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Silicon-modified ferric hydroxide for catalytic ozonation of nitrobenzene in aqueous solution

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ABSTRACT

Si–FeOOH heterogeneous catalytic ozonation has been effectively used to degrade Nitrobenzene (NB) in the wastewater treatment facilities. Based on the experimental results and theoretical analysis, the mechanism of catalytic ozonation was investigated in this study. Results show that the introduction of Si-FeOOH as a catalyst is beneficial to the enhancement of NB degradation compared with ozonation alone. The addition of Si was to improve the physical and chemical properties of FeOOH. The efficiency of NB degradation by Si-FeOOH/O_3 could reach 81.2% after 20 min of reaction time at pH 7, 25°C, 1.0 mg/L of O_3, 0.33 of Si/Fe molar ratio and 500 mg/L dosage of Si–FeOOH. Moreover, the assumption is that the enhanced NB degradation should be, substantially, attributed to hydroxyl radicals generated with the interaction of hydroxyl groups on the surface of catalyst and ozone, which was verified by the presence of t-BuOH.

Keywords: Catalytic ozonation; Si–FeOOH; Nitrobenzene; Hydroxyl radical; Reaction mechanism

1. Introduction

Heterogeneous catalytic ozonation has been a promising advanced oxidation method and has received more and more attention due to its potentially high effectiveness in the removal of hard-to-degraded organic pollutants in water and wastewater as well as its low negative effect on aqueous environment compared with the conventional ozonation [1–3].

To develop a catalyst with high efficiency and stability is of great importance in the process of heterogeneous catalytic ozonation. Recent researches mainly focus on innovative catalytic materials such as TiO_2, MnO_2, and Cu/Al_2O_3 [4–7].

FeOOH, due to its simple preparation process, low cost, high surface area, and stable chemical properties, has been widely used as a catalyst in water treatment processes, such as catalytic ozonation of benzene compounds, control of trihalomethane formation potential, and degradation of methyl orange [8–11]. However, studies have shown many discrepancies of FeOOH. For instance, it has a relatively low physical strength and is brittle in solution. Moreover, the amorphous structured FeOOH can be gradually transformed into crystalline structured iron oxides, such as goethite (α-FeOOH) and hematite (α-Fe_2O_3), which will cause the decrease of surface area and is disadvantageous to the catalysis. Therefore, different transition elements have been used as dopants to prepare modified FeOOH to

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improve the physical and chemical properties of FeOOH [12,13].

In this study, sodium silicate was selected as the dopant, and the catalyst of Si–FeOOH was investigated in combination of ozone. Nitrobenzene (NB) was chosen as a model organic contaminant because it reacts quickly with hydroxyl radical, but slowly with molecular ozone (i.e. $k_{OH,\ NB} = 2.2 \times 10^{8}\ M^{-1}\ s^{-1}$; $k_{O3,\ NB} = 0.09 \pm 0.02\ M^{-1}\ s^{-1}$) [14,15]. This experimental research aims at investigating the effectiveness and the optimal operational conditions of Si–FeOOH in improving the degradation of NB, as well as the mechanism of catalytic ozonation.

2. Experimental procedure

2.1. Laboratory instruments and materials

All the chemicals used in the experiments were analytical grade reagents. S odium silicate (1344-09-8), NB (98-95-3), tert-butanol (t-BuOH, 75-65-0), and ferric trichloride (7705-08-0) were purchased from Fuchen Chemical Reagent Company, Tianjin. Sodium hydroxide (1310-73-2), sulfuric acid (7664-93-9), potassium iodide (7681-11-0), anhydrous sodium sulfite (7757-83-7), and sodium thiosulfate (7772-98-7) were purchased from Chemical Reagent Company, Guangzhou. The phosphate buffer was prepared by mixing potassium dihydrogen phosphate (7778-77-0) and disodium hydrogen phosphate (7558-79-4) in different amounts to keep the aqueous solution at a constant pH of 7.0. Boiled Milli-Q water was used for dilution and rinsing.

2.2. Preparation of Si–FeOOH

Samples of Si–FeOOH were synthesized according to a method described by Zeng [16]. A certain amount of sodium silicate, according to the molar ratio of Si/Fe, was dissolved into 100 mL 10 mol/L NaOH solution with a stirring speed of 120 rpm (Magnetic stirrer). After that, 10 mol/L of prepared $FeCl_3$ solution was slowly added into the mixture to precipitate gel-like Fe–Si complexes under the stirring condition of 300 rpm. While the pH of the sedimentation process could range from 3 to 12, the final pH should be kept between 6 and 8 to ensure the integrity of the reaction. Subsequently, the suspension was stirred for 2–3 h, and then aged at 70℃ for 24 h. The product was thoroughly rinsed with distilled water and separated by centrifugation, and this procedure should be repeated for at least 2–3 times in order to guarantee a constant pH value of the solution and a complete removal of Cl^{-}. The made-up sample was then dried at 105℃ in the oven for 12 h and grinded afterwards. Particles with diameters ranging from 0.1 to 0.3 mm were screened and used in the following experiments.

2.3. Experimental procedure

The experimental facility is shown in Fig. 1. The ozone was generated from dried oxygen with a laboratory ozone generator (DHX-SS-1G, Harbin Jiujiu co. LTD). The ozone gas measured by a rotameter, firstly, flew through the experimental facility for at least 5 min to empty the interfering gas. Then, the gas was introduced into the reactor containing a certain amount of distilled water until it reached a constant concentration. At that time, the aqueous ozone was quickly sampled and then measured with the indigo method. Subsequently, the NB solution, the catalyst, and the t-BuOH (if necessary) were quickly added into the ozone bearing water, and the reaction was launched with a stirring speed of 180 rpm. In the experiment, phosphate buffer of 1.0 mmol/L was used to adjust the pH value, sodium sulfite solution of 0.1 mol/L was used to terminate the reaction, while potassium iodide solution to absorb the off-gas. At regular intervals, the samples were taken and filtrated by 0.45 μm filter membrane. The concentration of NB was measured by HPLC.

2.4. Analysis

Quantification of NB was carried out on a Waters HPLC system. Chromatographic conditions: Symmetry C18 silica gel column (4.6 × 250 mm, Waters), methanol/distilled water (50:50, V/V) as mobile phase at a flow rate of 1.0 mL/min with detection wavelength at 220 nm, and retention time of NB was 4.591 min [17]. Aqueous ozone concentration was measured with the indigo method [18].

Beaker experiments were carried out to test the practical application of the catalysts. Firstly, catalysts

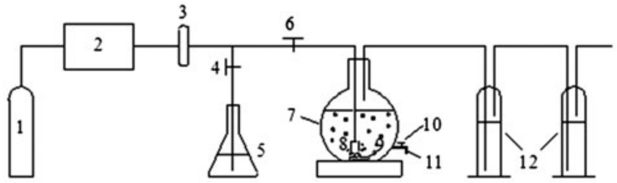

Fig. 1. Scheme of experimental facility.
Notes: 1. Oxygen bottle; 2. Ozonator; 3. Rotameter; 4. Valve one; 5. Oxygen absorption bottle; 6. Valve two; 7. Reactor; 8. Aerator; 9. Stirrer; 10. Valve three; 11. Sample connection; 12. Off-gas absorption bottle.

with different Si/Fe molar ratio of 0.15 g were put into 250 mL beakers with 100 mL distilled water. Then the beakers were placed on magnetic stirrers at 150 rpm for 1 h. After stirring, the cloudiness of the solution was observed visually. The catalysts' physical properties of crushing resistance and crushing rate were tested with the standard test method for determination of crush resistance using the particle strength tester (KHKQ-100) [19].

3. Results and discussion

3.1. Single ozonation process

3.1.1. Effect of O_3 dosage on the NB degradation

Experiments were performed to determine the optimal concentration of ozone in the following research. It can be easily seen from Fig. 2 that the removal rate of NB increases with an increase in the concentration of ozone. The ozone's mass transfer efficiency from gaseous to liquid phase which can help improve the chain reaction of ozone is enhanced, therefore will lead to the boost in the formation of hydroxyl radicals which can improve the degradation efficiency of NB. When the concentration of NB is fixed, it can be completely degraded by abundant ozone, with the removal rate growing approximately up to 100%.

The figure also indicates a good linear correlation between the removal rate of NB and the ozone concentration, which ranges from 0.5 to 2.0 mg/L. However, since the decomposition capability of ozone is limited when dissolved in water, superfluous ozone cannot be fully used and the growing rate of hydroxyl radicals does not increase in the same pace with the enhanced ozone concentration. As a consequence, when the concentration of ozone continues to increase from 2.0 mg/L to 3.0 mg/L, the increase of NB removal rate slows down. As the introduction of catalyst would enhance the degradation efficiency of NB and plenty amount of ozone would cost too much, the ozone concentration of 1.0 mg/L was chosen in the following experiments.

3.1.2. Effect of NB concentration on the NB degradation

Fig. 3 illustrates the effect of different initial NB concentrations on its removal rate. Under the condition of a constant ozone concentration and an increasing initial concentration of NB, the amount of NB which has not been fully degraded increases gradually due to the inadequate hydroxyl radicals, causing the decrease of NB removal rate.

It can also be observed from Fig. 3 that the removal efficiency manifests an obvious difference as the initial concentration of NB increases from 3 to 5 mg/L. However, the difference becomes smaller and smaller when it reaches 7 mg/L, indicating that the oxidation capacity of ozone is already close to the limit. Accordingly, the removal rate of NB decreases and reaches a stable point. That is to say, there exists an optimal molar ratio between ozone and NB. In consideration of the oxidation capacity of ozone as well as the requirement of the removal rate of NB, the NB initial concentration selected for this study is 5.0 mg/L.

3.2. Catalytic ozonation process

3.2.1. Effectiveness of catalyst in improving NB degradation

In order to verify the effectiveness of catalyst in improving NB degradation, three different reaction conditions under O_3, O_3/FeOOH, and O_3/Si–FeOOH (Si/Fe = 0.33, the molar ratio) were evaluated, respectively.

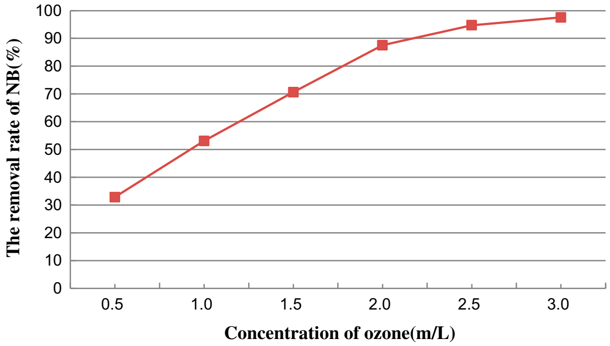

Fig. 2. Effect of O_3 dosage on the NB degradation. $[NB]_0$ = 5.0 mg/L, pH = 7, T = 25℃, and t = 20 min.

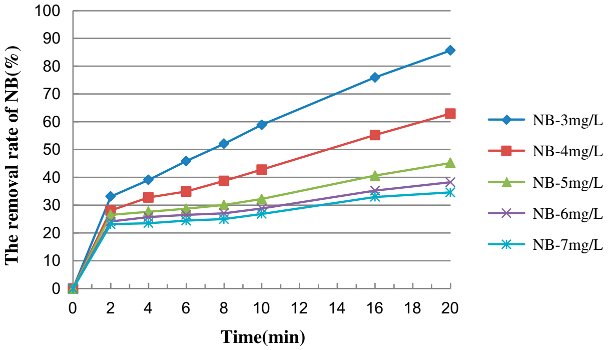

Fig. 3. Effect of NB concentration on the NB degradation. $[O_3]_0$ = 1.0 mg/L, pH = 7, T = 25℃, and t = 20 min.

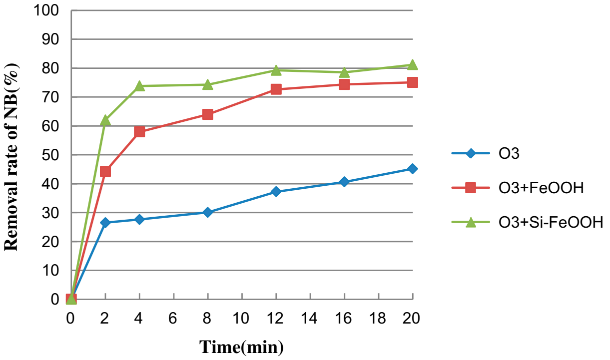

Fig. 4. Effects of O_3, O_3/FeOOH, O_3/Si–FeOOH on the degradation of NB. Si/Fe = 0; 0.33, catalyst dosage = 500 mg/L, $[O_3]_0 = 1.0$ mg/L, $[NB]_0 = 5.0$ mg/L, pH = 7, $T = 25$℃, and $t = 20$ min.

From Fig. 4, it is obvious that NB degrades quickly within the initial 2 min in the three different reactions and slows down afterwards. The results correspond with the two-phase theory of ozone decomposition in water [20]. A large number of hydroxyl radicals are generated at the initial phase of ozonation called instantaneous ozone decomposition and react quickly and non-selectively with NB. The secondary reaction rate constant is up to $2.2 \times 10^8 \, M^{-1} s^{-1}$. After 20 min reactions, the removal rates of NB reached 81.2 and 75.0%, respectively, in catalytic ozonation with Si–FeOOH and FeOOH, which are about 1.5 times higher than that of about 52.3% in ozonation alone, showing that catalysts are effective for improving NB degradation. Moreover, it is assumed that the hydroxyl radicals generated in the process of catalytic ozonation have played a leading role in NB degradation.

3.2.2. Effect of Si/Fe molar ratios on the NB degradation

The $FeCl_3$ solution, mixed with the mixture of Na_2SiO_3 and NaOH provide both the source of silica and FeOOH sol, and the gel-like Fe–Si complexes were eventually formed with the close contact of these two sols. As is shown in Table 1, the physical strength of catalyst shows an increasing trend with the increase of Si/Fe molar ratio, and FeOOH is easier to be crushed than Si–FeOOH, which indicates that the adding of FeOOH is less stable and more likely to cause secondary pollution. It is assumed that the coordination bond between Fe and Si enhances the physical strength of the catalyst. Meanwhile, the crystallization of iron oxides is strongly retarded by the presence of silicate species. As a result, the catalyst of Si–FeOOH tends to be of high surface area and stability, which is of great importance in catalytic oxidation.

The effect of the Si/Fe molar ratios on its different levels (0 (i.e. FeOOH), 0.2, 0.33, and 0.5) on the degradation of NB is shown in Fig. 5. The results reveal that NB degradation is enhanced with catalyst of either FeOOH or Si–FeOOH at different Si/Fe molar ratios.

However, the efficiency of the catalyst weakens with the further increasing of Si/Fe molar ratio, and 0.33 shows the best effectiveness with the removal rate up to 81.2%. It is assumed that the active site of FeOOH might be occupied by the increasing quantity of silicate species, which leads to the reduction of effective contacts between FeOOH and O_3, and hence impeding the generation of efficient hydroxyl radicals. Furthermore, as FeOOH plays the key role of a catalyst, the presence of silicate species decreases the effective content of catalyst. Take both the effect of physical factor and catalyst efficiency into consideration, 0.33 tends to be the optimal molar ratio of Si/Fe.

3.2.3. Effect of catalyst dosage on the NB degradation

The effect of catalyst dosage on the NB degradation is depicted in Fig. 6. The degradation rate of NB increases firstly with the increasing molar ratio of Si/Fe. It can be explained that the enlargement of surface area, which is due to the enhanced concentration of catalyst, results in the increasing number of active sites of Si–FeOOH. As a consequence, the generation of hydroxyl radicals which are of high catalytic efficiency is improved. However, as the concentration of catalyst continues to increase, the removal rate of NB is inclined to decrease. On the one hand, abundant catalyst hinders the mass transfer of ozone from gaseous to liquid phase, thus the concentration of ozone in liquid phase declines. On the other hand, the increasing number of hydroxyl radicals causes composite reaction among themselves, which leads to the reduction of effective hydroxyl radicals [21]. Consequently, there exists the optimal dosage of

Table 1
Effect of Si/Fe ratio on the physical properties of the catalysts

Si/Fe molar ratio	0	0.2	0.33	0.5
Cloudiness of solution after stir	Turbid	Cloudy	Clear	Clear
Crushing resistance (*N*)	94	117	141	183
Crushing rate (%)	15.4	12.7	9.9	8.2

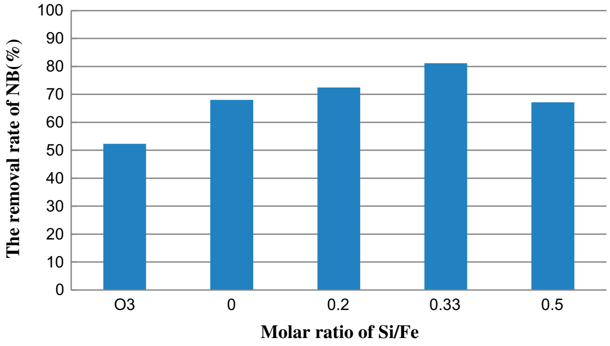

Fig. 5. Effect of the Si/Fe molar ratio on the degradation of NB. Catalyst dosage = 500 mg/L, $[O_3]_0 = 1.0$ mg/L, $[NB]_0 = 5.0$ mg/L, pH = 7, $T = 25$℃, and $t = 20$ min.

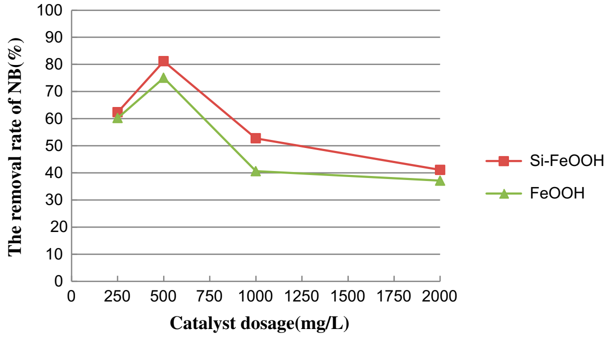

Fig. 6. Effect of catalyst dosage on the NB degradation. Si/Fe = 0; 0.33, $[O_3]_0 = 1$ mg/L, $[NB]_0 = 5$ mg/L, pH = 7, $T = 25$℃, and $t = 20$ min.

catalyst on the NB degradation, and 500 mg/L is eventually selected in this experiment.

3.2.4. Comparisons and economical evaluation

From the experiments above and previous researches, we made a comparison of different systems on the optimal conditions and removal rate of NB, and the results are shown in Table. 2.

As we can see from the table above, the removal rate of O_3/Si–FeOOH system is higher than that of other systems [22–24]. The advantages of high efficiency, time saving, and easy operation make it a better choice for NB degradation.

Taking the ozone, catalyst preparation cost, materials cost, testing cost, etc. into consideration, the raw wastewater treatment cost of the O_3/Si–FeOOH system was estimated at about 0.33 USD/ton.

3.3. Mechanism

From the experimental results above, the degradation efficiency of NB improved obviously after the introduction of metal oxides catalyst. The assumption is that the enhanced NB degradation should be, substantially, attributed to the generation of hydroxyl radicals [25,26]. Since the metal ions on the surface of metal oxide are coordinately unsaturated, it is easy for the H^+ and OH^- dissociated from water molecules to be absorbed on the surface of the catalyst, and hence forming the surface hydroxyl groups. The hydroxyl radicals are then generated from the interaction of hydroxyl groups and ozone, leading to the enhancement of NB degradation. The possible mechanism is concisely shown as follows:

$$M + H_2O \rightarrow M - OH + H^+ \tag{1}$$

$$O_3 + M - OH \rightarrow MOH - O_3 \tag{2}$$

$$MOH - O_3 \rightarrow M - HO_2^- + O_2 \tag{3}$$

$$M - HO_2^- + O_3 \rightarrow \cdot OH + 2O_2 \cdot^- + M \tag{4}$$

$$O_2 \cdot^- + O_3 + H_2O + 4H^+ \rightarrow 6 \cdot OH \tag{5}$$

In order to verify the theory above, t-BuOH, a well-known hydroxyl radical scavenger, was introduced into the catalytic oxidation process. Compared with the organic pollutants, it reacts quickly with hydroxyl radicals, which contributes to the quenching of ozone decomposition. The influences of t-BuOH on NB degradation of the ozone alone system as well as the Si–FeOOH/O_3 system are exhibited in Fig. 7.

The direct ozone oxidation, containing the decomposition of oxidant (ozone) and the degradation of organic pollutant (NB), is a second-order reaction. To put it simply, the degradation reaction of NB follows the pseudo-first-order kinetics. According to the experimental results, the curves of $-\ln(C/C_0)$-t are shown in Fig. 7, and the slopes reflect the rate constants of pseudo-first-order reactions.

As is exhibited in Fig. 7, in the presence of t-BuOH, the rate constants of both the ozonation alone system and the Si–FeOOH/O_3 system have decreased significantly, and there doesn't seem to be much difference between the two systems(0.202 and 0.216), suggesting that t-BuOH effectively restrains indirect ozonation. In addition, it is the ozone that has acted as the oxidant during these two oxidation processes. Contrastively, in the absence of t-BuOH, the rate constant of the Si–FeOOH/O_3 system (0.5624) ranks, distinctly, higher than that of the ozonation alone system (0.3352) due to the higher oxidizability of hydroxyl radicals generated during the indirect ozonation than that of ozone in the direct ozonation, which

Table 2
Comparison of different systems on the optimal conditions and removal rate of NB

Systems	Optimal conditions	Removal rate of NB (%)	Advantages and disadvantages
O_3	NB concentration = 5 mg/L, pH = 7, T = 25℃, t = 20 min,	45.19	Low efficiency
O_3/Si–FeOOH	Si/Fe = 0.33, catalyst dosage = 500 mg/L, O_3 concentration = 1.0 mg/L	81.17	High efficiency Time-saving Easy operation
Dual-pulse ultrasound enhanced electrochemical degradation (US-ECD)	NB concentration = 100 mg/L, pH = 3, t = 30 min, cell voltage = 10 V, ultrasonic power = 48.84 W, electrolyte concentration = 0.1 mg/L, energy consumption = 0.1413 kW h/LNB	80.08	High energy consumption
Electrochemistry/Fe_2O_3/γ-Al_2O_3	NB concentration = 60 mg/L, pH = 10, t = 45 min, cell voltage = 40 V, Na_2SO_4 = 500 mg/L, energy consumption = 301.8 kW h/kg NB	75.10	Low efficiency High energy consumption
Fenton/FeS_2	NB concentration = 20 mg/L, pH = 3, t = 30 min, H_2O_2 concentration = 250 mg/L, FeS_2 = 2 g/L	80	High efficiency Time-taking

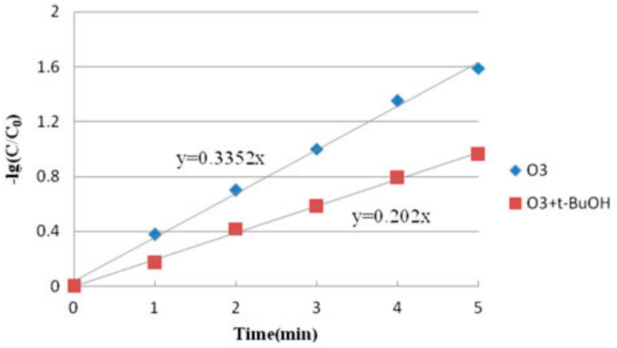

Fig. 7(a). Effect of t-BuOH on NB degradation in ozonation alone system.

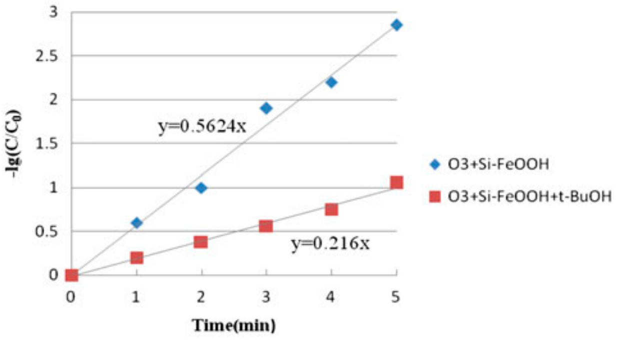

Fig. 7(b). Effect of t-BuOH on NB degradation in Si–FeOOH/O_3 system. Catalyst dosage = 500 mg/L, Si/Fe = 0.33, $[O_3]_0$ = 1 mg/L, $[NB]_0$ = 5 mg/L, pH = 7, T = 25℃, and t = 20 min.

indicates that direct ozonation plays the leading role in the ozonation alone system, while indirect ozonation dominates the Si–FeOOH/O_3 system.

4. Conclusion

The catalyst Si–FeOOH was synthesized successfully by the reaction of $FeCl_3$ with a mixture of Na_2SiO_3 and NaOH. An appropriate Si/Fe molar ratio of 0.33 was obtained taking both the effect of physical factor and catalyst efficiency into consideration. The presence of Si–FeOOH during the process of oxidation effectively enhanced the degradation of NB compared with ozonation alone. The efficiency of NB degradation with Si–FeOOH could reach 81.2% after 20-min reaction time at pH 7, 25℃, 1.0 mg/L of O_3, 0.33 of Si/Fe molar ratio and 500 mg/L dosage of Si–FeOOH. It was estimated that the raw wastewater treatment cost of the O_3/Si–FeOOH system would be about 0.33 USD/ton. Additionally, by the introduction of t-BuOH, it was confirmed that hydroxyl radicals generated with the interaction of hydroxyl groups on the surface of catalyst and ozone played an important role in the enhancement of NB degradation.

Acknowledgments

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