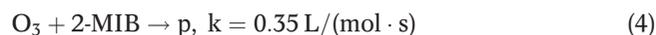
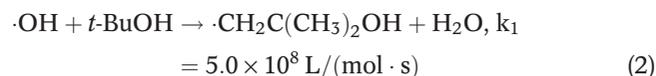


Figure 8 | Effect of tert-butanol concentration on the degradation of 2-MIB. $C_0(2\text{-MIB}) = 25 \mu\text{g/L}$, $C_0(\text{O}_3) = 1.4 \text{ mg/L}$, ZnOOH dosage: 200 mg, $T = 18 \pm 2 \text{ }^\circ\text{C}$. Concentration of tert-butanol: ■: 0 mg/L, ▲: 0.5 mg/L, ×: 5 mg/L, *: 50 mg/L.

that *t*-BuOH at low concentration resulted in a significant reduction of 2-MIB degradation. This is consistent with our suggestion that hydroxyl was generated in the O_3/ZnOOH and the reaction process in the system followed the mechanism of hydroxyl radical reaction.

Figure 8 shows the inhibition effects of *t*-BuOH at different concentrations in the reaction of ozone and 2-MIB; the inhibition ability became stronger when more *t*-BuOH was added. *t*-BuOH and 2-MIB competitively reacted in the same system, as shown in reactions (1)–(4).



Reaction rate constants of *t*-BuOH and 2-MIB with ozone could be ignored as they were very small (Buxton *et al.* 1988; von Gunten 2003; Andreas & von Gunten 2007). Reaction rate of 2-MIB and *t*-BuOH are expressed in Equations (1) and (2).

$$r(2\text{-MIB}) = d(2\text{-MIB})/dt = k_1 \cdot [2\text{-MIB}] \cdot [\cdot\text{OH}] \quad (1)$$

$$r(t\text{-BuOH}) = d(t\text{-BuOH})/dt = k_2 \cdot [t\text{-BuOH}] \cdot [\cdot\text{OH}] \quad (2)$$

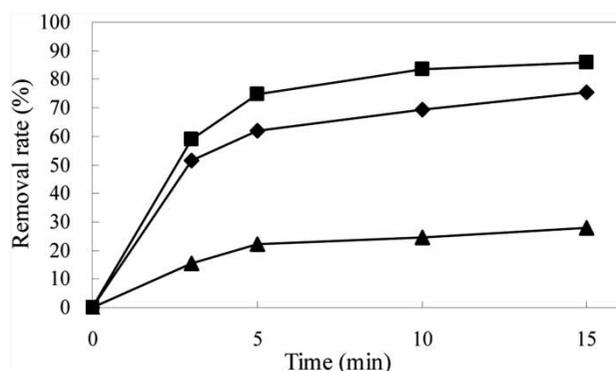
In order to inhibit the degradation of 2-MIB, we should let $r(t\text{-BuOH}) \gg r(2\text{-MIB})$ (suppose 2-MIB is completely inhibited when $r(t\text{-BuOH})/r(2\text{-MIB}) \geq 50$). Comparing Equations (1) and (2), the free radicals could be completely inhibited by *t*-BuOH when $[t\text{-BuOH}] \geq 500[2\text{-MIB}]$. Figure 8 shows that 2-MIB was still degraded when $[t\text{-BuOH}] = 500 [2\text{-MIB}]$.

Effect of different water quality

The water quality parameters of filtered water (from the local water treatment plant) and Songhua River water

Table 2 | Water quality parameters of filtered and Songhua River water

	pH	DOC (mg/L)	UV ₂₅₄ (cm ⁻¹)
Filtered water	6.28	2.941	0.012
Songhua River	7.21	12.975	0.197

**Figure 9** | Effect of different background on removal. $C_0(2\text{-MIB}) = 25 \mu\text{g/L}$, $C_0(\text{O}_3) = 1.4 \text{ mg/L}$, catalyst dosage: 200 mg, $T = 18 \pm 2 \text{ }^\circ\text{C}$, pH = 7. Background ◆: distilled water, ■: filtered water, ▲: Songhua River water.

are presented in Table 2. It is accepted that the reaction of 2-MIB with O_3/ZnOOH followed the hydroxyl radical mechanism. The effect of different water quality on the removal of 2-MIB in O_3/ZnOOH system cannot be ignored. The rate constants for reactions between hydroxyl and dissolved organic matter isolates from different water were found to be three to four orders of magnitude higher than for the reaction with ozone (Critenden *et al.* 1999; Westerhoff *et al.* 2007). Compared to the filtered water, Songhua River water has higher dissolved organic carbon (DOC) and UV₂₅₄ meaning that complex organic matter may inhibit the reaction between 2-MIB and O_3/ZnOOH .

Figure 9 shows the removal rate of 2-MIB in the O_3/ZnOOH system under different water quality backgrounds. When using filtered water, distilled water and Songhua River as background, the removal rate at 15 min is 86, 75 and 28%, respectively.

Based on the above results, the O_3/ZnOOH system is more suitable for advanced stages of water purification. It is likely that it would be difficult to get satisfactory results if O_3/ZnOOH system served as a pretreatment.

CONCLUSIONS

Laboratory-made ZnOOH is a mixture of ZnO and Zn(OH)₂. ZnOOH, which has a grainy nanostructure, has high catalytic activity but lacks the capacity to adsorb organics. As a heterogeneous catalyst for degradation of 2-MIB in water, laboratory-made ZnOOH significantly improved the removal of 2-MIB compared to single ozonation oxidation. Increasing the concentration of catalyst and ozone load had negligible influences on 2-MIB removal. Neutral pH was optimum for the catalytic ozonation of 2-MIB. The presence of tert-butanol had a negative effect on the removal rate of 2-MIB. The results confirmed the proposition that the degradation of 2-MIB by ZnOOH-catalyzed ozonation followed a radical-type mechanism. Water quality has an impact on catalyzed ozonation. The water quality of Songhua River resulted in the low removal rate of 2-MIB in O_3/ZnOOH system, especially as a result of the high DOC. DOC and 2-MIB have competitive reaction with hydroxyl generated in the O_3/ZnOOH system.

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