

Catalytic ozonation of trace nitrobenzene in water with synthetic goethite

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Abstract

This paper aims to reveal the effectiveness and the mechanism of catalytic ozonation with synthetic goethite (FeOOH) for the degradation of recalcitrant pollutants that cannot form surface complexes with surface metal sites of the catalyst in water. Nitrobenzene (NB) was used as the target pollutant. Results show that catalytic ozonation with FeOOH can substantially enhance NB degradation compared with ozonation alone. Scavenging test and quantification of the oxidation intermediates of NB reveal that the improved NB degradation is due to the enhanced hydroxyl radical generation. The activity of the FeOOH in water is related to its highly hydroxylated surfaces. The surface hydroxyl groups on the FeOOH in water are active sites in the catalytic ozonation. Moreover, the properties of the surface hydroxyl groups such as their quantity and charge states seem to have close relationship with the activity of the FeOOH in the catalytic ozonation of NB. We finally proposed a pathway that the uncharged surface hydroxyl groups on the FeOOH in water can induce aqueous ozone decomposition to generate hydroxyl radicals.

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1. Introduction

Recalcitrant organic pollutants are relatively difficult to be removed from water with traditional water treatment processes. Some of these pollutants are even difficult to be efficiently degraded by strong oxidants like ozone [1]. Advanced oxidation processes such as O_3/H_2O_2 , O_3/UV , and $O_3/UV/H_2O_2$, have been developed to improve the destruction of these pollutants with enhanced hydroxyl radical generation. Catalytic ozonation with heterogeneous catalysts is another alternative to improve the degradation of the recalcitrant pollutants. The catalysts are usually MnO_2 [2–5], TiO_2 [6,7], Al_2O_3 [8–10], noble metals [11], and mixed metal oxides [12–17]. In addition to its high activity in catalytic ozonation under neutral pH condition of water treatment, it is also necessary for the catalyst that its dissolution is very weak and the released metal ions pose no health problem to the water.

Ferric hydroxides are characterized by their extremely weak dissolution ($K_{sp} = 3 \times 10^{-39}$) in water. Moreover, the trace Fe^{3+} dissolved into water is nontoxic. Ferric hydroxides have been widely used as adsorbents and ion exchangers in water [18]. Up to date, there are only limited studies on their application as catalysts for water treatment. Commercial goethite (α -FeOOH) were found to be able to promote the oxidation of some contaminants by H_2O_2 [19–21], which suggests that goethite would be a promising catalyst for pollutant abatement. Lim et al. [22] noticed that the commercial goethite promoted the degradation of *p*-chlorobenzoic acid (*p*-CBA) during ozonation. Park et al. [23] further discussed the possible mechanism of the improved degradation of *p*-CBA by the commercial goethite. However, the researchers had not managed to remove the impurities from the commercial goethite before reactions. Alkalis, physically adsorbed by the goethite in its aging step of preparation, usually remain on the commercial product because of incompletely rinsing. For example, Park et al. [23] had mentioned that the water pH increased from 3 to 8 when 2 g of the commercial goethite was introduced into 1 L of acidified distilled water. Although the reaction solutions were buffered, the alkalis on the catalyst surface and at the water/catalyst interface still can react with ozone

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producing hydroxyl radicals [1], which makes it difficult to find out the actual effectiveness of catalytic ozonation with goethite and the catalysis pathway. Therefore, it is crucial to remove the adsorbed alkalis from the goethite to better reveal its activity in catalytic ozonation of refractory organic pollutants as well as the function of its surface sites in the catalytic ozonation.

In this study, goethite (FeOOH) particles were carefully synthesized to remove any alkalis that might be adsorbed during preparation. Nitrobenzene (NB) was selected as the target organic pollutant because it reacts slowly with molecular ozone ($k_{O_3, NB} = 0.09 \text{ M}^{-1} \text{ s}^{-1}$) [24], and also because it cannot form surface complexes with FeOOH and has very weak adsorption on the hydroxylated FeOOH surface. The objective is to reveal the effectiveness of FeOOH in improving the ozonation of NB and possible functions that surface hydroxyl groups on FeOOH in water played in the catalytic ozonation.

2. Experimental

2.1. Catalysts

FeOOH was prepared according to a method described by Kandori et al. [25]. Fe(OH)₃ was obtained by quickly adding 200 mL of 1 mol L⁻¹ NaOH solution into 200 mL of 0.25 mol L⁻¹ Fe(NO₃)₃ with magnetic stirring. The suspension was aged at 60 °C and pH 12 for over 48 h. Then, the precipitate was repeatedly rinsed with boiled Milli-Q water until the pH of leachate remained constant in three consecutive rinses. The precipitate was further dried at 70 °C for 16 h and grinded afterwards. Particles with diameters ranging from 0.075 to 0.3 mm were used in this experiment.

Other oxides of copper, cobalt, iron, nickel, and manganese were obtained by the calcination of the nitrates at 450 °C for 2 h. Grinded particles with diameters ranging from 0.075 to 0.3 mm were used.

2.2. Experimental procedure

Experiments were carried out in batch mode with circulated water bath. Ozone was generated from dried oxygen with a laboratory ozone generator (XFZ-58I, Tsinghua Tongli). The ozone gas was introduced into distilled water through a silica dispenser in a cylindrical glass reactor with a diameter of 6 cm and a volume of 1000 mL. The gas flow was switched off when aqueous ozone reached a steady concentration. Then, the NB stock solution and the catalyst were quickly added into the ozone bearing water, and the reaction was started with magnetic stirring. The initial aqueous ozone concentration can be controlled through changing the electric current of the ozone generator. Phosphate buffer of 1.0 mmol L⁻¹ was used in most of the experiments, which was sufficient to keep the pH constant during the reactions. Acidified Na₂SO₃ solution was used to quench the residual ozone in the samples. Then, the samples were instantly filtered with glass fiber filters, which had no influence on the NB concentration. In the case of quantification of the NB intermediates, we used a high initial NB concentration (19.7 μmol L⁻¹) dissolved in Milli-Q water.

2.3. Analysis

2.3.1. Ozone, nitrobenzene, and oxidation intermediates of NB

Aqueous ozone concentration was measured with the indigo method [26]. Examination of NB in water followed a method described in a previous paper [5]. The relative standard deviation (R.S.D.) of this method was less than 5% for NB. Quantification of the oxidation intermediates of NB was carried out on a Waters HPLC system (717 plus Autosampler, 1525 Binary Pump, and 2478 Dual λ Absorbance Detector). A Symmetry C18 column (3.9 mm × 150 mm, Waters) was used to separate and quantify aromatic fractions of the intermediates, while an Atlantis dC18 column (4.6 mm × 250 mm, Waters) was used to separate and quantify carboxylic fractions. For the examination of aromatic intermediates, the detection wavelength was 280 nm, the column temperature was set at 40 °C, and the eluent consisted of a 70:30 (phosphate buffer solution (320 μL H₃PO₄ in 1 L Milli-Q water) /methanol) isocratic mixture. For the examination of carboxylic intermediates, the wavelength was set at 220 nm, the column temperature was 30 °C, and the eluent was a mixture of phosphate buffer solution (320 μL H₃PO₄ in 1 L Milli-Q water) and acetonitrile with a volume ratio of 80:20.

2.3.2. Surface characterization

BET surface area, pore volume, and average pore size of the catalyst were obtained on a surface area and porosity analyzer (ASAP 2020, Micromeritics). The density of surface hydroxyl groups, expressed in mmol per unit gram, was measured according to a method described by Tamara and Tanaka [27]. The pH_{pzc} (pH of point-of-zero charge) of the catalyst was measured with a powder addition method [28].

2.3.3. Crystallographic confirmation

Thermogravimetry and differential thermal analysis (TG-DTA) for the dried FeOOH particle was carried out on a Rigaku TAS 100 thermal analyzer with temperature rising rate of 10 °C min⁻¹. Crystallite structures were confirmed with a Rigaku D/MAX-rA powder diffractometer (XRD) using Cu Kα radiations.

3. Results and discussion

3.1. Effectiveness in improving NB degradation

Fig. 1 shows the degradation of NB in ozonation, catalytic ozonation, and adsorption by FeOOH. It is clear that ozonation degraded NB slowly except the initial 2 min of the reaction. According to the references [29,30], instantaneous ozone decomposition occurs at the initial phase of ozonation which generates a significant amount of hydroxyl radicals. The NB degradation at the initial phase of ozonation can thus be attributed to the generation of hydroxyl radicals which react quickly with NB at a secondary reaction rate constant of $7.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [31]. Catalytic ozonation with FeOOH degraded 65 percent of NB within 20 min, which is about two times higher than the NB degraded in ozonation alone. In addi-

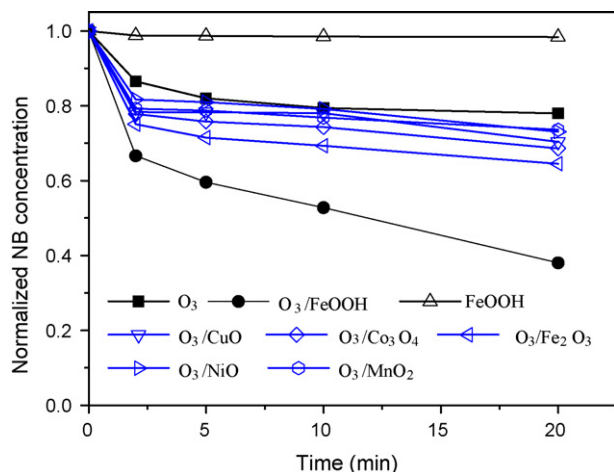


Fig. 1. Degradation of NB in ozonation and catalytic ozonation. $[O_3]_0 = 0.40 \pm 0.02 \text{ mg L}^{-1}$; $[NB]_0 = 0.37 \mu\text{mol L}^{-1}$; FeOOH dose = 100 mg L^{-1} ; 1.0 mmol L^{-1} phosphate buffered pH 6.7; $T = 18^\circ\text{C}$.

tion, only less than 1.6% of the NB can be adsorbed by the FeOOH in this experiment. The results reveal that the FeOOH is quite effective in enhancing the ozonation of NB.

The FeOOH was also compared with other typical catalysts (i.e., CuO, Co_3O_4 , Fe_2O_3 , NiO, and MnO_2) for their effectiveness in catalytic ozonation of NB. Fig. 1 indicates that FeOOH is more effective than these oxides in NB degradation.

The FeOOH was further used repeatedly in the catalytic ozonation in order to find out whether its activity would deplete. The FeOOH particles used in the batch experiment were reclaimed by filtration through a glass fiber filter, dried at 120°C , and reused for different times in the catalytic ozonation. NB degradation rate in the catalytic ozonation decreased slightly as the reuse times of FeOOH increased (Fig. 2). When the FeOOH was reused for seven times, the NB degradation slightly decreased by about 8–11% compared with that when the FeOOH was reused for the first time. It was noted that there was a slight loss of the catalyst during the repeated filtration,

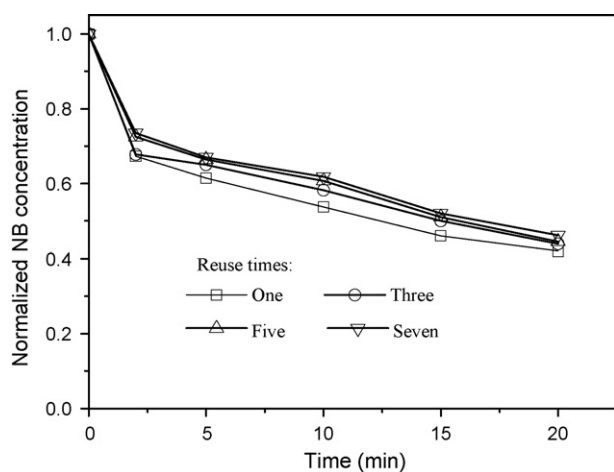


Fig. 2. Influence of consecutive reutilization of FeOOH on NB degradation in catalytic ozonation. $[O_3]_0 = 0.40 \pm 0.02 \text{ mg L}^{-1}$; $[NB]_0 = 0.37 \mu\text{mol L}^{-1}$; FeOOH dose = 200 mg L^{-1} ; 1.0 mmol L^{-1} phosphate buffered pH 6.7; $T = 18^\circ\text{C}$.

which occupied about 10% of the initial dose after seven times of repeated circulation. Then, the weight loss of the FeOOH is likely to be responsible for the slight decrease of NB degradation in the repeated catalytic ozonation. The results indicate that the activity of the FeOOH is relatively stable.

As mentioned in the introduction, if the alkalis adsorbed on FeOOH during preparation were not removed, they can react with ozone at the catalyst surface or catalyst/water interface producing hydroxyl radicals. However, the alkalis will deplete quickly in consecutive ozonation because of dilution as well as their fast reaction with ozone [1]. The stable activity of FeOOH in the repeated catalytic ozonation, therefore, confirms that the alkalis are well removed from the FeOOH in the preparation of the catalyst. The results also reveal that the activity of FeOOH is due to its surface properties but not the alkalis.

3.2. Discussion on the mechanism

3.2.1. Influence of hydroxyl radical scavenger

Since NB adsorption on FeOOH was very weak and the direct ozone oxidation of NB is quite slow, the enhanced NB degradation by the catalytic ozonation is possibly ascribed to accelerated hydroxyl radical generation from ozone. The influences of *tert*-butanol (*t*-BuOH), a well-known hydroxyl radical scavenger, on ozone decomposition and NB degradation for ozonation alone and the catalytic ozonation are shown in Fig. 3a and b. FeOOH enhanced ozone decomposition in water. In the presence of *t*-BuOH, both ozone decomposition rate and NB degradation rate significantly decreased in ozonation and catalytic ozonation. Moreover, the two oxidation processes had similar ozone decomposition rate as well as NB degradation rate in the presence of *t*-BuOH. The *t*-BuOH is characterized by its reaction with hydroxyl radicals [31], generating inert intermediates and consequently quenching aqueous ozone decomposition. The results indicate that the improved NB degradation in the catalytic ozonation is due to the enhanced ozone decomposition which generates more hydroxyl radicals.

3.2.2. Yields of the oxidation intermediates

The intermediates of NB that can be quantified after ozonation and FeOOH-catalyzed ozonation were 4-nitrophenol (4-NP), 3-nitrophenol (3-NP), 2-nitrophenol (2-NP), and oxalic acid. Fig. 4 shows the evolution of the concentrations of these intermediates during ozonation and catalytic ozonation. It is noted that catalytic ozonation produced the same kinds of intermediates with ozonation alone. Furthermore, the yields of the intermediates in catalytic ozonation are higher than those in ozonation alone. According to Hoigné and Bader [24], the nitrophenols are the products that hydroxyl radicals react with NB by means of addition reactions. Oxalic acid is formed in the direct oxidation of the nitrophenols by molecular ozone [32]. The results indicate that the catalytic ozonation follows a similar oxidation pathway with ozonation, i.e. hydroxyl radical oxidation in combination with direct oxidation by molecular ozone. The enhanced accumulation of the intermediates in the catalytic ozonation also indicates that the FeOOH promotes NB degradation through the enhanced hydroxyl radical generation.

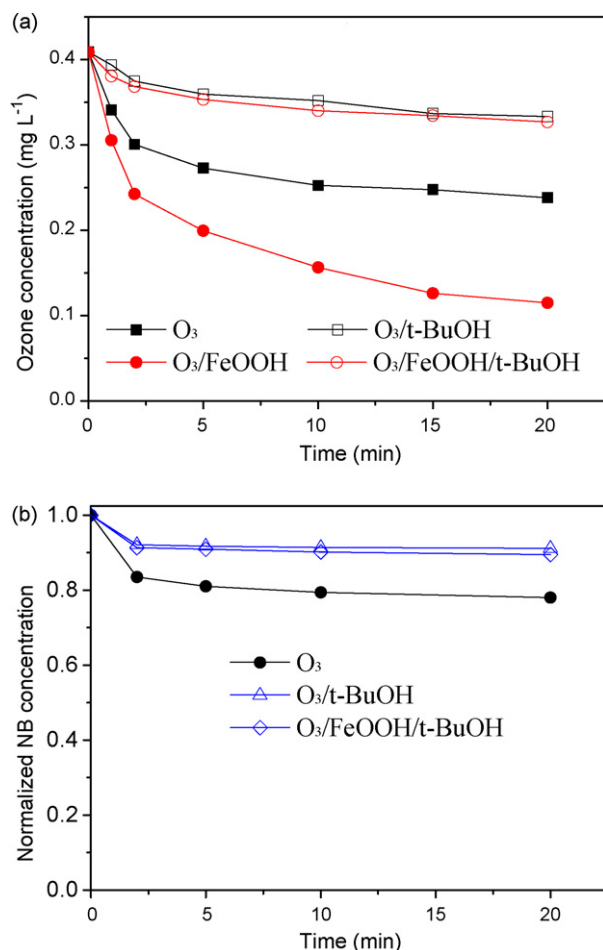


Fig. 3. Influence of t-BuOH on ozone decomposition (a) and NB degradation (b). $[O_3]_0 = 0.40 \pm 0.02 \text{ mg L}^{-1}$; $[NB]_0 = 0.37 \mu\text{mol L}^{-1}$; $[t\text{-BuOH}]_0 = 50 \text{ mg L}^{-1}$; FeOOH dose = 200 mg L^{-1} ; 1.0 mmol L^{-1} phosphate buffered pH 6.7; $T = 18^\circ \text{C}$.

In addition, the total organic carbon (TOC) of the NB solution was nearly not reduced after either ozonation or catalytic ozonation (not shown here), which means that the oxalic acid is difficult to be mineralized by molecular ozone and hydroxyl radicals under the experimental conditions here. However, since the intermediates are more biodegradable than NB, the catalytic ozonation combined with a flow-up bio-filtration process will degrade more TOC than the conventional ozonation/bio-filtration process used in water treatment plants.

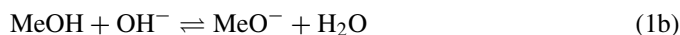
3.2.3. Influence of pH

Water pH is one of the most important factors that influence the efficiency of ozonation, as OH^- can initiate aqueous ozone decomposition to generate hydroxyl radicals. Moreover, the water pH is also an important factor that determines the charge properties of surface hydroxyl groups at oxide/water interface (Eqs. (1a) and (1b)) [33]. The oxide is nearly not surface charged at water pH near its pH_{pzc} . The oxide surface becomes protonated or deprotonated when water pH is below or above its pH_{pzc} .

Table 1
Major characteristics of FeOOH and hematite

	$\alpha\text{-FeOOH}$	$\alpha\text{-Fe}_2\text{O}_3$
BET surface area ($\text{m}^2 \text{g}^{-1}$)	54.78	58.12
Pore volume ($\text{cm}^3 \text{g}^{-1}$) ^a	0.250	0.497
Average pore diameter (nm)	24.5	30.1
Density of surface hydroxyl groups (mmol g^{-1})	0.502	0.380
pH_{pzc}	7.0	8.8

^a Cumulative volume of pores between 1.7 and 300 nm diameter.



The effect of water pH on the catalytic ozonation of NB is depicted in Fig. 5. The catalytic ozonation substantially enhanced NB degradation at pH close to 7. However, the enhancement of NB degradation by the catalytic ozonation compared with ozonation alone significantly decreased as the solution became acidic or basic.

Andreozzi et al. [2] reported that MnO_2 had no activity in catalytic ozonation of oxalic acid when solution pH was higher than its pH_{pzc} . Tong et al. [34] observed similar phenomena when different types of MnO_2 were used to improve the ozonation of sulfosalicylic acid. Furthermore, they both proposed the mechanism of surface complex formation and its subsequent oxidation by aqueous ozone. This mechanism cannot be used to interpret the catalytic ozonation of NB with FeOOH, because surface complexes cannot be formed between NB molecules and the FeOOH. However, the surface charge states determined by the pH_{pzc} and water pH seem also very important to the catalytic ozonation. Since the pH_{pzc} of FeOOH is 7.0 (Table 1), its surface hydroxyl groups would be mostly zero charged near neutral pH and charged under acidic or basic water pH conditions. The results indicate that the zero-charged surfaces of FeOOH are more active than the protonated or deprotonated in promoting hydroxyl radical generation.

3.2.4. Influence of thermal-treatment for FeOOH

Thermal-treatment for FeOOH above certain temperature will make it transform to ferric oxide. Some changes on the properties of the hydroxylated surface in water will subsequently take place. In an effort to understand the function of the hydroxylated surface in the catalytic ozonation of NB, the effect of thermal-pretreatment for FeOOH on its activity was examined.

Thermal-pretreatment at the temperatures of 70, 120, 180, and 240°C had no significant effect on NB degradation in the catalytic ozonation (Fig. 6). However, a significant decrease of NB degradation rate occurred after FeOOH having been pretreated at 300 or 500°C .

Thermal behavior analysis with TG-DTA for FeOOH is shown in Fig. 7. There was a weight loss of 5 percent with the increment of temperature below 200°C , which is caused by the evaporation of water molecules physically adsorbed on the FeOOH. A significant weight loss and an endothermic peak

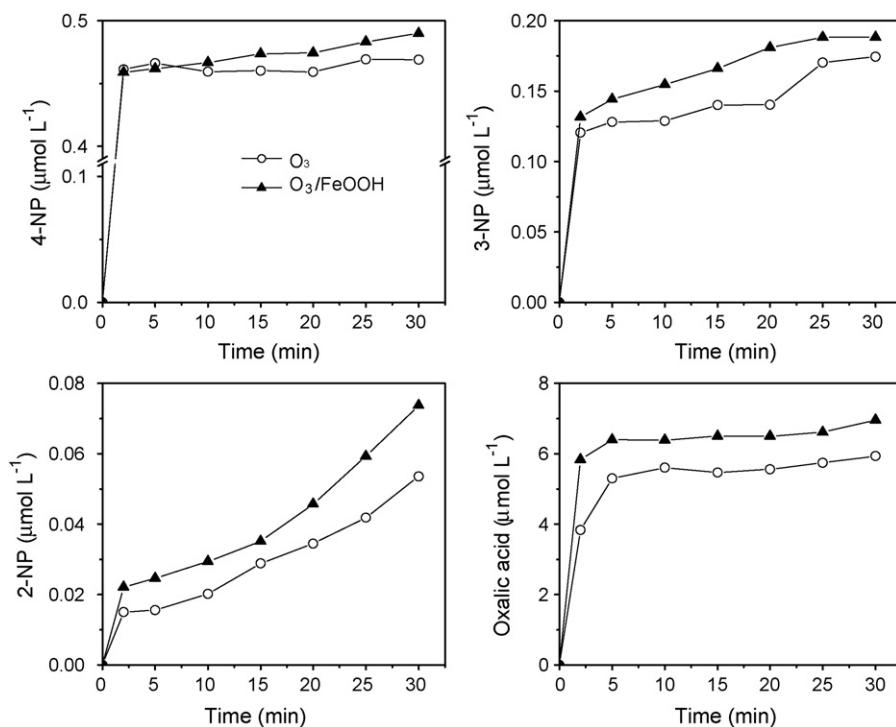


Fig. 4. NB intermediates formed in ozonation and catalytic ozonation. $[O_3]_0 = 10.0 \pm 0.02 \text{ mg L}^{-1}$; $[NB]_0 = 19.7 \mu\text{mol L}^{-1}$; FeOOH dosage = 100 mg L^{-1} ; pH 6.3; $T = 18^\circ\text{C}$.

emerged near 270°C , which can be attributed to the dehydroxylation of the FeOOH and the formation of a new crystalline. The XRD diffractograms (Fig. 8) demonstrate that the FeOOH had transformed to hematite ($\alpha\text{-Fe}_2\text{O}_3$) at the thermal-treatment of 300 or 500°C .

As the FeOOH was transformed to $\alpha\text{-Fe}_2\text{O}_3$ at the thermal-treatment, its BET surface area, pore volume, average pore size, and pH_{pzc} were increased (Table 1). The density of surface hydroxyl groups in water was decreased with the value on FeOOH being 1.32 times of that on $\alpha\text{-Fe}_2\text{O}_3$. The less surface hydroxyl groups on $\alpha\text{-Fe}_2\text{O}_3$ in water would provide fewer chances for the interaction between ozone and the surface

hydroxyl groups. Moreover, the charge properties or acid/base properties of the surface hydroxyl groups were also changed with the increase of pH_{pzc} from 7.0 to 8.8. At pH 6.7 of this study, most of the surface hydroxyl groups on FeOOH were nearly not charged. Most of them on the $\alpha\text{-Fe}_2\text{O}_3$, however, would be positively charged (protonated) because of its much higher pH_{pzc} value than the water pH. Therefore, the decrease of the catalytic activity as the FeOOH was transformed to $\alpha\text{-Fe}_2\text{O}_3$ possibly can be ascribed to two reasons: (1) the decrease of surface hydroxyl groups' quantity; and (2) the increase in the proportion of protonated surface hydroxyl groups.

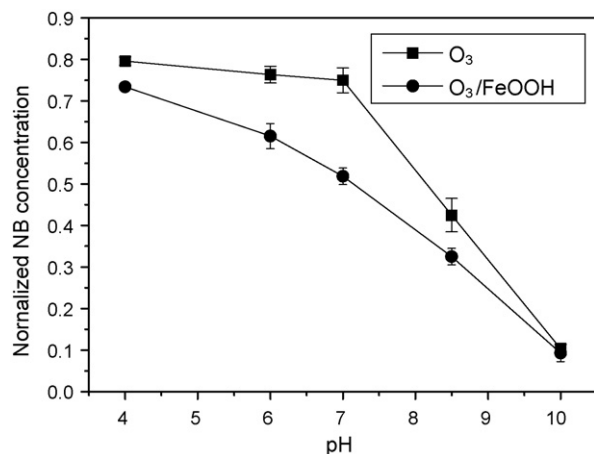


Fig. 5. Influence of pH on NB degradation. $[O_3]_0 = 0.40 \pm 0.02 \text{ mg L}^{-1}$; $[NB]_0 = 0.37 \mu\text{mol L}^{-1}$; FeOOH dose = 500 mg L^{-1} ; 1.0 mmol L^{-1} phosphate buffered pH 6.7; $T = 18^\circ\text{C}$; reaction time of 10 min.

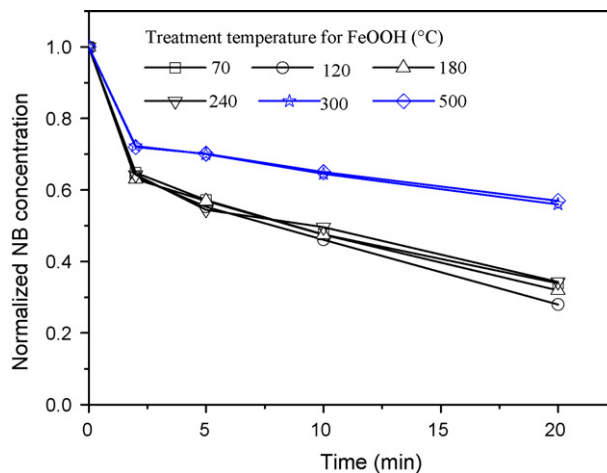


Fig. 6. Influence of thermal-pretreatment for FeOOH on catalytic ozonation of NB. $[O_3]_0 = 0.40 \pm 0.02 \text{ mg L}^{-1}$; $[NB]_0 = 0.37 \mu\text{mol L}^{-1}$; catalyst dose = 100 mg L^{-1} ; 1.0 mmol L^{-1} phosphate buffered pH 6.7; $T = 18^\circ\text{C}$.

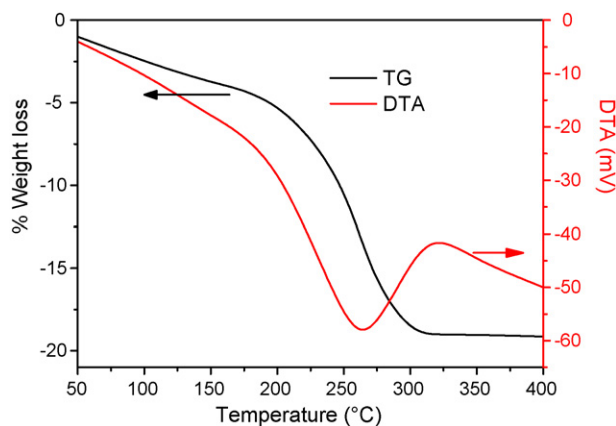


Fig. 7. TG–DTA curves of FeOOH at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$.

3.2.5 Influence of substitution of surface hydroxyl groups by different anions

Some inorganic anions can be adsorbed onto metal oxide in water through ligand exchange with surface hydroxyl groups, which is specific adsorption (Eq. (2)). If the specific adsorption inhibits the catalytic ozonation of NB, it will prove in a more direct way that the activity of FeOOH is related to its surface hydroxyl groups.



Phosphate, sulfate, and nitrate have different coordination affinity for surface Fe(III) of FeOOH [35]. Fig. 9 shows the inhibition effects of the increment dose of sodium phosphate, sodium sulfate, and sodium nitrate on NB degradation of catalytic ozonation, respectively. The “Reduced extent” of NB degradation was used for the y-axis to level off differences in NB degradation rates caused by the increase of ionic strength. It was expressed as:

$$\frac{(C_{01} - C_{c1}) - (C_{02} - C_{c2})}{C_0}$$

“ C_0 ” is the initial NB concentration. “ C_{01} ” and “ C_{02} ” are final NB concentrations after ozonation in the presence of

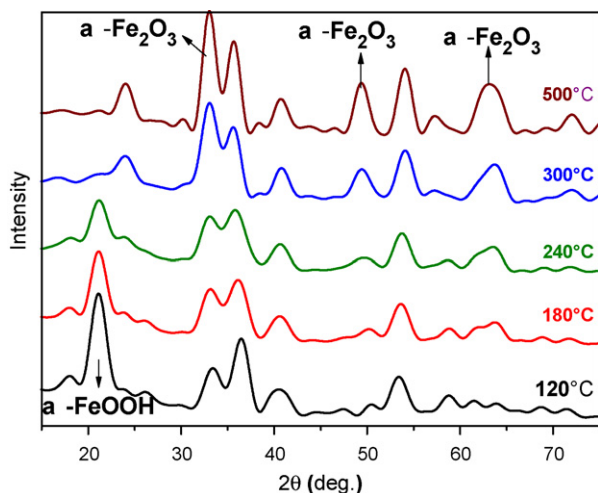


Fig. 8. XRD for FeOOH treated at different temperatures.

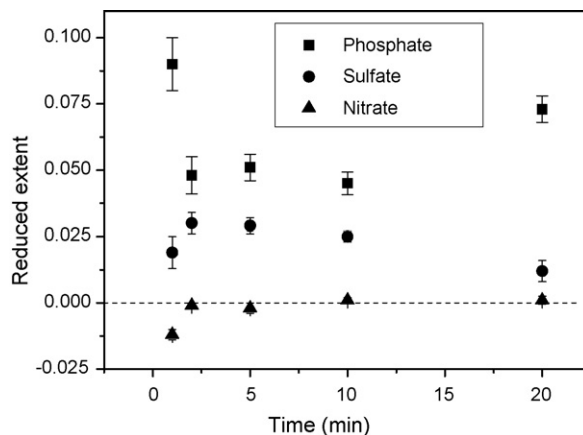


Fig. 9. Influence of the increase of anions from 2 mmol L^{-1} to 10 mmol L^{-1} on NB degradation in catalytic ozonation relative to that in ozonation. $[\text{O}_3]_0 = 1.20 \pm 0.02\text{ mg L}^{-1}$; $[\text{NB}]_0 = 2.96\text{ }\mu\text{mol L}^{-1}$, FeOOH dose = 200 mg L^{-1} , pH 7.30, $T = 16\text{ }^{\circ}\text{C}$.

2 mmol L^{-1} and 10 mmol L^{-1} anions, respectively. “ C_{c1} ” and “ C_{c2} ” are final NB concentrations after catalytic ozonation in the presence of 2 mmol L^{-1} and 10 mmol L^{-1} anions, respectively. Results indicate that the increment of phosphate significantly inhibits NB degradation in the catalytic ozonation. The increase of sulfate has much less negative effect on the NB degradation. However, the increment of nitrate has nearly no negative effect on the NB degradation in the catalytic ozonation.

Phosphate has the highest coordination affinity for surface Fe(III) on FeOOH among these anions [33,36]. According to Ler and Stanforth [37], it forms inner-sphere complex with the surface Fe(III), which leads to its maximum substitution for surface hydroxyl groups on the FeOOH in water. Sulfate adsorbs on FeOOH mainly as outer-sphere complex at neutral water pH [38,39]. Nitrate has very weak coordination affinity for the Fe(III), which leads to nearly no substitution of surface hydroxyl groups of the FeOOH by this anion [33]. Therefore, the inhibition degree of the catalytic ozonation by these anions is closely related with the extent of their substitution for surface hydroxyl groups of the FeOOH. The results further reveal that the surface hydroxyl groups of FeOOH in water play an important role in the catalytic ozonation of NB.

3.2.6 Pathway of FeOOH-induced hydroxyl radical generation

In the previous paper of catalytic ozonation with manganese hydroxide, the authors proposed that OH^{-} in water would be electro-statically attracted to the surface of the hydroxide when the solution pH was above its pH_{pzc} . The attracted OH^{-} would initiate radical chain decomposition of ozone at the hydroxide/water interface [4]. However, this hypothesis cannot explain the relatively low activity of some oxides with much lower pH_{pzc} than water pH in the catalytic ozonation. For example, MnO_2 with the pH_{pzc} of 4 [40], has extremely low activity in promoting hydroxyl radical generation from ozone.

Metal oxides adsorb water molecules strongly in water, because the surface cations are not saturatedly coordinated. The adsorbed water molecules dissociate into OH^{-} and H^{+} ,

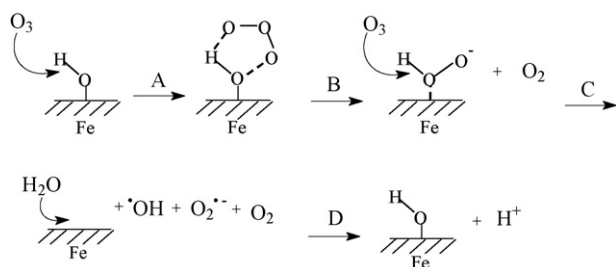


Fig. 10. Scheme of the proposed pathway of hydroxyl radical generation when aqueous ozone interacts with surface hydroxyl group of FeOOH in water.

forming surface hydroxyl groups with surface cations and oxygen anions, respectively [41]. The surface hydroxyl groups at the water/oxide interface will interact with O_3 and the substrate in catalytic ozonation. The FeOOH has much higher surface hydroxyl density ($0.502 \text{ mmol g}^{-1}$) in water than other oxides (surface hydroxyl density = $0.1\text{--}0.3 \text{ mmol g}^{-1}$) used in this study. This property of the FeOOH seems to have contributed to its high activity in the catalytic ozonation of NB. The important function of the surface hydroxyl groups is further confirmed when the substitution of surface hydroxyl groups by inorganic anions inhibited the catalytic ozonation. Moreover, the influences of water pH and FeOOH transformation on the catalytic ozonation of NB indicate that both the quantity of surface hydroxyl groups and their charge states have relationship with the activity of the catalyst in enhancing ozone decomposition to generate hydroxyl radicals.

Fig. 10 illustrates the possible pathway of hydroxyl radical generation induced by the surface hydroxyl groups of the FeOOH. Since ozone has both nucleophilic site and electrophilic site as a dipole agent [42], the ozone molecule can be combined with the surface hydroxyl group as its H and O are electrophilic and nucleophilic respectively (step A). The combined species further decomposes into surface HO_2^- (step B). The surface HO_2^- reacts with another O_3 forming $\bullet OH$ and $O_2^{\bullet -}$ (step C). The $O_2^{\bullet -}$ can further reacts with O_3 , which finally will yield another $\bullet OH$ [1]. The vacant surface Fe(III) site adsorbs another water molecule, which subsequently dissociates into surface hydroxyl group (step D).

As far as the protonated surface hydroxyl group is concerned, its O is weaker in nucleophilicity than the O of neutral state hydroxyl group. Therefore, the protonation of the surface hydroxyl group will disadvantage the surface binding of ozone (step A). On the other hand, the deprotonated surface hydroxyl group cannot provide the electrophilic H, which would also handicap the proposed process. Then, it will explain why the presence of FeOOH significantly improved the ozonation of NB only nearly neutral water pH.

In addition to the quantities and the charge states of the surface hydroxyl groups, their chemical properties, such as the Brønsted acidity and coordination states with surface metal sites of the catalyst, should be further studied to get more detailed information on their relationship with the activity in the catalytic ozonation.

4. Conclusions

The careful preparation well removed the alkalis from the synthetic goethite (FeOOH). Catalytic ozonation with the prepared FeOOH substantially improved the degradation of NB in water through enhanced generation of hydroxyl radicals. The activity of the FeOOH in this case is due to its highly hydroxylated surfaces in water. The surface hydroxyl groups on the FeOOH in water play an important role in the catalytic ozonation. It seems that the uncharged surface hydroxyl groups are more active in the catalytic ozonation than the protonated or deprotonated ones. Results indicate that the uncharged surface hydroxyl groups of FeOOH in water can induce aqueous ozone decomposition to generate hydroxyl radicals during the catalytic ozonation of NB.

Further researches are still needed to find out the relationship between the acidity as well as the coordination states of the surface hydroxyl groups and their activity in inducing hydroxyl radical generation from aqueous ozone.

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