

## Supporting Information

### **Activation peroxymonosulfate by iron-based catalysts for orange G degradation: Role of hydroxylamine**

Jing Zhang<sup>1,\*</sup>, Mengyan Chen<sup>1</sup>, Liang Zhu<sup>1</sup>

1. Key Laboratory of Integrated Regulation and Resource Development on Shallow  
Lakes of Ministry of Education, College of Environment, Hohai University, Nanjing,  
210098, China

Contact information for corresponding author:

Jing Zhang

E-mail: zhang\_jing@hhu.edu.cn, telephone: 86-15050556980

## Table of Contents

Text S1 Materials	S3
Text S2 Detailed parameters and procedures of EPR experiments	S4
Text S3 Experiments about the stability of Fe <sub>3</sub> O <sub>4</sub>	S5
Text S4 Synthetic method of 1.5wt% Fe/Al <sub>2</sub> O <sub>3</sub> catalyst	S6
Text S5 Quantification of NH <sub>2</sub> OH and its degradation products	S7
Text S6 Preparation of iron sludge	S8
Fig. S1 Catalyst packed column reactor	S10
Fig. S2 XRD patterns for virgin Fe <sub>3</sub> O <sub>4</sub> , Fe <sub>3</sub> O <sub>4</sub> used after Fe <sub>3</sub> O <sub>4</sub> /PMS process and Fe <sub>3</sub> O <sub>4</sub> reduced by NH <sub>2</sub> OH	S11
Fig. S3 Mineralization of OG in NH <sub>2</sub> OH/Fe <sub>3</sub> O <sub>4</sub> /PMS process	S12
Fig. S4 Time courses of PMS and NH <sub>2</sub> OH in different processes	S13
Fig. S5 Degradation of OG in NH <sub>2</sub> OH/Fe <sub>2</sub> O <sub>3</sub> /PMS process	S14
Fig. S6 Degradation of OG in NH <sub>2</sub> OH/Iron sludge/PMS process	S15
Fig. S7 Effect of pH on the distribution of hydroxylamine at 25 °C	S16
Fig. S8 Effect of PMS concentration on OG degradation in NH <sub>2</sub> OH/Fe <sub>3</sub> O <sub>4</sub> /PMS process	S17
Fig. S9 Consumption of PMS in NH <sub>2</sub> OH/Fe <sub>3</sub> O <sub>4</sub> /PMS process	S18
Fig. S10 Effect of temperature on OG degradation	S19
Fig. S11 Concentrations of hydroxylamine and its end degradation products in NH <sub>2</sub> OH/Fe <sub>3</sub> O <sub>4</sub> /PMS process	S20
Fig. S12 Degradation of OG in batch experiment with 1.5wt%Fe/Al <sub>2</sub> O <sub>3</sub> as catalyst	S21

## **Text S1 Materials**

Oxone ( $\text{KHSO}_5 \cdot 0.5\text{KHSO}_4 \cdot 0.5\text{K}_2\text{SO}_4$ , PMS), hydroxylamine ( $\text{NH}_2\text{OH}$ , 99.9%), orange G (OG, 99.5%) and 5,5-dimethyl-1-pyrrolin-N-oxide (DMPO) were of analytical grade and supplied by J&K Chemical. Perchloric acid (99.0%), sodium hydroxide (99.0%), potassium iodide (99.5%) and sulfuric acid (98.0%) were of analytical reagent grade and purchased from Sinopharm Chemical Reagent Co., Ltd. Tert-butyl alcohol (TBA), methanol and tert-Butyl methyl ether (MTBE) were of guaranteed reagent grade and supplied by Tianjian Chemical Reagent Co., China. The magnetite nanoparticles were purchased from Nanjing Emperor Nano Material Co., Ltd. All of these chemicals were used as received without further purification. All solutions were prepared with ultrapure water.

## **Text S2 Detailed parameters and procedures of EPR experiments**

The 5,5-dimethyl-1-pyrrolidine-N-oxide (DMPO) was used as the spin trapping agent in EPR experiments. The DMPO solution, PMS solution,  $\text{NH}_2\text{OH}$  solution, and  $\text{Fe}_3\text{O}_4$  were mixed for 30 seconds and transferred into a 100  $\mu\text{L}$  capillary tube, which was then inserted into the cavity of the EPR spectrometer (Bruker A200). The EPR experiments were performed on the EPR spectrometer under the following conditions: a center field of 351.5 mT, a sweep width of 6.0 mT, a microwave frequency of 9.867 GHz, a microwave attenuator of 20 dB, a microwave power of 2.39 mW, a temperature of 300.0 K, a receiver gain of  $5.02 \times 10^4$ , a modulation amplitude of 0.1 mT, and a sweep time of 20.48 seconds.

### **Text S3 Experiments about the stability of Fe<sub>3</sub>O<sub>4</sub>**

To assess the catalytic property and stability of Fe<sub>3</sub>O<sub>4</sub>, 10 successive experiments were conducted at pH 3.0. The samples, collected at fix time interval for OG analysis, were filtered with a 0.22- $\mu$ m membrane filter to collect the catalyst and the filtrate was terminated with methanol following filtration. The collected Fe<sub>3</sub>O<sub>4</sub> catalyst was washed with DI water, dried in vacuum at 40 °C and then reused in the next cycle.

#### **Text S4 Synthetic method of 1.5wt% Fe/Al<sub>2</sub>O<sub>3</sub> catalyst**

Laboratory synthetic 1.5 wt% Fe/Al<sub>2</sub>O<sub>3</sub> catalyst was prepared as follow. Briefly, 202 g of Fe(NO<sub>3</sub>)<sub>3</sub> • 9H<sub>2</sub>O was dissolved in a 2-L glass flask and diluted with ultrapure water to 1.0 L, followed by a dropwise addition (at a rate of 10 mL min<sup>-1</sup>) of 240 mL of 2.5 M L<sup>-1</sup> KOH while keeping the solution constantly stirred. Then 269 g activated aluminium oxide (Al<sub>2</sub>O<sub>3</sub>) was added to the slurry and the mixture was aged for 10 h at 60 °C, and dialyzed for several times until the dialysate pH reached ~7.0 to remove dissolved potassium nitrate and excess potassium hydroxide. Finally, the synthetic Fe/Al<sub>2</sub>O<sub>3</sub> catalyst was dried at 105 °C for the subsequent qualitative analysis.

Metal compositions of fresh and used catalysts from column experiments were determined by ICP-AES following microwave-assisted acid digestion. BET measurements showed that the synthesized Fe/Al<sub>2</sub>O<sub>3</sub> catalyst had a specific surface area of 203 m<sup>2</sup> g<sup>-1</sup>, which was lower than that of Al<sub>2</sub>O<sub>3</sub> (272 m<sup>2</sup> g<sup>-1</sup>). The decrease of specific surface might be caused by mouth blockage during the impregnation of ferric hydroxide. The diameter of Fe/Al<sub>2</sub>O<sub>3</sub> catalyst was 3-4 mm, which was almost the same as that of Al<sub>2</sub>O<sub>3</sub>, indicating that the impregnation layer had barely impact on the size of supports.

### **Text S5 Quantification of NH<sub>2</sub>OH and its degradation products**

NH<sub>2</sub>OH was measured by gas chromatography (Agilent 7890A) with a flame ionization detector (FID) following the first derivation to acetoxime by acetone <sup>S1, S2</sup>.

In order to quantify the production of N<sub>2</sub> in NH<sub>2</sub>OH/Fe<sub>3</sub>O<sub>4</sub>/PMS process, the batch experiment was carried out in a serum bottle sealed with rubber stopper, the head space of which was purged with He before starting the reaction. After the reaction was finished, the mixture gas of N<sub>2</sub> and He was sampled by a six-way valve and determined with the gas chromatography (Agilent 7890A) equipped with a thermal conductivity detector (TCD) and a HP PLOT Q column (30 m×0.53 mm×40 μm). He was used as the carrier gas with the flow rate of 4.0 mL min<sup>-1</sup>. The column temperature was initially held at 120 °C for 2 min, followed by a linear heating program to 200 °C with the rate of 30 °C min<sup>-1</sup> and held for 4 min. The injector temperature was set at 250 °C with the injection volume of 20 μL and the split ratio of 1:3.

The concentration of dissolved N<sub>2</sub>O was determined with a gas chromatograph (Agilent 7890A) according to the method reported by Butler and Elkins <sup>S3</sup>.

The concentrations of NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> were measured with an ion chromatography (Dionex ICS-3000), which was equipped with a SP gradient pump, a Dionex AS19 column (4×250 mm), a Dionex guard column (4×50 mm), an anion

self-regenerating suppressor (ASRS 300, 4 mm), a conductive detector, and an AS40 autosampler. KOH solution (30 mM) and ultrapure water (30:70, v/v %) were used as the mobile phase with the flow rate of 1.0 mL min<sup>-1</sup>. The suppressor current and the injection volume were set as 75 mA and 100 µL, respectively.

## References

- [S1] J. Zou, J. Ma, L.W. Chen, X.C. Li, Y.H. Guan, P.C. Xie, C. Pan, *Environ. Sci. Technol.*, 47 (2013) 11685-11691.
- [S2] S.X. Peng, M.J. Strojnowski, J.K. Hu, B.J. Smith, T.H. Eichhold, K.R. Wehmeyer, S. Pikul, N.G. Almstead, *J. Chromatogr. B*, 724 (1999) 181-187.
- [S3] J.H. Butler, J.W. Elkins, *Mar. Chem.*, 34 (1991) 47-61.



### **Text S6 Preparation of iron sludge**

The iron sludge was obtained from a typical Fenton process. The Fenton experiment was performed in 1 L borosilicate glass beaker with a constant stirring rate at  $25 \pm 1$  °C. The reaction solution with 0.2 mM OG and 1.0 mM  $\text{Fe}^{2+}$  was prepared with ultrapure water and adjusted to pH 3.0 with 6 M sulfuric acid. The desired  $\text{H}_2\text{O}_2$  (10 mM) was then added to start the reaction. After the reaction was completed, the pH of the reaction solution was adjusted to 8.0 with the addition of 1.0 M sodium hydroxide. The coagulation of ferric hydroxide was enhanced by 1 min rapid mixing stage at 200 rpm followed by a 20 min flocculation stage at 40 rpm and a 20 min settlement period. Then the solid was separated by centrifugation, washed with ultrapure water for several times until pH of the filtrate was  $\sim 7.0$ , and then dried at 40 °C in a vacuum drying oven.

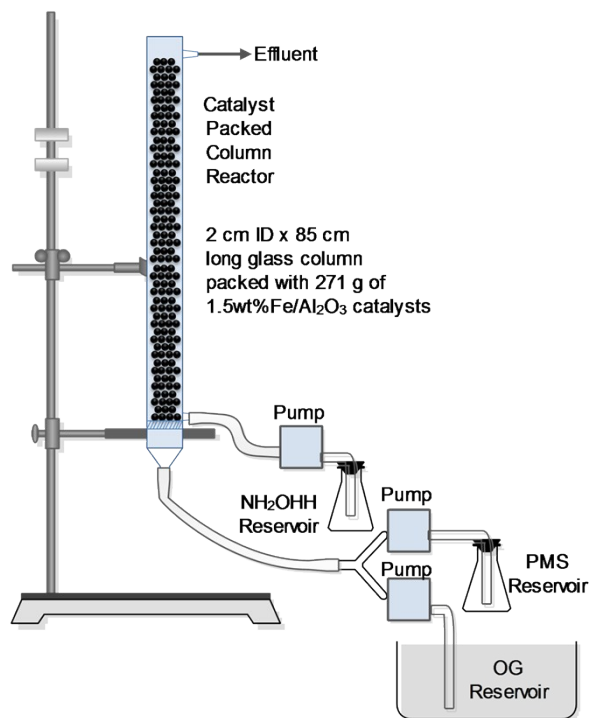


Fig. S1 Catalyst packed column reactor.

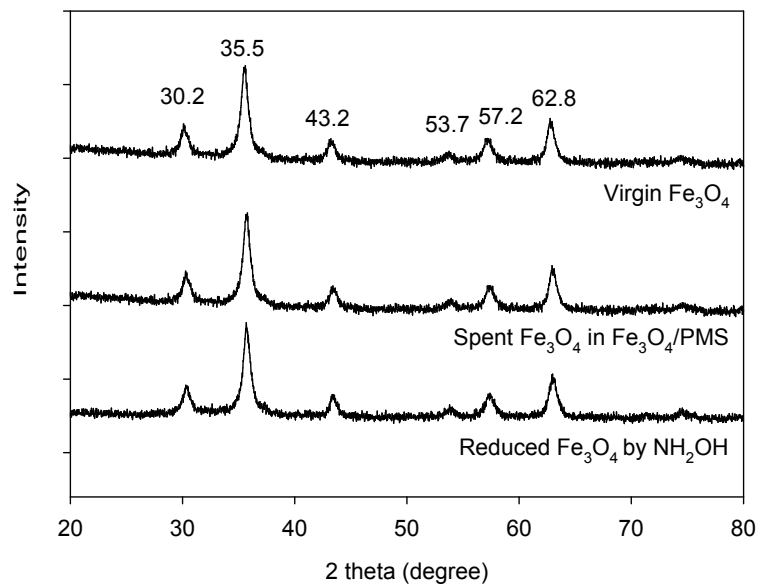


Fig. S2 XRD patterns for virgin Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub> used after Fe<sub>3</sub>O<sub>4</sub>/PMS process and Fe<sub>3</sub>O<sub>4</sub> reduced by NH<sub>2</sub>OH.

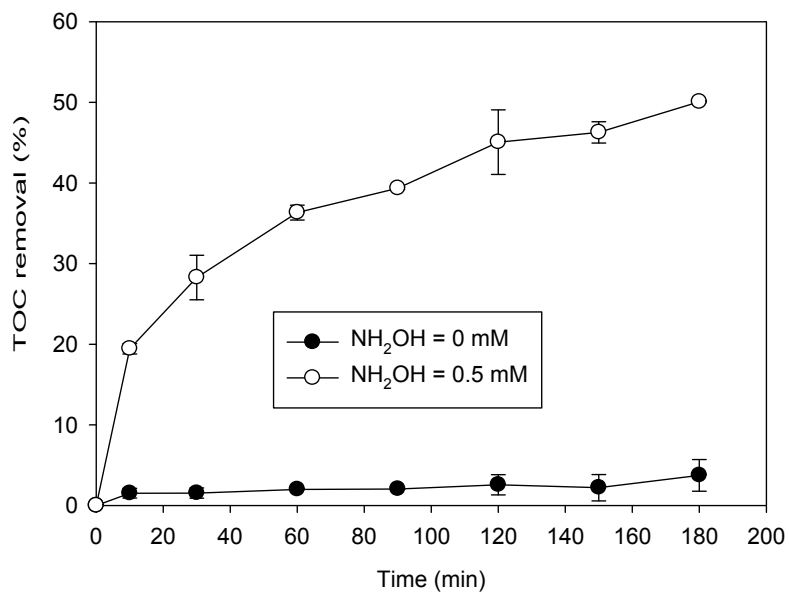


Fig. S3 Mineralization of OG in NH<sub>2</sub>OH/Fe<sub>3</sub>O<sub>4</sub>/PMS process. Conditions: [NH<sub>2</sub>OH]<sub>0</sub> = 1.0 mM (no addition for Fe<sub>3</sub>O<sub>4</sub>/PMS process), [Fe<sub>3</sub>O<sub>4</sub>]<sub>0</sub> = 0.5 g L<sup>-1</sup> for NH<sub>2</sub>OH/Fe<sub>3</sub>O<sub>4</sub>/PMS and Fe<sub>3</sub>O<sub>4</sub>/PMS process, [PMS]<sub>0</sub> = 1.0 mM, [OG]<sub>0</sub> = 0.1 mM, pH = 3.0, 25 °C.

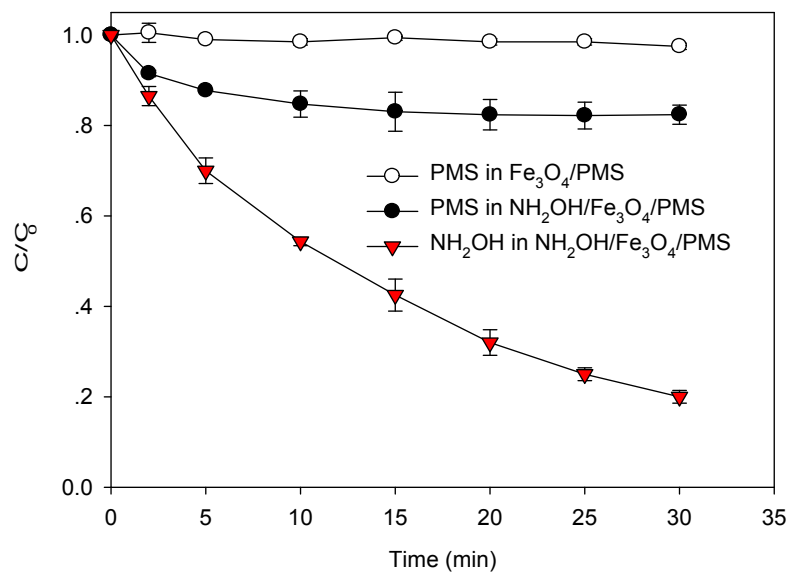


Fig. S4 Time courses of PMS and  $NH_2OH$  in different processes. Conditions:  $[NH_2OH]_0 = 0.5$  mM (no addition in  $Fe_3O_4$ /PMS process),  $[Fe_3O_4]_0 = 0.5$  g  $L^{-1}$ ,  $[PMS]_0 = 1.0$  mM,  $[OG]_0 = 0.1$  mM, pH = 3.0, 25 °C.

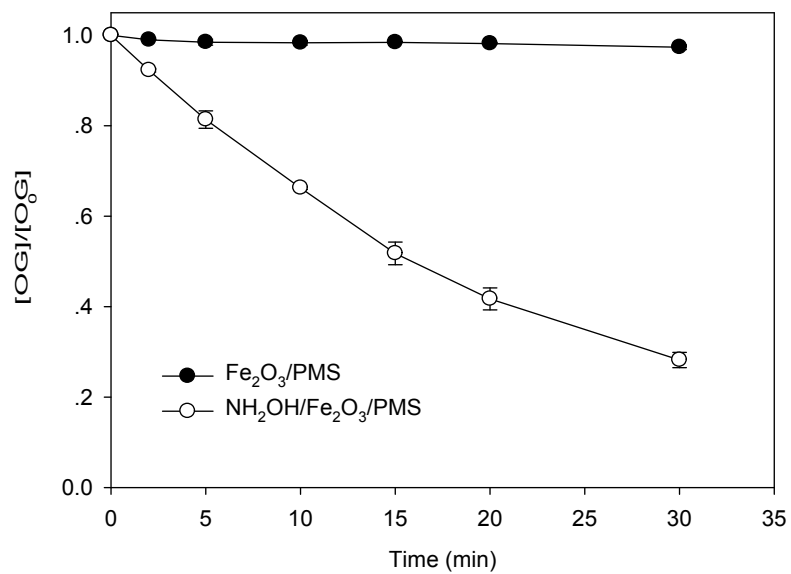


Fig. S5 Degradation of OG in  $\text{NH}_2\text{OH}/\text{Fe}_2\text{O}_3/\text{PMS}$  process. Conditions:  $[\text{NH}_2\text{OH}]_0 = 0.50 \text{ mM}$  (no addition for  $\text{Fe}_2\text{O}_3/\text{PMS}$  process),  $[\text{Fe}_2\text{O}_3]_0 = 0.5 \text{ g L}^{-1}$ ,  $[\text{PMS}]_0 = 1.0 \text{ mM}$ ,  $[\text{OG}]_0 = 0.1 \text{ mM}$ ,  $\text{pH} = 3.0$ ,  $25 \text{ }^\circ\text{C}$ .

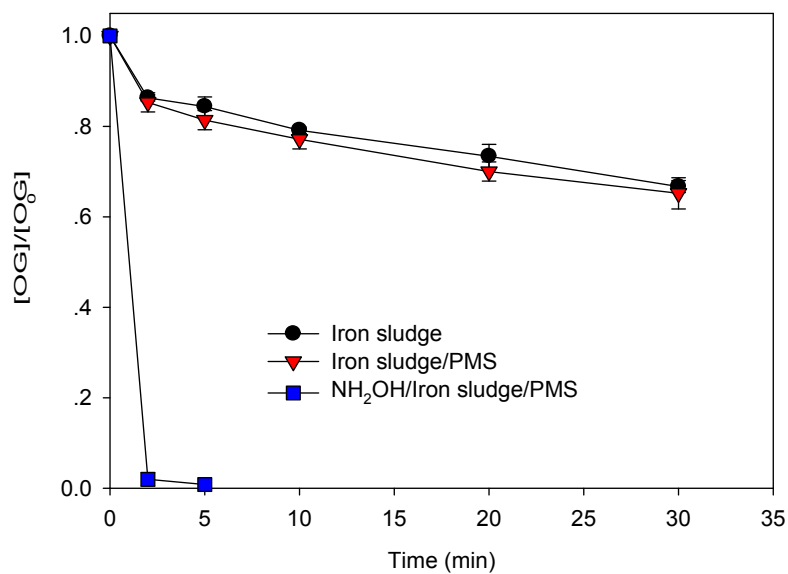


Fig. S6 Degradation of OG in NH<sub>2</sub>OH/iron sludge/PMS process. Conditions:  $[NH_2OH]_0 = 0.50$  mM (no addition for iron sludge or iron sludge/PMS process),  $[iron\ sludge]_0 = 0.5$  g L<sup>-1</sup>,  $[PMS]_0 = 1.0$  mM,  $[OG]_0 = 0.1$  mM, pH = 3.0, 25 °C.

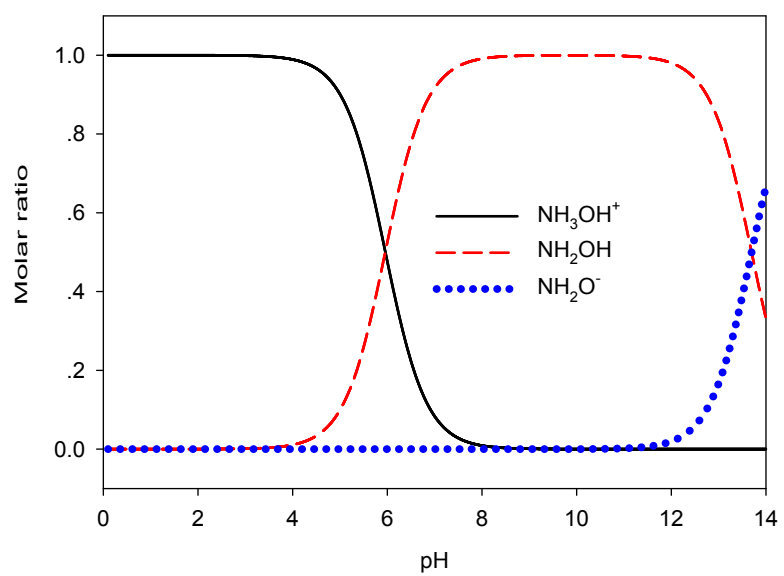


Fig. S7 Effect of pH on the distribution of hydroxylamine at 25 °C.



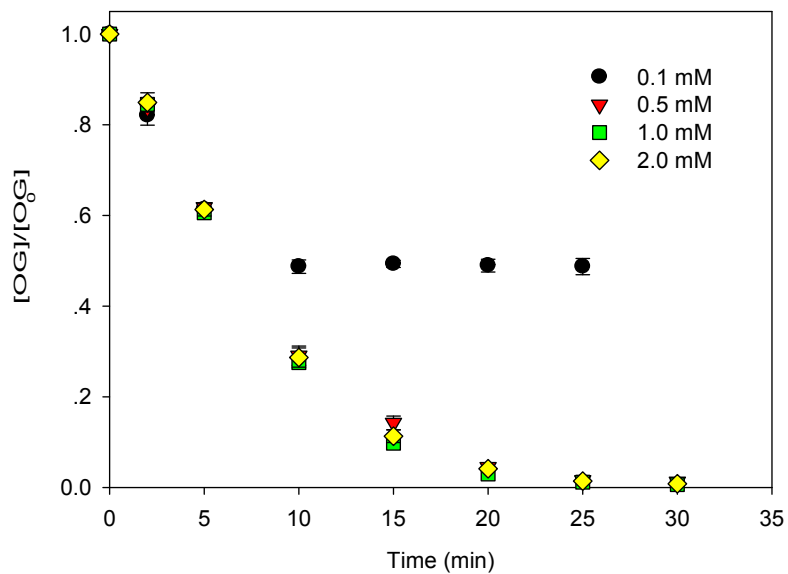


Fig. S8 Effect of PMS concentration on OG degradation in  $\text{NH}_2\text{OH}/\text{Fe}_3\text{O}_4/\text{PMS}$  process. Conditions:  $[\text{NH}_2\text{OH}]_0 = 0.5 \text{ mM}$ ,  $[\text{Fe}_3\text{O}_4]_0 = 0.5 \text{ g L}^{-1}$ ,  $[\text{PMS}]_0 = 0.1\text{-}2.0 \text{ mM}$ ,  $[\text{OG}]_0 = 0.1 \text{ mM}$ ,  $\text{pH} = 3.0$ ,  $25 \text{ }^\circ\text{C}$ .

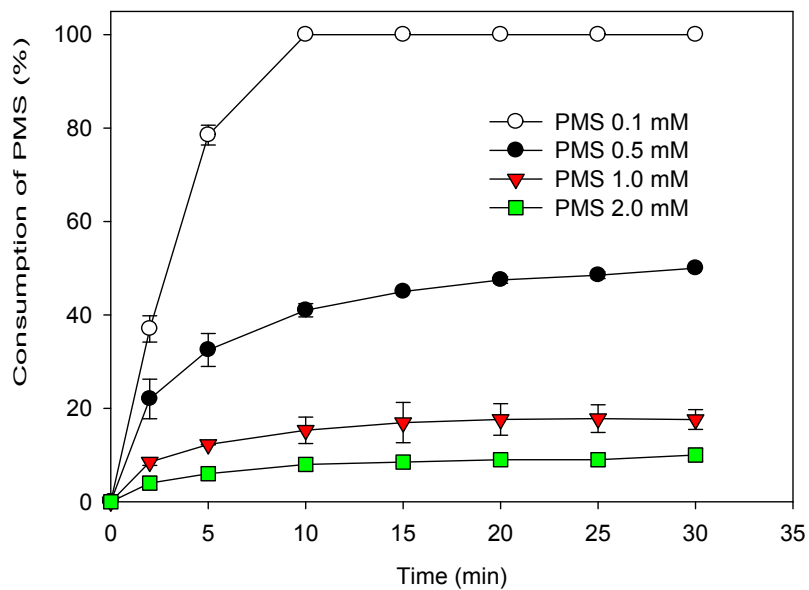


Fig. S9 Consumption of PMS in  $\text{NH}_2\text{OH}/\text{Fe}_3\text{O}_4/\text{PMS}$  process. Conditions:  $[\text{NH}_2\text{OH}]_0 = 0.5 \text{ mM}$ ,  $[\text{Fe}_3\text{O}_4]_0 = 0.5 \text{ g L}^{-1}$ ,  $[\text{OG}]_0 = 0.1 \text{ mM}$ ,  $[\text{PMS}]_0 = 0.1\text{-}2.0 \text{ mM}$ ,  $\text{pH} = 3.0$ ,  $25^\circ\text{C}$ .

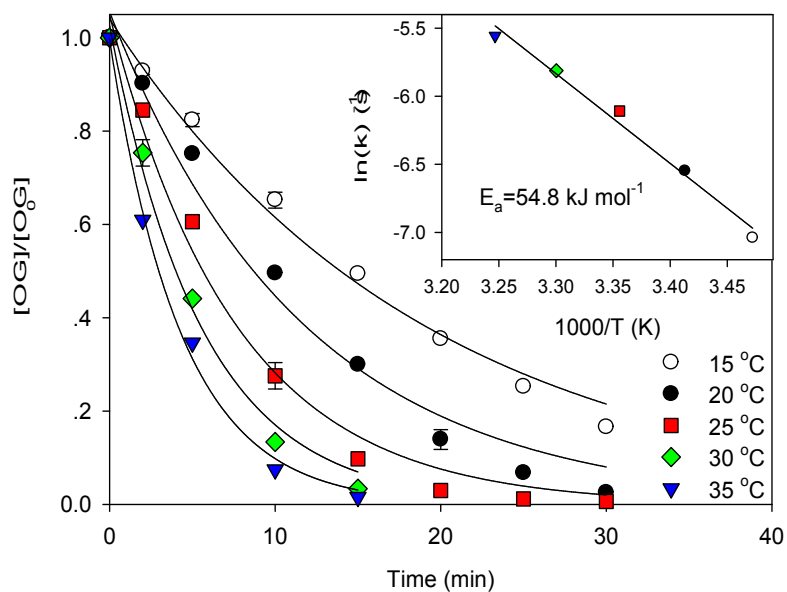


Fig. S10 Effect of temperature on OG degradation in  $\text{NH}_2\text{OH}/\text{Fe}_3\text{O}_4/\text{PMS}$  process.

Inset indicates the Arrhenius plot for the OG degradation rate constants at 15, 20, 25, 30 and 35 °C. Conditions:  $[\text{NH}_2\text{OH}]_0 = 0.5 \text{ mM}$ ,  $[\text{Fe}_3\text{O}_4]_0 = 0.5 \text{ g L}^{-1}$ ,  $[\text{PMS}]_0 = 1.0 \text{ mM}$ ,  $[\text{OG}]_0 = 0.1 \text{ mM}$ ,  $\text{pH} = 3.0$ .

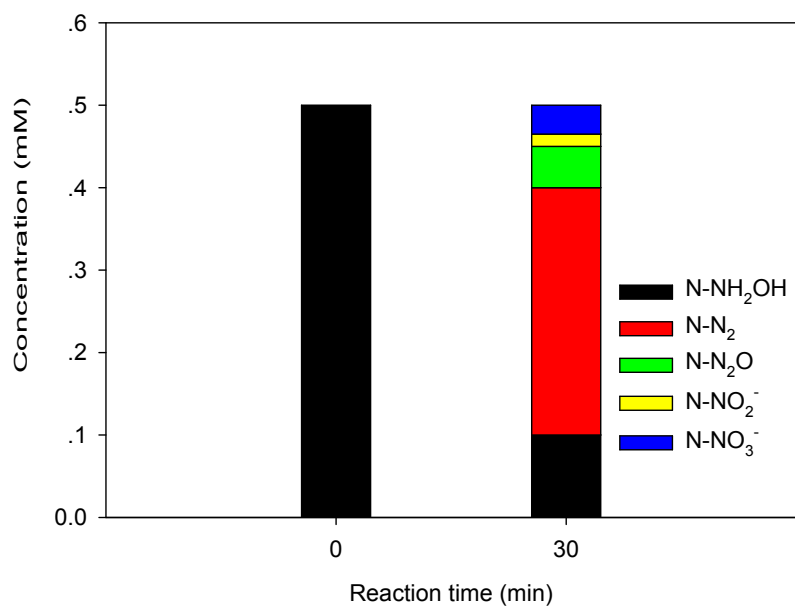


Fig. S11 Concentrations of hydroxylamine and its end degradation products in NH<sub>2</sub>OH/Fe<sub>3</sub>O<sub>4</sub>/PMS process. [N-NH<sub>2</sub>OH], [N-N<sub>2</sub>O], [N-NO<sub>2</sub><sup>-</sup>], [N-NO<sub>3</sub><sup>-</sup>], and [N-N<sub>2</sub>] were calculated as follows: [N-NH<sub>2</sub>OH] = [NH<sub>2</sub>OH], [N-N<sub>2</sub>O] = 2[N<sub>2</sub>O], [N-NO<sub>2</sub><sup>-</sup>] = [NO<sub>2</sub><sup>-</sup>], [N-NO<sub>3</sub><sup>-</sup>] = [NO<sub>3</sub><sup>-</sup>], and [N-N<sub>2</sub>] = 2[N<sub>2</sub>]. Conditions: [NH<sub>2</sub>OH]<sub>0</sub> = 0.5 mM, [Fe<sub>3</sub>O<sub>4</sub>]<sub>0</sub> = 0.5 g L<sup>-1</sup>, [PMS]<sub>0</sub> = 1.0 mM, [OG]<sub>0</sub> = 0.1 mM, pH = 3.0, 25 °C, and reaction time = 30 min.

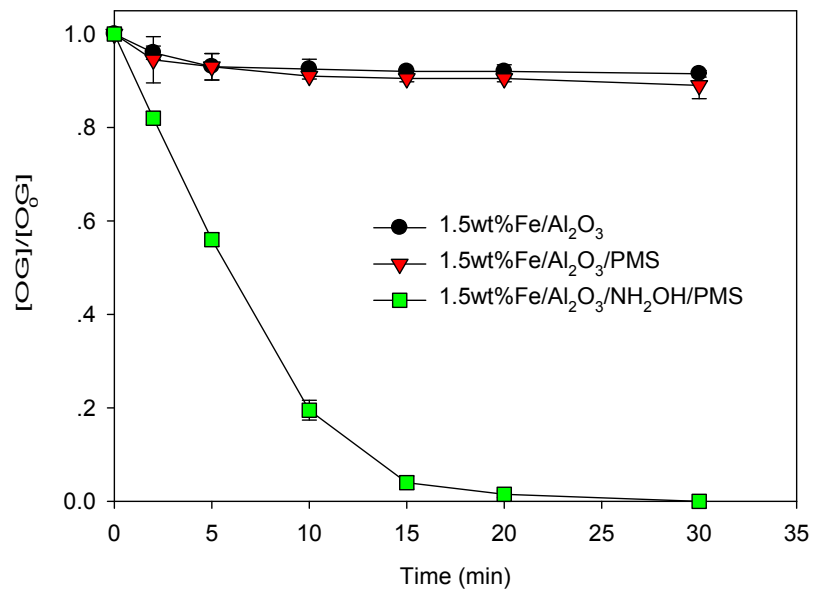


Fig. S12 Degradation of OG in batch experiment with 1.5wt%Fe/Al<sub>2</sub>O<sub>3</sub> as catalyst.

Conditions:  $[NH_2OH]_0 = 0.5 \text{ mM}$  (no addition for 1.5wt%Fe/Al<sub>2</sub>O<sub>3</sub> and 1.5wt%Fe/Al<sub>2</sub>O<sub>3</sub>/PMS),  $[1.5wt\%Fe/Al_2O_3]_0 = 5.0 \text{ g L}^{-1}$ ,  $[PMS]_0 = 1.0 \text{ mM}$ ,  $[OG]_0 = 0.1 \text{ mM}$ , pH = 3.0, 25 °C.