



# A Mechanistic Study of Goethite-Based Fenton-Like Reactions for Imidacloprid Degradation

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## Abstract

Biotic transformation of imidacloprid (IMD) has been widely investigated in the environments. However, little was known about IMD degradation via abiotic pathways, such as reactive oxygen species (ROS)-based oxidation processes. Here we systematically investigated the mechanism of hydroxyl radical ( $\cdot\text{OH}$ ) production and the associated IMD degradation in the goethite ( $\alpha\text{-FeOOH}$ )-based Fenton-like systems. Results showed that IMD can be efficiently degraded in the  $\alpha\text{-FeOOH}/\text{H}_2\text{O}_2$  systems, with degradation rate exceeded 80% within 48 h. Based on the examination of electron paramagnetic resonance (EPR) and chemical probes,  $\cdot\text{OH}$  was identified as the key ROS that responsible for IMD degradation. IMD can be decomposed via hydroxylation or removal of  $-\text{N}-\text{NO}_2$  to produce hydroxylated IMD, cyclic urea and 6-chloronicotinic acid, with the associated toxicities also evaluated. In addition, the increasing  $\text{H}_2\text{O}_2$  concentration and decreasing solution pH both significantly increased IMD degradation. This study provides theoretical understanding for the implications of soil mineral-based Fenton-like reactions in the abiotic transformation of pesticide pollutants.

**Keywords** Fenton-like reaction ·  $\alpha\text{-FeOOH}$  · Hydrogen peroxide · Hydroxyl radical · Imidacloprid degradation

## Introduction

With the rapid development of agricultural production, the application of insecticides becomes increasingly extensive in the agricultural fields, especially for neonicotinoid insecticides, the most widely used insecticides in the world (Simon-Delso et al. 2015). As one of the highly effective neonicotinoid insecticides, imidacloprid (IMD) is a synthetic compound with a structure similar to nicotine and it kills insects by affecting their central nervous system (Bass et al. 2015; Schaeffer and Wijntjes 2022). The residual average levels of IMD were documented in the range of  $< 1$  to  $10 \text{ ng g}^{-1}$  (Jones et al. 2014, Stewart, Lorenz et al. 2014),

and the half-life of IMD was approximated ranged from 3 to  $> 1000$  days (Hladik et al. 2018) in different types soils, such as sandy and silty clay soil (Goulson 2013). It has been reported that microbial processes played an important role in IMD transformation in soil. Specifically, Anhalt et al. found that IMD can be degraded by microorganisms using it as the nitrogen source (Anhalt et al. 2007). Besides, bacterial types also affected the pathways and degradation products of IMD (Akoijam and Singh 2015, Kandil, Trigo et al. 2015). The current studies on the transformation and degradation of IMD are mainly focused on the microbial processes in soil (Hussain et al. 2016, Pang, Lin et al. 2020), and little was known about the kinetics and associated mechanisms to IMD transformation via abiotic pathways, such as reactive oxygen species (ROS)-based oxidation processes.

As one of the most powerful oxidants in natural environment, hydroxyl radical ( $\cdot\text{OH}$ ,  $E^\circ=2.8 \text{ V}$ ) can degrade a wide range of organic pollutants in atmosphere, surface water and soil environments (Oturán and Aaron 2014; Gligorovski et al. 2015), including diethyl phthalate (DEP), 2-chlorobiphenyl (2-CB), etc. (Fang et al. 2013, Chen, Fang et al. 2016, Liu, Yuan et al. 2017, Zeng, Dong et al. 2017, Chen, Fang et al. 2019, Chen, Huang Chen et al. 2021a, b). Since superoxide radical ( $\text{O}_2^{\cdot-}$ ) are broadly produced by soil

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microorganisms (Diaz et al. 2013), the formation of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) can be accomplished via  $\text{O}_2^{\cdot-}$  protonation and oxidase enzymes mediated by functional microbes (Hayyan et al. 2016). Hence,  $\cdot\text{OH}$  production through the reactions between  $\text{H}_2\text{O}_2$  and catalysts (e.g.,  $\text{Fe}^{2+}$ , Fe (oxyhydr)oxides) via Fenton and Fenton-like mechanisms was an omnipresent phenomenon in soil environments. The traditional Fenton reactions used dissolved  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  to produce  $\cdot\text{OH}$  and degrade organic pollutants effectively (Dalla Villa and Nogueira 2006, Chen, Wei et al. 2022). Besides, iron-bearing minerals-based heterogeneous Fenton-like reactions were also explored (Garrido-Ramirez et al. 2010), which is capable to degrade organic pollutants effectively within the wide pH range and prevent the precipitation of iron ions (Huang et al. 2001, Matta, Hanna et al. 2007, Pham, Lee et al. 2009). Although papers have reported that Fe bearing mineral-based Fenton-like systems (e.g., Fe-bearing minerals/ $\text{H}_2\text{O}_2$ ) were active to induce the organic pollutants degradation, such as alachlor (Hou et al. 2017), acetamiprid (Mitsika et al. 2013), dimethyl sulphoxide (Wu et al. 2006) etc., current studies are mainly focused on exploring applicable strategies for enhancing the efficiency of ROS formation and contaminants degradation in the goethite/ $\text{H}_2\text{O}_2$  systems, such as the introducing hydroxylamine (Hou et al. 2017), and ascorbate (Wang et al. 2021, Chen et al. 2021a, b). Hence, systematic studies involving organic contaminants degradation in the goethite/ $\text{H}_2\text{O}_2$  systems are still needed, especially the degradation of organic contaminants that rarely reported. Besides, imidacloprid (IMD) is one of the highly effective neonicotinoid insecticides with production of ten thousands of tons per year (Bass et al. 2015). Many studies have reported the microbial degradation of IMD in soil environments (Hussain et al. 2016, Pang, Lin et al. 2020), whereas its transformation via abiotic pathways, such as reactive oxygen species (ROS)-based oxidation processes, was rather limited. Accordingly, our study was conducive to predicting the abiotic degradation of IMD in soil environments through iron bearing mineral-based Fenton-like reactions.

Accordingly, goethite was selected as the model iron-bearing mineral to examine IMD degradation during Fenton-like reactions. Based on this, our study mainly aims to investigate the mechanisms of  $\cdot\text{OH}$  formation and IMD degradation by goethite-based Fenton-like reactions, and examine the effect of associated environmental factors. The obtained results will be conducive to understanding the kinetics and mechanisms of  $\cdot\text{OH}$ -mediated abiotic transformation of pesticide pollutants in soil environments.

## Materials and Methods

### Chemicals and Materials

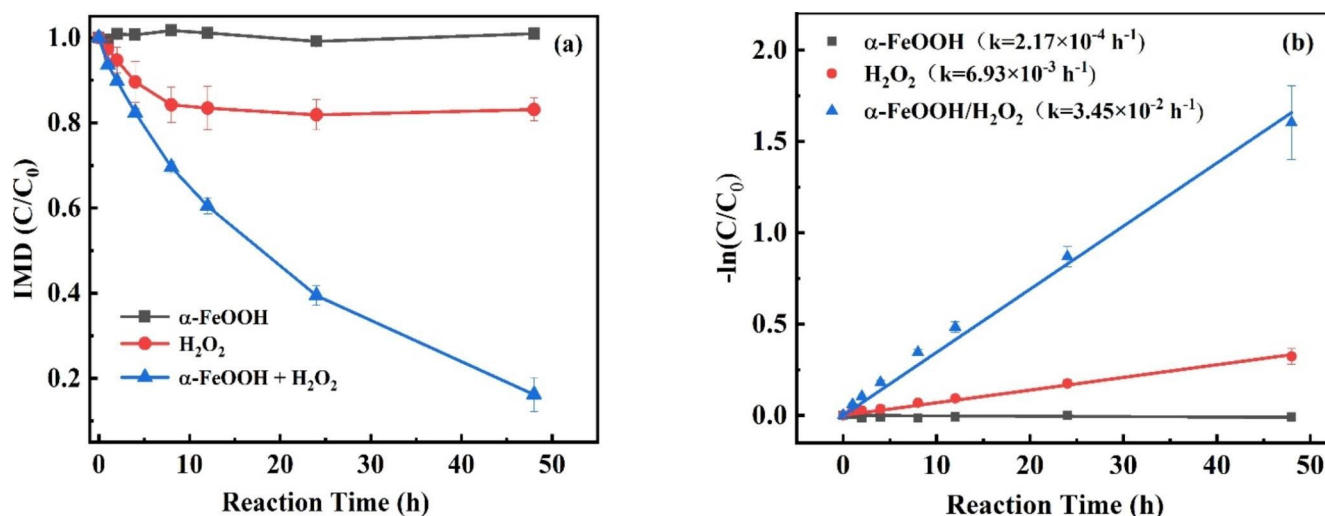
Imidacloprid (IMD,  $\geq 98\%$ ) was purchased from Sigma-Aldrich (USA). Sodium hydroxide (NaOH, 97%), sulfuric acid ( $\text{H}_2\text{SO}_4$ , 98%), potassium titanium oxalate ( $\text{C}_4\text{H}_2\text{K}_2\text{O}_{10}\text{Ti}$ , 98%), potassium hydroxide (KOH, 85%), ferric nitrate nonahydrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , 98%), tert-butanol (TBA, 99%) were obtained from China National Medicines Corporation Ltd. (Beijing, China). Hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30%), benzoic acid (BA, 99.5%), and *p*-hydroxybenzoic acid (*p*-HBA, 99.5%) were provided by Nanjing Chemical Reagents Co., Ltd. (Nanjing, China). 5, 5-dimethyl-1-pyrroline N-oxide (DMPO, 97%) and HPLC grade methanol were supplied by J&K Scientific Ltd., China (Shanghai).

### Synthesis of Goethite

Goethite ( $\alpha\text{-FeOOH}$ ) was synthesized based on the well-established method (Shuai et al. 2019). Briefly, 30 mL 5 M KOH was added to 1.5 L 0.1 M  $\text{Fe}(\text{NO}_3)_3$  solution with pH adjusted to 12.0. The suspension was placed in an oven at 70°C for 40 h, and then cooled to room temperature. After that, the suspension was put into 3 K Dalton dialysis bags in ultrapure water bath for 3 days with continuous stirring, and the ultrapure water was renewed three times daily. Finally, the obtained solids were poured into glass vials and freeze-dried to gain  $\alpha\text{-FeOOH}$  particles. The obtained  $\alpha\text{-FeOOH}$  samples were characterized by transmission electron microscopy (TEM, JEM-2100 F) and X-ray diffraction (XRD, Ultima IV, Japan; Fig. S1).

### Experimental Procedure

Degradation experiments were performed in 40 mL glass vials, which were placed in a constant temperature shaker (150 rpm,  $25 \pm 2$  °C) for oscillation reaction. Typical experimental suspensions were consisted of different contents of  $\alpha\text{-FeOOH}$ ,  $\text{H}_2\text{O}_2$  and 10  $\mu\text{M}$  IMD, using 0.1 M  $\text{H}_2\text{SO}_4$  and NaOH to adjust the solution pH. All experiments were performed in triplicates with standard deviations reported. At predetermined time intervals, a certain volume of suspension was withdrawn and mixed with 50% methanol to quench the reaction. Then, the suspension was filtered with 0.22  $\mu\text{m}$  PTFE membrane for IMD analysis. Benzoic acid (BA) was added to probe the produced  $\cdot\text{OH}$  via formation of hydroxybenzoic acid (HBA) without IMD addition. The concentration of *p*-hydroxybenzoic acid (*p*-HBA) was analyzed to quantify the  $\cdot\text{OH}$  accumulation with the conversion factor of 5.87 (Chen et al. 2021). The effects of  $\alpha\text{-FeOOH}$



**Fig. 1** Kinetics of IMD degradation in the  $\alpha$ -FeOOH Fenton-like reactions: (a) IMD degradation; (b) pseudo first-order fitting for IMD degradation. Reaction conditions:  $[\alpha\text{-FeOOH}]_0 = 1 \text{ g L}^{-1}$ ,  $[\text{H}_2\text{O}_2]_0 = 2 \text{ mM}$ ,  $[\text{IMD}]_0 = 10 \text{ }\mu\text{M}$ , initial  $\text{pH} = 3.0 \pm 0.2$ , and  $25 \text{ }^\circ\text{C}$

dosages ( $0.5\text{--}5 \text{ g L}^{-1}$ ),  $\text{H}_2\text{O}_2$  concentration ( $0.2\text{--}2 \text{ mM}$ ) and  $\text{pH}$  ( $3.0\text{--}11.0$ ) on IMD degradation were also performed under same conditions. All experiments were conducted in triplicates, with mean values and standard errors reported.

## Analytical Methods

The concentrations of IMD, BA and *p*-HBA were analyzed by HPLC (Agilent 1200, USA) equipped with a Supelcosil LC-18 column ( $25 \text{ cm} \times 4.6 \text{ mm}$ ) and a diode-array detector (DAD). The mobile phase was consisted of 60% ultrapure water and 40% methanol at a flow rate of  $1.0 \text{ mL min}^{-1}$  for IMD analysis. The detection wavelength of DAD was at  $270 \text{ nm}$ . The mobile phase was consisted of 35% methanol and 65% phosphate buffer ( $0.1\%$ ) at a flow rate of  $1.0 \text{ mL min}^{-1}$  for BA and *p*-HBA analyses. The detection wavelength of DAD was at  $254$  and  $300 \text{ nm}$ . The LODs of BA and IMD were  $25$  and  $91 \text{ nM}$ , respectively. The recovery of IMD was in the range of  $91.0\text{--}99.5\%$ , with standard deviation in the range of  $0.7\text{--}6.1\%$ . The IMD products were identified by liquid chromatographic time-of-flight mass spectrometer (LC-TOF-MS, AB SCIEX, USA).

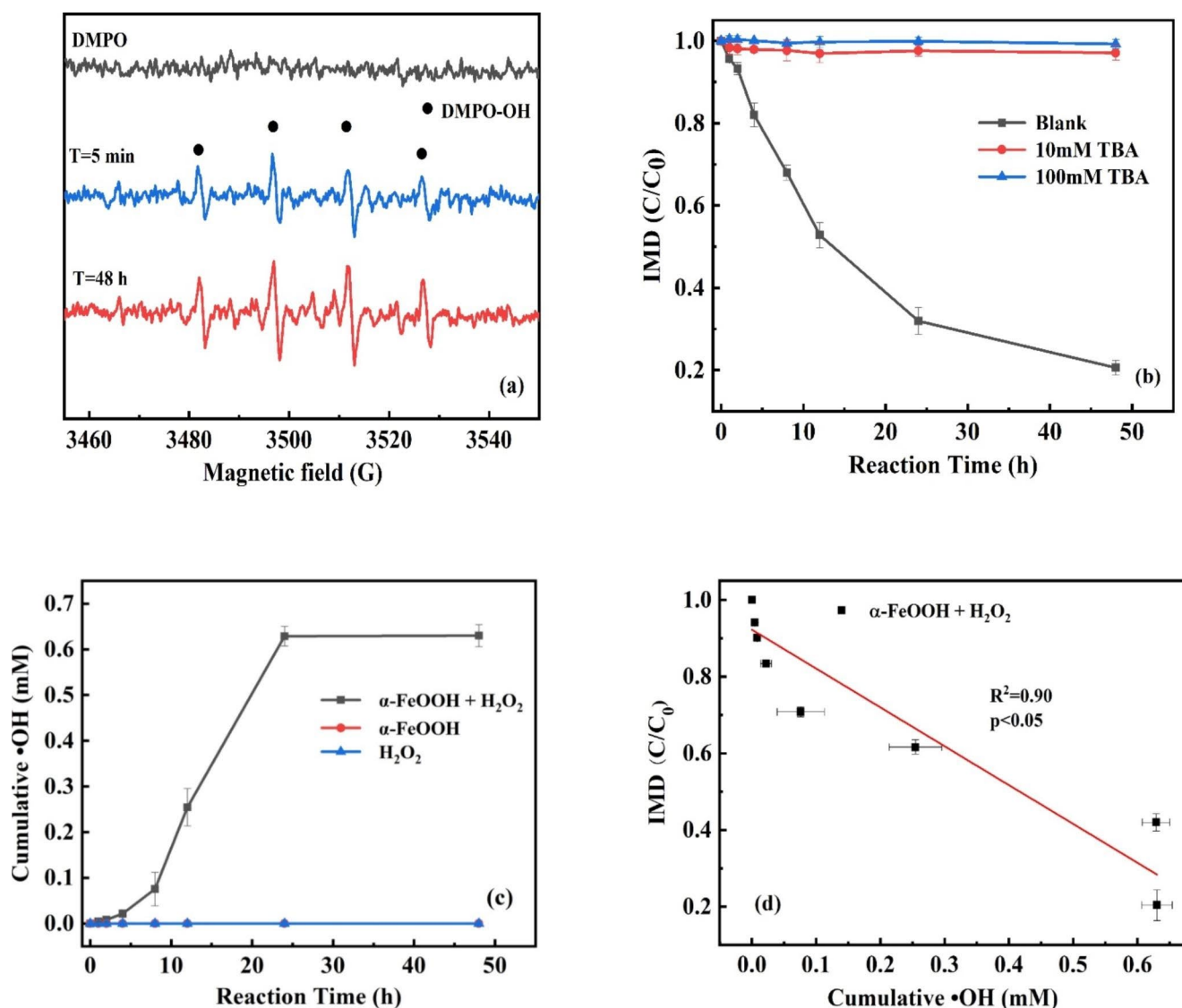
$\text{H}_2\text{O}_2$  concentration was analyzed based on the potassium titanium oxalate method and detect the  $\text{H}_2\text{O}_2$  concentration by spectrophotometer (UV 2700, Shimadzu, Japan) at  $400 \text{ nm}$  wavelength (Pham et al. 2009). The  $\cdot\text{OH}$  production was examined using an electron paramagnetic resonance (EPR, Bruker E500-9.5/12) with  $0.1 \text{ M}$  5, 5-dimethyl-1-pyrroline N-oxide (DMPO) as the trapping agent. The operational condition of EPR was set at X-band with a microwave power of  $6.33 \text{ mW}$ , modulation frequency of  $100 \text{ kHz}$ , resonance frequency of  $9.42 \text{ GHz}$ , and modulation amplitude of  $1.0 \text{ G}$ .

## Results and Discussion

### IMD Degradation in the $\alpha$ -FeOOH/ $\text{H}_2\text{O}_2$ Systems

The degradation kinetics of IMD ( $10 \text{ }\mu\text{M}$ ) were firstly examined in the  $\alpha$ -FeOOH/ $\text{H}_2\text{O}_2$  systems (Fig. 1a). The IMD concentration negligibly changed with  $\alpha$ -FeOOH alone, which indicated that IMD was relatively stable in the presence of  $\alpha$ -FeOOH. The IMD concentration decreased by approximated 20% within 48 h in the presence of  $\text{H}_2\text{O}_2$ , suggesting that IMD was oxidized by  $\text{H}_2\text{O}_2$ . However, IMD degradation exceeded 80% within 48 h in the  $\alpha$ -FeOOH/ $\text{H}_2\text{O}_2$  system, indicating IMD degradation was greatly enhanced due to the Fenton-like reaction between  $\alpha$ -FeOOH and  $\text{H}_2\text{O}_2$ .

The IMD degradation of were well fitted with the pseudo first-order kinetics, with the results shown in Fig. 1b. The degradation rate constant ( $k_{\text{obs}}$ ) of IMD was  $0.035 \pm (9.1 \times 10^{-4}) \text{ h}^{-1}$  in the  $\alpha$ -FeOOH and  $\text{H}_2\text{O}_2$  system, which was much higher than that of  $\alpha$ -FeOOH ( $2.2 \pm 1.5 \times 10^{-4} \text{ h}^{-1}$ ) and  $\text{H}_2\text{O}_2$  ( $6.9 \pm 0.2 \times 10^{-3} \text{ h}^{-1}$ ) alone. These results further demonstrated that IMD degradation was significantly enhanced in the  $\alpha$ -FeOOH and  $\text{H}_2\text{O}_2$  system. Meanwhile, the amount of dissolved  $\text{Fe}^{3+}$  was measured by O-phenanthroline colorimetry (Fang et al. 2013), and results showed that the dissolved  $\text{Fe}^{3+}$  concentration was undetectable after reaction. Hence, IMD degradation was mainly induced by the heterogeneous Fenton processes rather than homogeneous reactions (Lin et al. 2014).



**Fig. 2** (a) EPR spectra of ROS in the  $\alpha$ -FeOOH/ $\text{H}_2\text{O}_2$  system at different time intervals; (b) effects of TBA on IMD degradation; (c)  $\cdot\text{OH}$  accumulation in different reaction systems; (d) correlation analyses between  $\cdot\text{OH}$  accumulation and IMD concentration in the

$\alpha$ -FeOOH/ $\text{H}_2\text{O}_2$  system. Reaction conditions:  $[\alpha\text{-FeOOH}]_0 = 1 \text{ g L}^{-1}$ ,  $[\text{H}_2\text{O}_2]_0 = 2 \text{ mM}$ ,  $[\text{IMD}]_0 = 10 \text{ }\mu\text{M}$ ,  $[\text{TBA}]_0 = 10 \text{ mM}$  and  $100 \text{ mM}$ ,  $[\text{DMPO}]_0 = 0.1 \text{ M}$ ,  $[\text{BA}]_0 = 10 \text{ mM}$ , initial  $\text{pH} = 3.0 \pm 0.2$ , and  $25 \text{ }^\circ\text{C}$

## Mechanism of IMD Degradation in The $\alpha$ -FeOOH and $\text{H}_2\text{O}_2$ System

### The Identification of Key ROS

To investigate key ROS in the  $\alpha$ -FeOOH/ $\text{H}_2\text{O}_2$  system, EPR examination was applied with DMPO as trapping agent (Fang et al. 2013). The signals of free radical formation in the  $\alpha$ -FeOOH/ $\text{H}_2\text{O}_2$  system was measured at different times (Fig. 2a). As shown in Fig. 2a, there are strong 4-fold characteristic peaks with an intensity ratio of 1:2:2:1, which was the characteristic signal of DMPO-OH (Zhou et al. 2018). This result indicated the  $\cdot\text{OH}$  signal production in the  $\alpha$ -FeOOH/ $\text{H}_2\text{O}_2$  system. The DMPO-OH signal was slightly

increased at 48 h versus that at 5 min, suggesting  $\cdot\text{OH}$  production was sustained during reaction. The TBA was further added to reaction system as the scavenger of  $\cdot\text{OH}$ . Results showed that IMD degradation was significantly inhibited ( $< 1\%$ ) with addition of TBA, further indicating that the produced  $\cdot\text{OH}$  was responsible for IMD degradation.

The  $\cdot\text{OH}$  formation was further quantified with BA (Fig. 2c), which showed that  $630.2 \text{ }\mu\text{M}$   $\cdot\text{OH}$  was accumulated within 48 h. Besides, correlation analyses between  $\cdot\text{OH}$  accumulation and IMD concentration was performed in Fig. 2d. Results showed that IMD concentration was negatively correlated ( $R^2 = 0.90$ ) with  $\cdot\text{OH}$  accumulation. These combined results demonstrated that  $\cdot\text{OH}$  was the key ROS for IMD degradation in the  $\alpha$ -FeOOH/ $\text{H}_2\text{O}_2$  system.

## The Proposed Degradation Pathways of IMD Induced by $\cdot\text{OH}$

The total of five products of IMD were identified after  $\cdot\text{OH}$  oxidation (Fig. S2), including the hydroxylated IMD, cyclic urea and 6-chloronicotinic acid, etc. Accordingly, IMD degradation pathways were proposed based on the identified products and previous studies (Malato et al. 2001, Wang, Shu et al. 2022). As shown in Fig. S3, there are two main pathways for IMD degradation, showing that IMD was hydroxylated by  $\cdot\text{OH}$  to produced products I and II. Meanwhile, the removal of  $-\text{N}-\text{NO}_2$  from IMD can generate products III and IV. Finally, all intermediate products were converted into 6-chloronicotinic acid.

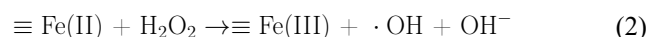
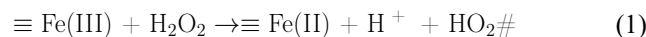
To evaluate the ecological risk of IMD and its products, ECOSAR program was used to predict the toxicity of IMD and its products. Table S1 shows that the median lethal concentration ( $\text{LC}_{50}$ ), median effect concentration ( $\text{EC}_{50}$ ) and chronic value (ChV) of 4-hydroxy derivative for fish and green algae exceed 100 mg/L, which indicated that 4-hydroxy derivative was lower toxicity than IMD. The  $\text{LC}_{50}$  of cyclic urea for daphnia was 39.68 mg/L, and the  $\text{EC}_{50}$  of cyclic urea for green algae was 0.02 mg/L. Besides, the ChV of cyclic urea for fish, daphnia and green algae were 0.94, 9.64, 0 mg/L, respectively. Additionally, the  $\text{LC}_{50}$  of 6-chloronicotinic acid for fish and daphnia were 21.09, 12.8 mg/L, and the ChV of 6-chloronicotinic acid for fish and daphnia were 10.89, 0.69 mg/L respectively. The  $\text{LC}_{50}$ ,  $\text{EC}_{50}$  and ChV of parameters of cyclic urea and 6-chloronicotinic acid were lower than those of IMD, which indicated that these two products were much more toxic than IMD. Therefore, the toxicity of IMD intermediate products increased or decreased depending on its structures.

## Effects of Environmental Factors on IMD Degradation

### $\alpha$ -FeOOH Dosages

The effect of  $\alpha$ -FeOOH dosages on IMD degradation were investigated under ambient conditions (Fig. S4a). Results showed that IMD degradation increased from 65 to 80% with  $\alpha$ -FeOOH dosages increasing from 0.5 to 1 g  $\text{L}^{-1}$ , and changed negligibly at 2 g  $\text{L}^{-1}$ . With  $\alpha$ -FeOOH dosage increased to 5 g  $\text{L}^{-1}$ , IMD degradation efficiency declined to 60%. Correspondingly, the  $k_{\text{obs}}$  value increases from  $2.2 \pm 0.1 \times 10^{-2} \text{ h}^{-1}$  (0.5 g  $\text{L}^{-1}$ ) to  $3.1 \pm 0.1 \times 10^{-2} \text{ h}^{-1}$  (1 g  $\text{L}^{-1}$ ), but then gradually decreased to  $1.7 \pm 0.1 \times 10^{-2} \text{ h}^{-1}$  at 5 g  $\text{L}^{-1}$  (Fig. S4b). These combined results further indicated that 1 g  $\text{L}^{-1}$  of  $\alpha$ -FeOOH was the optimal dosage for IMD degradation. These results might be mainly because that increasing dosages of  $\alpha$ -FeOOH was contributed to

producing more  $\cdot\text{OH}$  (Le-Tuan et al. 2012, Lin, Ma et al. 2014). But large amounts of  $\alpha$ -FeOOH adsorbed more surface  $\text{Fe}^{3+}$  and consequently induced more  $\text{HO}_2\cdot$  production via  $\text{H}_2\text{O}_2$  decomposition (Eqs. 1 and 2) (Usman et al. 2022), which finally inhibited IMD degradation.



### Effect of pH

The effect of pH (3.0–11.0) on IMD degradation was further investigated in the  $\alpha$ -FeOOH/ $\text{H}_2\text{O}_2$  system (Fig. S5a). Results showed that IMD degradation rate significantly decreased from 80 to 15% with pH increasing from 3.0 to 11.0. Correspondingly, the  $k_{\text{obs}}$  decreased from  $2.9 \pm 0.0 \times 10^{-2} \text{ h}^{-1}$  to  $3.0 \pm 0.4 \times 10^{-3} \text{ h}^{-1}$  (Fig. S5b), indicating IMD degradation was intensively inhibited under neutral and alkaline conditions. Two possible reasons might be responsible for this phenomenon. Firstly, lower pH was conducive to activating more  $\text{H}_2\text{O}_2$  to produce more  $\cdot\text{OH}$  (Burbano et al. 2005). However,  $\text{H}_2\text{O}_2$  was easily decomposed into  $\text{H}_2\text{O}$  and  $\text{O}_2$  under alkaline conditions, which inhibited  $\cdot\text{OH}$  production (Buthiyappan et al. 2016, Zong, Xu et al. 2020). Another probable reason was probably due to the changed surface charge of  $\alpha$ -FeOOH, with point of zero charge ( $\text{pH}_{\text{pzc}}$ ) of 7.7 (Nezamzadeh-Ejhih and Amiri 2013). When pH is higher than  $\text{pH}_{\text{pzc}}$  (Lin and Gurol 1998), the surface of  $\alpha$ -FeOOH is negatively charged (Nezamzadeh-Ejhih and Zabihi-Mobarakeh 2014). Hence,  $\text{H}_2\text{O}_2$  decomposition was increasingly impeded with the increase of pH due to the repellency between  $\text{H}_2\text{O}_2$  and negatively charged surface. Consequently,  $\cdot\text{OH}$  production was significantly declined and induced less IMD degradation.

### $\text{H}_2\text{O}_2$ Concentration

Figure S6a shows the effect of  $\text{H}_2\text{O}_2$  concentrations on IMD degradation. The degradation efficiency increased from 30 to 80% with the  $\text{H}_2\text{O}_2$  concentration increased from 0.2 to 2 mM. Meanwhile,  $k_{\text{obs}}$  values also increased from  $6.5 \pm 0.5 \times 10^{-3} \text{ h}^{-1}$  to  $2.8 \pm 0.1 \times 10^{-2} \text{ h}^{-1}$  (Fig. S6b), which indicated that the increased  $\text{H}_2\text{O}_2$  concentration enhanced IMD degradation. Previous studies also documented that increased  $\text{H}_2\text{O}_2$  concentration was contributed to  $\cdot\text{OH}$  production (Fang et al. 2018, Wang, Ding et al. 2020), which was responsible for the enhanced IMD degradation. Meanwhile,  $\text{H}_2\text{O}_2$  concentration also decreased during reaction (Fig. S7a,b), indicating the decomposition of  $\text{H}_2\text{O}_2$  for  $\cdot\text{OH}$  production. These combined results demonstrated that the



increased  $\text{H}_2\text{O}_2$  concentration was conducive to IMD degradation in the  $\alpha\text{-FeOOH}/\text{H}_2\text{O}_2$  system.

## Conclusion

This study systematically investigated the processes and mechanisms of  $\cdot\text{OH}$  production and associated IMD degradation in the  $\alpha\text{-FeOOH}/\text{H}_2\text{O}_2$  systems. Results showed that the lower pH and increasing  $\text{H}_2\text{O}_2$  concentration significantly improved IMD degradation. The  $\cdot\text{OH}$  was key ROS in the  $\alpha\text{-FeOOH}/\text{H}_2\text{O}_2$  system as demonstrated by EPR and chemical probes, which was responsible for the proposed initial hydroxylation products and following degradation of IMD. IMD can be decomposed via hydroxylation or removal of  $-\text{N}-\text{NO}_2$  to produce hydroxylated IMD, cyclic urea and 6-chloronicotinic acid. The toxicities of these intermediates increased or decreased depended on the properties of organic compounds. All these results provides theoretical understanding to  $\alpha\text{-FeOOH}$ -based Fenton-like reactions that responsible for the abiotic transformation of pesticide pollutants, like IMD.

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## Declarations

**Conflict of Interest** The authors declare no competing financial interest.

**Supporting Information** Text of more detailed information on materials and methods as well as additional Figures.

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