CoFe-LDO Nanoparticles as a Novel Catalyst of Permonosulfate (PMS) for Amino Acid Removal

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Abstract

Dissolved organic nitrogen (DON) has been a subject of studies because of its potential to form nitrogenous disinfection byproducts (N-DBPs) in drinking water treatment. In our study, histidine was effectively degraded in the CoFe-LDO/PMS system. The results investigated that the removal of DON and histidine within 1 h in the CoFe-LDO/PMS system were up to 61% and 72%, respectively. Then the influences of CoFe-LDO dosage, PMS dosage and pH value for DON removal were elucidated. The optimum pH was 8, the optimal dosage of CoFe-LDO and PMS were 0.04 g/L and 0.5 mmol/L. It was found that SO$_4$$^-\cdot$ and •OH induced by the transformation of Co$^{2+}$-Co$^{3+}$ and Fe$^{2+}$-Fe$^{3+}$ on the catalyst surface were responsible for the degradation by ESR detection, in which SO$_4$$^-\cdot$ played a more important role. The degradation pathway of histidine indicated that it was partly oxidized to NH$_4$$^+$$-$N in the 60 min and no evident generation of N$_2$ during the whole process. Furthermore, degradation products of histidine have also been revealed by the analysis of HPLC-MS. In addition, the generation potentials of two typical N-DBPs were also clarified. The formation potential of dichloroacetonitrile (DCAN) decreased, while that of dichloroacetamide (DCAcAm) increased firstly after declining.

1. Introduction

The eutrophication of most natural lakes leads to excessive algae reproduction, especially at the later stage of algal growth, the DON is released into the water body causes the DON content in the water body to be higher than that of the general water body (Ambonguilat, et al., 2006; Choi and Valentine, 2002; Henderson, et al., 2008). The removal of algae source DON by conventional water treatment (coagulation - sedimentation - filtration - disinfection) is poor. At present, most domestic water plants are treated by liquid chlorine disinfection. On the one hand, the presence of DON can lead to the increase of chlorine consumption, on the other hand, it also forms toxic N-DBPs as precursors in the chlorination process. (Bellar, et al., 1974; Rook, 2002). Therefore, it is an urgent need for drinking water treatment to study the effective DON removal technology and its mechanism. Because of a wide variety of DON, it is particularly important to select the typical algal source DON as the research object. Amino acids are important components of organic compounds in algae, and are also the main precursors of N-DBPs, which are typical and representative (Chu, et al., 2015; Konstantinou and Albanis, 2004; Uyguner-Demirel and Bekbolet, 2011). Studies have shown that in Lake Taihu, the basic amino acid content is relatively high, and the basic amino acid is difficult to degrade compared to other amino acids under natural conditions (Cheng, et al., 2015; Gong, et al., 2015). Therefore, histidine is selected as a typical target due to its relatively high concentration and high potential to form N-DBPs (Dotson, 2009; Ueno, et al., 1996; Yang, et al., 2012).

Recently, advanced oxidation technology based on sulfate radicals (SO$_4$$^-\cdot$) has achieved much attention from studies on water treatment and in situ chemical oxidation. Compared with OH•, SO$_4$$^-\cdot$ has the characteristics of high redox potential, good stability and high utilization (Rodriguez, et al., 2014). In addition, the advanced oxidation technology of persulfate has become a hot spot in water treatment
research because of its wide application range, rapid reaction speed and high efficiency (Long, et al., 2014; Rodriguez, et al., 2014). Anipsitakis's study shows that Co$^{2+}$ and Fe$^{2+}$ can activate PMS better (Anipsitakis and Dionysiou, 2004). However, the toxicity of Co$^{2+}$ itself has limited its application in drinking water treatment.

In order to further improve the activation ability of Co to PMS and reduce the dissolution of Co, the solid base serves as a Co-carrier which improves the catalytic performance of the active substance Co(OH)$^+$ and restrains the dissolution of Co (<35 μg/L, limiting 1 mg/L, and GB5749-2006 on sanitary standards for drinking water) (Anipsitakis and Dionysiou, 2003; Chuang, et al., 2008). Similarly, hydrotalcite like compounds (LDH), which also belongs to solid bases and have similar functions. For this reason, low supersaturation coprecipitation method was used to optimize the preparation method of CoFe-LDO.

There have been few studies on using CoFe-LDO/PMS system to degrade typical amino acid. However, it is valuable to use CoFe-LDO/PMS system to study the removal of histidine due to the high generation potential of basic amino acids (histidine) as disinfection by-products and poor removal in the conventional treatment of drinking water. The main purpose of our research is: (1) Evaluate the degradation performance of histidine by peroxymonosulfate (PMS) activated by CoFe-LDO composite catalyst in heterogeneous catalytic process; (2) Investigate the effects of CoFe-LDO dosage, PMS dosage, and pH on the degradation of histidine; (3) Propose a possible reaction mechanism of histidine in the CoFe-LDO/PMS system; (4) Illustrate the main reactive substance and identify the intermediates via conducting electron spin resonance (ESR) experiments and high-performance liquid chromatography-mass spectrometry (HPLC-MS); (5) Explore the formation potential of the N-DBPs by Gas chromatography (GC) experiments.

2. Material And Methods

2.1 Materials

DCAcAm (98.5%) was obtained from Alfa Aesar (Karlsruhe, Germany). DCAN, Methanol (MeOH, HPLC grade) and DMPO were purchased from Sigma-Aldrich (Oakville, ON, Canada). A sodium hypochlorite solution (active chlorine >5%, Sinopharm Chemical Reagent Co., Ltd., China) was used for preparation free chlorine stock solutions. Oxone and other materials were at least analytical grade and obtained from Sigma-Aldrich Chemical Co., Ltd. (Shanghai, China) unless otherwise noted. Histidine was used because of its great potential for producing haloacetonitriles. Properties of histidine were shown in Table S1.

2.2 CoFe-LDO nanoparticles preparation

The low supersaturated coprecipitation method was used for the preparation of CoFe-LDO. The preparation method was as follows:

Solution A: Co(NO$_3$)$_2$$\cdot$6H$_2$O and Fe(NO$_3$)$_3$$\cdot$9H$_2$O are prepared with molar ratio of Co to Fe =1:1, 2:1, 3:1 and 4:1 and ensure that the sum of Co$^{2+}$ and Fe$^{3+}$ concentration is 1.2mol/L in the 100mL of mixed
Solution B: NaOH and Na$_2$CO$_3$ are weighed according to the ratio of $n$(NaOH): $n$(Na$_2$CO$_3$) =1:2 and the total concentration of NaOH and Na$_2$CO$_3$ is 1.8mol/L in the 100mL of mixed solution.

The solution A and the solution B were added to the beaker with 250mL distilled water and placed in a water bath pot (70°C) with stirring at the same time. and the pH=8.5 of the solution was controlled under the heated stirring at 70°C. The resultant suspensions were aged at 80°C for 48 h, then the product was centrifuged and washed with deionized water until the supernatant was neutral. Finally, the collected catalysts were dried at 80°C and calcined 3h in a muffle furnace at 550°C to get the corresponding compound oxide catalyst (CoFe-LDO).

2.3 Analytical methods

NO$_3^-$, NO$_2^-$, and NH$_4^+$ concentrations were determined using standard methods. DON content was calculated by subtracting the sum of dissolved inorganic nitrogen species from total dissolved nitrogen (TDN) content measured in experiment (Eqn.1).

$$\text{DON (mg/L)} = \text{TDN} - (\text{NO}_3^-\text{N} + \text{NO}_2^-\text{N} + \text{NH}_4^+\text{N}) \quad (1)$$

Amino acids were analyzed by high performance liquid chromatography (HPLC) using the derivatization of 6-aminoquinolyl-N-hydroxysuccinimidyl (AQC) (Díaz, et al., 1996). In the present study, we established a method for the determination of amino acid oxidation products using HPLC-MS. Gas chromatography were used to determine the formation potential of the N-DBPs (Chu, et al., 2016; Liew, et al., 2012). Specific experimental conditions for HPLC, HPLC-MS and GC were given in text S1. Electron spin resonance (ESR) were carried out on a Bruker EMX-E spectrometer (Germany) using DMPO as the spin-trapping agent. The surface morphologies of CoFe-LDO were analyzed by scanning electron microscopy (SEM; Hitachi-S4800; Japan). The surface functional groups were detected by a Fourier transform infrared (FTIR) spectrometer (Tensor 27; Bruker, Germany).

2.4 CoFe-LDO/PMS and chlorination treatment

For the catalytic oxidation experiments using the CoFe-LDO/PMS system, batch experiments were carried out in 250 mL glass brown bottles evenly placed in water bath shaker (190 rpm) at 25 °C. CoFe-LDO was added to 200 mL amino acid solution (10 mg/L) and stirred for 60 min to achieve degradation equilibrium. Then the reaction was then triggered by adding PMS. 0.5 mL samples were collected from each bottle at designated time intervals and immediately filtered through a 0.22 µm membrane. The sample bottles were pre-filled with 0.2 mL of MeOH solution to extinguish any residual oxidation caused by PMS. Residual water samples were used for DON testing.

After different time CoFe-LDO/PMS treatment, the water samples were filtered into the brown glass bottle, and the water samples were stored under the condition of pH 4.5-5.5. Before the experiment, the chlorine
reaction was carried out at room temperature, and the amount of chlorine added was obtained by the following formula: \( \text{Cl}_2 \ (\text{mg/L}) = 3 \times \text{DOC} \ (\text{mg/L}) + 7.6 \times \text{NH}_4^+ - \text{N} \ (\text{mg/L}) + 10 \), which was placed in the dark place to fully react 24h.

After 24h chlorination experiment, the disinfectant residual was quenched with a stoichiometric amount of ascorbic acid and was analyzed as soon as possible. All experiments were performed in triplicate. Data were reported as mean ± standard deviation (SD).

3. Results And Discussion

3.1 Characterization of CoFe-LDO

3.1.1 SEM analysis

SEM images of CoFe-LDO catalysts before and after catalytic degradation of amino acids were shown in Fig. 1 (a) and (b), respectively. SEM was carried out to investigate the morphology of the material surface. It could be seen that before the reaction, the catalyst CoFe-LDO was flaky, and its particle size was about 100 nm. It had sponge-like porous network structure, which was composed of interconnected nanoparticles. After the reaction, the flake part was destroyed to granular and the particle size was about 50nm. This phenomenon may lead to the reduction of the activity of the catalyst and influence the catalytic efficiency.

3.1.2 FTIR spectroscopy

The catalyst CoFe-LDO was characterized by FTIR in Fig. 1 (c) so as to test the structure of the sample surface. The absorption peak near 1633 cm\(^{-1}\) is caused by the vibration of the H-OH group (Jing, et al., 2019), the absorption peak of 834 cm\(^{-1}\) and 1383 cm\(^{-1}\) was ascribed to CO\(_3^{2-}\) (Zeng, et al., 2021).

Compared with the FTIR spectra of CoFe-LDH in the literature (Li, et al., 2017), the absorption peak of CO\(_3^{2-}\) is reduced and the peak was lower than the M-O absorption peak at 556 cm\(^{-1}\), indicating that after calcination, the material was converted to CoFe-LDO.

3.1.3 XRD

The X ray diffraction pattern can be used to characterize the crystallinity, regularity of the catalyst from Fig. 1 (d). The samples had diffraction peaks at \( \theta = 31.27^\circ, 36.85^\circ, 44.80^\circ, 55.6^\circ, 59.3^\circ \) and \( 74.1^\circ \), which were in accordance with Co\(_3\)O\(_4\) (JCPDS 43-1004) standard cards, and the diffraction peaks of \( \theta \) at 33.1°, 39.2° and 43.5° matched the Fe\(_2\)O\(_3\) (JCPDS 39-1346) crystal. The high intensity of the diffraction peak, which proved that the catalyst had good crystallinity, and there was no other diffraction peak, indicating the high purity of the catalyst.

3.1.4 XPS
The main purpose of the XPS analysis was to determine the chemical composition of the material surface. The XPS spectrum of the catalyst CoFe-LDO was displayed in Fig. 1 (e)-(g). According to the full pattern of Fig. 1 (g), there were three predominant elements of Co, Fe and O on the surface of the catalyst. The peak Co$_{2p3/2}$ was located at 778.9eV, and the peak Co$_{2p1/2}$ was located at 794.1eV in Fig. 1 (f), which was similar to the binding energy of standard map CoO and Co$_3$O$_4$ (standard value Co$_{2p3/2}$ (780.3eV) and Co$_{2p1/2}$ (795.9eV))(Jang, et al., 2013). Meanwhile, Co mainly existed in the form of Co$_3$O$_4$. The peak Fe$_{2p3/2}$ was located at 709.3eV, and the peak Fe$_{2p1/2}$ was located at 721.5eV, which was consistent with the binding energy of standard Fe$_2$O$_3$ (standard value Fe$_{2p3/2}$ (711.3eV) and Fe$_{2p1/2}$ (724.3eV)) as shown in Fig. 1 (e)(Yamashita and Hayes, 2008), consequently Fe was mainly in the form of Fe$_2$O$_3$.

3.1.5 Zeta potential

Zeta potential, as an important parameter for the particle stability in the reaction or colloidal suspension was tested. The catalyst was generally uniformly dispersed in the water, so that each catalyst particles had full contact and reaction in solution. As seen in Fig. 1 (h), the isoelectric point of CoFe-LDO was approximately 10. Therefore, the catalyst could be dispersed steadily in the solution with initial pH between 4.0 to 9.0.

3.2 Degradation efficiency

To evaluate the performance of degradation of histidine by CoFe-LDO/PMS system, several experiments including CoFe-LDO alone and PMS alone systems were conducted during 60 min by using 0.1 g/L CoFe-LDO, 1.5 mM PMS. As shown in Fig. 6, the concentration of histidine decreased from 10 mg/L to 3.9 mg/L during 60 min in the CoFe-LDO/PMS system. In contrast, almost no removal occurred in either Fe$_2$O$_3$|$Co_3$O$_4$|$CoFe-LDO or PMS alone system. The sorting of the degradation effects of amino acids and DON in the composite system was CoFe-LDO/PMS $>$ Fe$_3$O$_4$/PMS $>$ Co$_3$O$_4$/PMS $>$ Fe$_2$O$_3$/PMS. The result convincingly revealed that the combination of CoFe-LDO and PMS was conducive to the removal of histidine in aqueous solution and CoFe-LDO could be a favorable catalyst for PMS activation during the histidine removal process. Furthermore, the DON removal efficiency was slightly lower than that of histidine, which was explained by incomplete mineralization of amino acids into other organic nitrogen substances.

3.3 Influence of various factors

3.3.1 CoFe-LDO and PMS dosage

The initial conditions were as follows: the temperature was 25°C, the initial concentration of histidine was 10 mg/L, respectively. The results were shown in Fig. 3.

As seen in Fig. 3 (a), the removal of DON decreased with the increasing of the dosage of CoFe-LDO. The DON removal reached the highest when the dosage of catalyst CoFe-LDO was 0.04 g/L. This was because when the catalyst dosage increases to a certain extent, the catalyst was prone to agglomeration,
resulting in the reduction of contact area with the target and the effective reaction site of the catalyst. These will slow down the reaction rate. Therefore, the optimum dosage of catalyst CoFe-LDO was 0.04 g/L.

The effect of PMS dosage on the histidine degradation was presented in Fig. 3 (b). Generally, with the increase of the concentration of PMS, the removal of DON showed the tendency to rise and then fall. It was observed that the increase of PMS dose from 0.2 mmol/L to 0.5 mmol/L could significantly enhance DON removal, the concentration of DON dropped from 1.65 mg/L to 0.78 mg/L; while with the PMS concentration further increased from 1.5 mmol/L to 2 mmol/L, the DON concentration increased to 1.2 mg/L.

This was because the active site of the catalyst was sufficient when the concentration of PMS was low, the increase of PMS concentration in the reaction system could produce more $\text{SO}_4^{2-}\cdot$, so as to improve the removal rate of DON. However, the active sites of COFE-LDO surface equivalent amount had been saturated when the PMS concentration was high, and then the excessive PMS could not be involved in the reaction to produce more $\text{SO}_4^{2-}\cdot$ at this time. Similar inhibition appeared in the literature (Chen, et al., 2008).

### 3.3.2 Initial pH

It was reported that $\text{SO}_4^{2-}\cdot$ based AOPs could work in a wide range pH compared with Fenton oxidation process. Thus, for purpose of evaluating the influence of different initial pH on DON removal, a series of experiments were carried out with pH ranging from 4.0 to 9.0. The effect of pH value on the histidine degradation was presented in Fig. 3 (c). It could be seen that DON removal increased first and then decreased with the increase of pH value. The removal of DON was up to 60% when pH value reached to 8. According to the zeta potential, the isoelectric point of CoFe-LDO was 10.0 and that of histidine was 7.59. Due to the surface properties of CoFe-LDO, net positive charge would be shown on the surface of CoFe-LDO when the solution pH was lower than 10. When the pH value was lower than 8, both the catalyst surface and histidine were positively charged, which reduced the probability of collision due to electrostatic repulsion. However, when the alkalinity of the solution was more than 10, the catalyst surface was negatively charged to repel negative ions produced by PMS dissolution, which led to the decreased removal of DON. Moreover, it was favorable for the formation of hydrogen bond between $\text{H}^+$ and O which produced by the dissolution of PMS in the acidic environment (Cai, et al., 2020), thereby inhibiting the catalytic oxidation. In addition, the $\text{SO}_4^{2-}\cdot$ would react with the $\text{OH}^-$ to form the $\cdot\text{OH}$ in the alkaline condition. The redox potential of hydroxyl radical was lower than that of sulfate radical, which affected the degradation. When the pH value was about 8, the catalyst surface was positively charged while histidine was negatively charged. The catalyst and oxidant collided due to electrostatic attraction and the degradation efficiency was greatly improved, which was consistent with the results shown in the Fig. 3 (c).

### 3.4 Stability and reusability of CoFe-LDO


In order to verify the stability and reutilization of CoFe-LDO catalyst, the leaching of Co and Fe was detected by inductively coupled plasma chromatography (ICP-OES), and the catalyst CoFe-LDO was investigated after four successive runs. It could be seen from table S2, the leaching of Co and Fe were 0.028 mg/L (<0.1 mg/L) and 0.015 mg/L (<0.3 mg/L) respectively, which were in accord with the limit concentration in the drinking water sanitation standard. It confirmed that CoFe-LDO was stable and reusable in the process of reaction. Moreover, the CoFe-LDO catalysts were collected and recovered for four times. As seen in Fig. 3 (d), the removal efficiency was 60%, 56%, 52% and 47% for the first, second, third and fourth time, respectively. There were two reasons for the reduction of DON removal efficiency: (1) a fraction of CoFe-LDO catalysts was lost with water in the process of catalytic and recovery washing, resulting in mass reduction; (2) according to the results of ICP-OES, it was possible that the amount of cobalt and iron ions decreased after 4 cycles of recycling, which made the proportion of homogeneous reactions in heterogeneous catalysis decrease, resulting in the reduction of DON efficiency.

3.5 Proposed mechanisms of CoFe-LDO/PMS system

3.5.1 Existence of free radicals

For purpose of further identifying the free radicals produced in the system, ESR was used to qualitatively detect the class of free radicals. Fig. 4 indicated that in the presence of DMPO, free radicals were not detected in separate catalytic materials. The typical peaks of 1:2:2:1 with low peak value were detected in the Fe$_2$O$_3$/PMS system, indicating that hydroxyl radicals were generated from the Fe$_2$O$_3$/PMS system. In the Co$_3$O$_4$/PMS reaction system, both OH$^•$ and SO$_4$$^•$ were detected at the same time, and the peak value was higher than that of Fe$_2$O$_3$/PMS system. In addition, DMPO-X was detected in CoFe-LDO/PMS, and the peak intensity ratio of ESR spectrum was 1:2:1:2:1:2:1. It was revealed that DMPO-X was produced by direct oxidation of single electron source (Wang, et al., 2015).

In order to explore the main free radicals in CoFe-LDO/PMS system, methanol (MeOH) and tert butyl alcohol (TBA) were used as quenching agents in this study. Methanol (MeOH) was an alcohol-containing α-H, which could quickly quench ·OH and SO$_4$$^•$ by reacting with them. Tert-butyl alcohol (TBA) did not contain α-H, and it could only react rapidly with ·OH, while its reaction with SO$_4$$^•$ was much slower (Xie, et al., 2015). The result of the quenching of free radicals was shown in Fig. 5. The content of sulfate radical accounted for a high proportion in the total free radical. The removal efficiency reached 60% without quenching agent after 1 h. Under the conditions of 0.02 M TBA and 0.02 M MeOH respectively, the removal of DON decreased by 10% and 30%, respectively. The reduction of DON removal was substantial in the presence of MeOH compared with TBA, indicating that SO$_4$$^•$ as oxidizing species were mainly formed during the CoFe-LDO/PMS system.

3.5.2 Degradation pathway

The concentrations of total dissolved nitrogen (TDN), ammonium nitrogen (NH$_4^+$-N), nitrite nitrogen (NO$_3^-$-N), and nitrate nitrogen (NO$_2^-$-N) were determined to confirm the oxidation extent of DON in the different
reaction time. The results were shown in Fig. 6.

It was shown that the main categories of nitrogen had different variation tendency due to the degradation pathway involved in the reaction. It was obvious that the concentration of DON decreased within 60 minutes, while the concentration of NH$_4^+$ increased and the content of TN and NO$_3^-$ remained unchanged during the whole oxidation process. According to the variation value of DON and NH$_4^+$ (1.65 mg/L vs. 0.67 mg/L and 0.043 mg/L vs. 0.78 mg/L), it was found that the increase of the NH$_4^+$ was caused by the oxidation of histidine, and NH$_4^+$ was not converted to nitrogen at last. It was because that the reaction system was a multiphase catalytic oxidation reaction, which was the reaction of transition metal ions to activate persulfate to produce free radicals to oxidize the target. And there was no mutual transformation between NH$_4^+$ and NO$_3^-$ during the reaction process.

According to the previous study (Chen, et al., 2019; Chen, et al., 2020), the mechanism of DON degradation in CoFe-LDO/PMS system could be described as follows:

![Diagram of DON degradation mechanism]

Co$^{2+}$ + HSO$_5^-$ $\rightarrow$ Co$^{3+}$ + SO$_4^{2-}$ + OH$^-$

Co$^{3+}$ + HSO$_5^-$ $\rightarrow$ Co$^{2+}$ + SO$_5^{2-}$ + H$^+$

Fe$^{3+}$ + HSO$_5^-$ $\rightarrow$ Fe$^{2+}$ + SO$_5^{2-}$ + H$^+$

Fe$^{2+}$ + HSO$_5^-$ $\rightarrow$ Fe$^{3+}$ + SO$_4^{2-}$ + OH$^-$

Fe$^{2+}$ + Co$^{3+}$ $\rightarrow$ Fe$^{3+}$ + Co$^{2+}$

Fe$^{3+}$ + e$^-$ $\rightarrow$ Fe$^{2+}$ E$^0$=0.77V

Co$^{3+}$ + e$^-$ $\rightarrow$ Co$^{2+}$ E$^0$=1.81V
SO₄⁻• + H₂O → SO₄²⁻ + •OH + H⁺

DON + SO₄⁻• + •OH + SO₅⁻• + H₂O → NH₄⁺ + OH⁻ + Intermediate products

According to the reaction mechanism, it could be found that Co³⁺ and Co²⁺ were converted into each other through the reaction with persulfate, which was the same with Fe²⁺ and Fe³⁺. Co³⁺ was more likely to oxidize Fe²⁺ to Fe³⁺ in the system due to the stronger oxidation of Co³⁺ (E₀=1.81V), which led to the change of Co³⁺ to Co²⁺. It might be difficult to form the effective cyclic transformation from Fe³⁺ to Fe²⁺ due to its low redox potential.

In addition, the degradation intermediates of histidine oxidation were identified by HPLC-MS. The results were shown in Fig. S1.

Fig. S1 investigated that the main mass-to-charge ratios (m/z) for mass spectrum of histidine after catalytic treatment are 154.0, 139.9, 112.9 and 222.0. The molecular formula of these substances can be tentatively determined according to the m/z and structure of amino acids (Table 1).

Table 1 Identification of histidine oxidation products

| Amino acid | Monitoring ion | m/z   | Molecular formula          |
|------------|----------------|-------|----------------------------|
| Histidine  | [M+Na]⁺        | 154.0 | C₆H₉N₃O₂                   |
|            | [M+H]⁺         | 139.9 | C₆H₉N₃O                   |
|            | [M+H]⁺         | 112.9 | C₅H₆N₂O                   |
|            | [M+H]⁺         | 222.0 | Co²⁺–Xaa complex           |

Referring to the molecular weight in Table 1, it is presumed that the transformation process follows the following rules. It can be seen from Fig. 15 that after the catalytic degradation of 60min by CoFe-LDO/PMS system, histidine degrades in two ways under the action of OH• and SO₄⁻•. In the pathway (a), amino acid carboxyl groups are protonated, and Co²⁺ and amino acids react to form Co²⁺–Xaa complexes. The Co²⁺ in the Co²⁺ - Xaa complex was oxidized by HSO₅⁻ to Co³⁺ - Xaa complex, generating SO₄⁻• and SO₅⁻• at the same time. A hydrogen atom was extracted from the α-carbon of amino acid to form an amino acid radical centered on the carbon atom by SO₄⁻•, which was generated near the amino acid of the complex. The free radical reacted with Co³⁺ in the complex and generated Co²⁺ and amino acid derivatives, which produced spontaneous hydrolysis of alpha ketoacids and NH₄⁺. In the pathway (b), the anions were oxidized to carboxyl groups. Here, the alpha amino radical could be converted to alpha amino carbocation, thus forming protonated imines. In the end, aldehydes could be produced by hydrolysis.

3.6 N-DBPs formation and intermediate products
Fig. 8 revealed the formation of N-DBPs during chlorination of histidine oxidized by persulfate in the CoFe-LDO/PMS system. The concentration of DCAN decreased with the increasing of the reaction time. However, at the same time, the formation potential of DCAcAm increased first and then decreased, which was mainly due to the varying structure of R group.

The side chains of histidine contained imidazole ring, which had certain aromaticity and was prone to carry out electrophilic substitution reaction and ring opening reaction. There were two N atoms in imidazole heterocycle, which might be converted to DCAN by ring opening reaction. DCAN hydrolyzed to produce DCAcAm and the precursor of DCAcAm decreased. Finally, the reaction of DCAcAm formation was complete, and because of its own instability, hence it could be seen that the formation of DCAcAm during chlorination of histidine shows first increased and then decreased (Chu, et al., 2014; Yimeng, et al., 2017).

Moreover, it could be seen from Fig. S2 that the variation trend of intermediate products of the mass to charge ratio at different time accordance with histidine chlorination to DCAcAm. According to the result of Fig. 7 and Fig. S2, it was predicted that \( \text{and} \) the two intermediate products might be the source of increasing the concentration of histidine chloride to DCAcAm.

4. Conclusions

In this study, CoFe-LDO is used as a heterogeneous catalyst to activate PMS for degradation of amino acid as the precursor of N-DBPs. The results of experiments apparently showed that CoFe-LDO could effectively catalyze PMS to remove DON. The catalyst was stable and reusable without any significant leaching, which provided great significance for practical applications. ESR results showed that hydroxyl radical (OH•) and sulfate radical (SO\(_4^{−}\)) were detected and SO\(_4^{−}\) was dominant in the CoFe-LDO/PMS system. Therefore, the degradation of DON was ascribed to the free radicals. After the chlorination of histidine, the formation potential of DCAN decreased, while the formation potential of DCAcAm first increased and then decreased. The unstable changes of DCAcAm were mainly caused by the increase of the generation potential of N-DBP of histidine degradation intermediate products. Although the concentrations of DON and amino acids were both removed, the labile changes of N-DBPs still needed to be further controlled.

Declarations

Ethics approval and consent to participate
Not applicable

Consent for publication

Not applicable

Availability of data and materials

Not applicable

Competing interests

The authors declare that they have no competing interests

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Authors' contributions

YL: Methodology, Validation, Formal analysis, Data Curation, Writing - Original Draft, Writing - Review & Editing. CL: Conceptualization, Methodology, Resources, Supervision, Writing - Review & Editing. MZ: Writing - Review & Editing

All co-authors contributed in all parts of the manuscript.

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**Figures**
Figure 1

(a) and (b) SEM images of CoFe-LDO before and after use, respectively (×50k); (c) FTIR of CoFe-LDO; (d) XRD of CoFe-LDO; (e) Fe 2p core level of XPS spectra; (f) Co 2p core level of XPS spectra; (g) full-range scan of XPS spectra; (h) Zeta potential of CoFe-LDO
Figure 2

Changes in histidine and DON concentration in different reaction systems: 10 mg/L histidine; 0.1 g/L CoFe-LDO; 1.5 mM PMS; 190 r/min.
Figure 3

(a) Effect of CoFe-LDO dosage (0.04-0.5 g/L CoFe-LDO, 1.5 mmol/L PMS); (b) Effect of PMS dosage (0.04 g/L CoFe-LDO; 0.2-1.5 mmol/L PMS); (c) Effect of pH value (0.04 g/L CoFe-LDO; 0.5 mmol/L PMS); (d) Effect of catalyst cycles on the degradation of DON (10 mg/L histidine; 0.04 g/L CoFe-LDO; 0.5 mmol/L PMS)

Figure 4

ESR spectra obtained for (a) Separate catalyst; (b) Fe2O3/PMS; (c) Co3O4/PMS; (d) CoFe-LDO/PMS ([DMPO] = 0.1 M)
Figure 5

Effect of different free radical scavengers on the degradation of histidine (10 mg/L histidine; 0.04 g/L CoFe-LDO; 0.5 mmol/LPMS; 190 r/min)
Figure 6

Changes of TDN, NO₃⁻, NH₄⁺ in the Fe₃O₄/PMS system (10 mg/L histidine; 0.04 g/L CoFe-LDO; 0.5 mmol/L PMS; 190 r/min)
Figure 7

Degradation pathway of histidine in the CoFe-LDO/PMS system
Figure 8

Formation of two N-DBPs (DCAN and DCAcAm) during chlorination of Histidine in the CoFe-LDO/PMS system (10 mg/L histidine; 0.04 g/L CoFe-LDO; 0.5 mmol/L PMS)

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