

Supporting Information for

**Heterogeneous catalytic ozonation of natural organic matter with
goethite, cerium oxide and magnesium oxide**

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This PDF file includes:

4 Texts, 2 Figures and 1 Table are available for further information addressing experimental procedures, and additional data.

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Text S1. Calculation of tert-butanol (TBA) dosage in the bulk solution

TBA was used to capture HO· in the catalytic ozonation and single ozonation. The concentration of TBA should be in excess of the substrate (i.e., at least tenfold). It was calculated by Eq. (1) as showed below.

$$[TBA] = \frac{10 \sum k_i [s_i]}{k_{HO \cdot, TBA}} \quad (1)$$

where [TBA] represents the concentration of TBA; $[s_i]$ represents the concentration of natural organic matter s_i in the filtered water; k_i represents the rate constant of the reaction between HO· and s_i ; $k_{HO \cdot, TBA}$ represents the rate constant of the reaction between HO· and TBA.

$[s_i]$ can be calculated by [DOC], which is $2.68 \text{ mg} \cdot \text{L}^{-1}$ as showed in Table 1. $k_i \approx 2.5 \times 10^4 \text{ (mg} \cdot \text{L}^{-1})^{-1} \cdot \text{s}^{-1}$, $k_{HO \cdot, TBA} = 5 \times 10^8 \text{ M}^{-1} \cdot \text{s}^{-1}$, and then the concentration of TBA can be calculated to be $1.34 \times 10^{-3} \text{ M}$. Thus, 13.5 mM TBA was introduced into the reactor in the batch experiments.

Text S2. The detailed information for batch experimental procedures

1 L of the water sample was added into the reactor followed by TBA solution (13.5 mM). In the catalytic ozonation, after addition of TBA solution, MgO, FeOOH or CeO₂ (0.1 g) was added into the reactor. 36.56 mL of aqueous ozone was introduced into the reactor after the saturated ozone concentration (ca. $32 \text{ mg} \cdot \text{L}^{-1}$) reached. The reactor was then sealed and magnetically stirred. The samples withdrawn at predetermined intervals were filtered through 0.45- μm glass fiber filters (Whatman) to remove the catalyst particles after the residual ozone has been quenched by pure nitrogen.

Text S3. The detailed information for evaluating the stability and recyclability of the catalysts

Pre-experiments were needed to obtain the recycled catalysts. In the pre-experiments, after the dose of $2 \mu\text{M}$ atrazine solution, a large amount of the catalysts (ca. 3g) was introduced into the reactors to avoid the insufficient of the catalysts in the subsequent runs due to the loss of the catalysts during reclamation processes. And then, 36.56 mL of aqueous ozone was introduced into the reactor after the saturated ozone concentration (ca. $32 \text{ mg} \cdot \text{L}^{-1}$) reached. The reactor was then sealed and magnetically stirred. After 20 min, the catalysts were reclaimed by filtration through glass fiber filters and rinsed with methanol and Milli-Q water several times. And then, the catalysts were dried at $70 \text{ }^\circ\text{C}$ for 12 h. The reclaimed catalysts were divided into two parts. 100 mg of the catalysts was taken out to be used in the second run and the residual catalysts were used and reclaimed again according to the above steps. And then, the catalysts for the third, fourth and fifth run were obtained, respectively. The fresh catalysts were used as catalysts in the first run, and the reclaimed particles were used as catalysts in the second, third, fourth and fifth run. In these runs, the samples withdrawn at predetermined intervals were filtered through 0.45- μm glass fiber filters (Whatman) to remove the catalyst particles after the residual ozone has been quenched by pure nitrogen.

Text S4. Calculation of R_{ct} in the catalytic ozonation and single ozonation

The R_{ct} is defined as the ratio of the exposures of HO radicals and ozone. The exposures O_3 -ct and HO-ct are the integrals of concentration (O_3 or HO·) vs. time plots. The calculation is described in Eq. (S1).

$$R_{ct} = \frac{\int [HO\cdot] dt}{\int [O_3] dt} \quad (S1)$$

The integral of O_3 concentration vs time plots corresponds to the area under this curve. The integral of HO· concentration vs time plots can be determined by measuring the decrease of atrazine (ATZ). The rate constants $k_{O_3,ATZ}$ and $k_{HO,ATZ}$ were found to be $6.0 \text{ M}^{-1}\cdot\text{s}^{-1}$ and $3 \times 10^9 \text{ M}^{-1}\cdot\text{s}^{-1}$, respectively. And thus, the degradation of ATZ can be calculated as described in Eq. (S2).

$$\frac{d[ATZ]}{dt} = k_{O_3,ATZ} [ATZ][O_3] + k_{HO,ATZ} [ATZ][HO\cdot] \quad (S2)$$

Eq. (S2) can be rewritten as:

$$\ln \frac{[ATZ]}{[ATZ]_0} = - \left(\int k_{O_3,ATZ} [O_3] dt + \int k_{HO,ATZ} [HO\cdot] dt \right) \quad (S3)$$

After further simplify, Eq. (S4) can be obtained by substituting Eq. (S1) into Eq. (S3):

$$\ln \frac{[ATZ]}{[ATZ]_0} = - \left(k_{O_3,ATZ} + k_{HO,ATZ} \cdot R_{ct} \right) \int [O_3] dt \quad (S4)$$

And thus, the R_{ct} value can be calculated as Eq. (S5):

$$R_{ct} = \frac{\left(\ln \frac{[ATZ]}{[ATZ]_0} \right)}{\int [O_3] dt + k_{O_3,ATZ}} \quad (S5)$$

The first item of the denominator is the slope of the curve $\left(\ln \frac{[ATZ]}{[ATZ]_0} \right)$ vs. $\int [O_3] dt$.

Combined with Fig. S1, the R_{ct} values in the catalytic ozonation and single ozonation are summarized in Table S1.

Fig. S1. Apparent first order kinetics for ATZ degradation in the catalytic ozonation and single ozonation

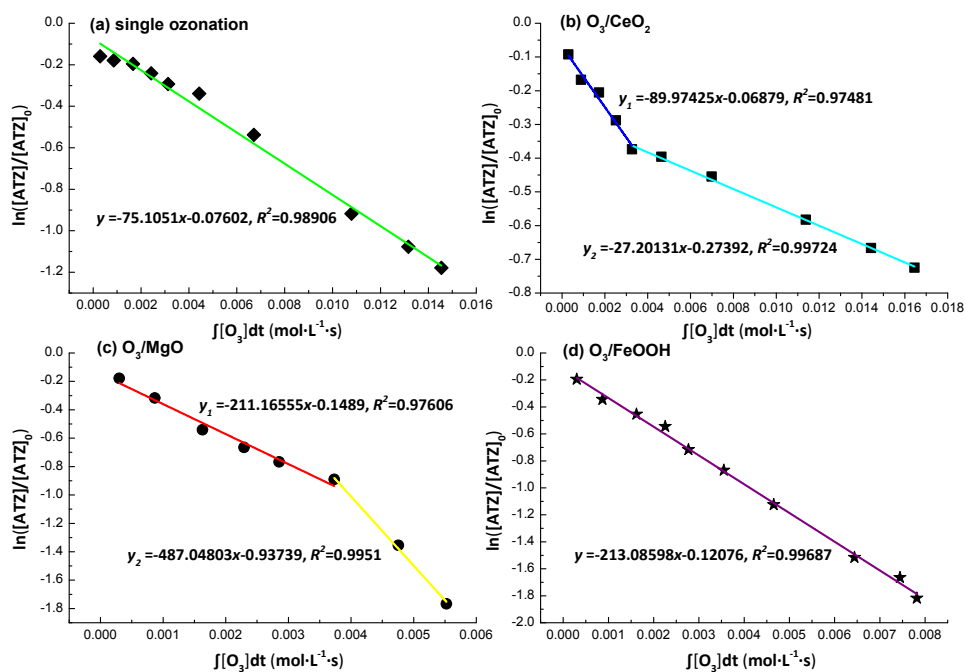


Fig. S1. Apparent first order kinetics for ATZ degradation in (a) single ozonation, (b) CeO₂ catalytic ozonation, (c) MgO catalytic ozonation and (d) FeOOH catalytic ozonation. Catalyst dose= 100 mg·L⁻¹, T= 20 °C, pH= 7.53, [O₃]₀= 1.17 ± 0.03 mg·L⁻¹, [ATZ]₀= 2 μm, reaction time = 20 min.

Figure S2. Comparison of XRD patterns of the catalysts before and after reactions

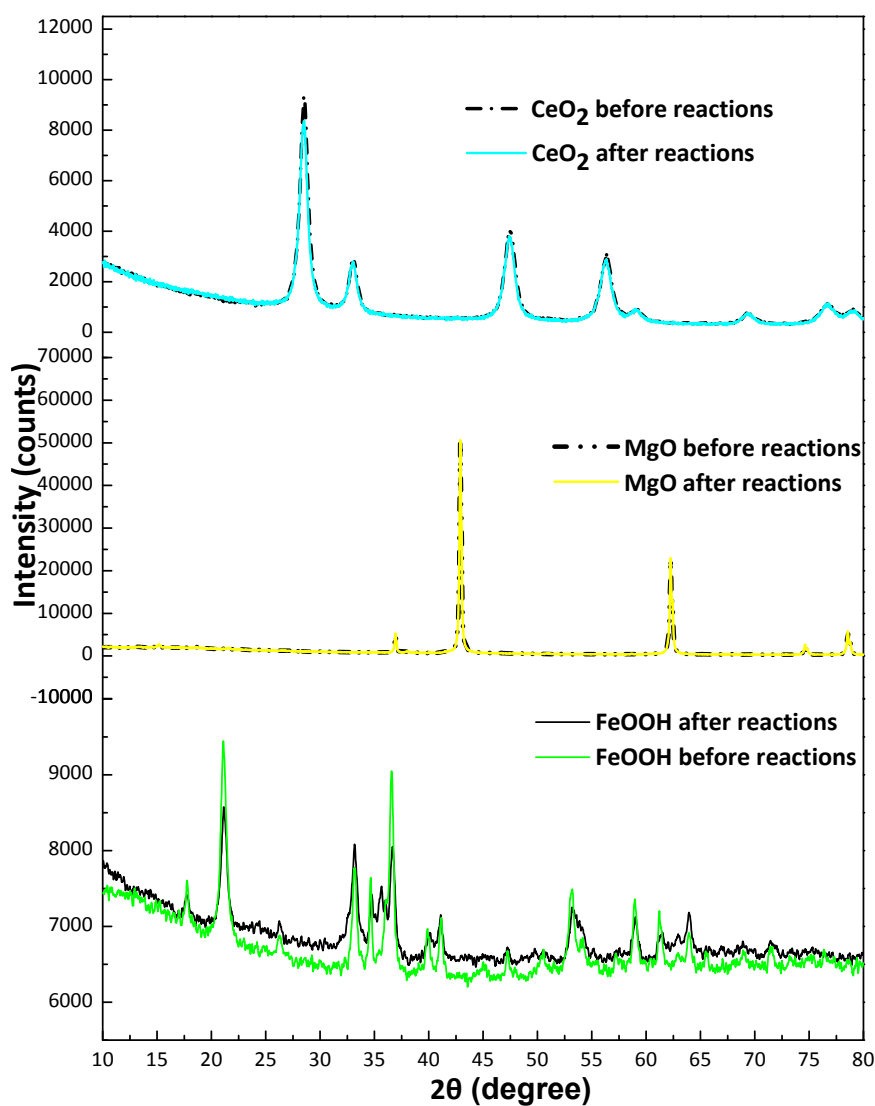


Fig. S2 Comparison of XRD patterns of the catalysts before and after reactions

Table S1. The R_{ct} values in the catalytic ozonation and single ozonation

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Processes	R_{ct} values	
	The first phase	The second phase
Single ozonation	2.3035×10^{-8}	
CeO ₂ catalytic ozonation	2.7991×10^{-8}	7.0671×10^{-9}
MgO catalytic ozonation	6.83885×10^{-8}	1.6035×10^{-7}
FeOOH catalytic ozonation	6.90287×10^{-8}	