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Degradation Effect and Mechanism of Dinitrotoluene Wastewater by Magnetic Nano-Fe₃O₄/H₂O₂ Fenton-like

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ABSTRACT

The characteristics and influencing factors for dinitrotoluene degradation by nano-Fe₃O₄-H₂O₂ were studied, and the nano-scale Fe₃O₄ catalyst was prepared by the coprecipitation method, with dinitrotoluene wastewater as the degradation object. The results showed that the catalytic reaction system within the pH value range of 1 to 9 could effectively degrade dinitrotoluene, and the optimal pH value was 3; with the increase of catalyst dosage, the degradation efficiency and the catalytic reaction rate of dinitrotoluene grew as well. The optimal catalyst dosage was 1.0 g/L when the H₂O₂ dosage was within the range of 0 to 0.8 mL/L; the degradation efficiency and reaction rate grew with the increase of H₂O₂ dosage. With further increase of H₂O₂ dosage, degradation efficiency and reaction rate decreased; under the best conditions with the H₂O₂ dosage of 0.8 mL/L, the catalyst concentration of 1 g/L and the pH value of 3 at room temperature (25 °C), the degradation rate of the 100-mg/L dinitrotoluene in 120 min reached 97.6%. Through the use of the probe compounds n-butyl alcohol and benzoquinone, it was proved that the oxidation activity species in the nano-Fe₃O₄-H₂O₂ catalytic system were mainly hydroxyl radical (•OH) and superoxide radicals (HO₂•), based on which, the reaction mechanism was hypothesized.

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Hydroxyl Radical; Nano-Fe₃O₄

Introduction

Dinitrotoluene is a type of widely-applied basic chemical material and an intermediate in the fine chemical industry, characterized with carcinogenicity, teratogenicity and mutagenicity. If entering the water, it will deteriorate the sensory properties of water over the long term, causing substantial harm to the environment and the organisms. China has included it as one of 58 harmful chemicals under the priority control for environmental protection. Such substances have a high stability in the water, so it is difficult to degrade and remove dinitrotoluene in the water with conventional wastewater treatment methods.

Advanced oxidation technology is an effective way to treat the organic wastewater that is difficult to degrade. Of such technologies, the widely applied Fenton technology utilizes Fe²⁺ to catalyze H₂O₂ and produce hydroxyl radicals with strong oxidability, which can then oxidize organics unconditionally (Xue et al. 2009). The latest study has found that not only can the heterogeneous Fenton reaction with the iron-based solid as the catalyst achieve efficient degradation

but it can also overcome the shortcomings in terms of the homogeneous reaction conditions, such as the required presence of acid environment, generation of iron sludge and impossible reuse of iron salts (Sun, Zeng, and Lemley 2013; Jie et al. 2015).

As one iron-based solid, magnetite (Fe₃O₄) belongs to the cubic crystal lattice, with the lattice constant $a = 0.8396$ nm. It has an octahedral interstice structure in which Fe²⁺ and Fe³⁺ co-exist, so the redox of Fe²⁺ can be done thereby (Wei and Wang 2008). Meanwhile, magnetite (Fe₃O₄) has a stable structure, easy for separation and recovery in addition to other advantages such as thermal stability (Wang et al. 2010). Therefore, the heterogeneous Fenton technology with Fe₃O₄ as the catalyst has become a hotspot of research on advanced oxidation technologies. The studies carried out by Moura FCC et al. show that: Fe₃O₄ is ferrous, so it can catalyze hydrogen peroxide to produce hydroxyl radicals (Moura et al. 2005). Hua et al. prepared nano-Fe₃O₄/graphite oxide, and obtained the degradation rate of 90% of bisphenol A (20 mg/L) via 6 h reaction under the conditions with the catalyst dosage of 1.0 g/L, the H₂O₂ concentration of 20 mmol/L and

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the pH value of 6 (Hua et al. 2014). Zhang et al. studied the catalytic oxidation of phenol and aniline by superparamagnetic nano-Fe₃O₄ and investigated the reaction conditions and intermediates (Zhang et al. 2009). Existing research suggests that the catalytic activity of Fe₃O₄ can be effectively improved by reducing the size of catalyst. However, as for the mechanism of H₂O₂ catalytic decomposition by nano-Fe₃O₄ for degradation of organics and the effects of Fe₃O₄ surface properties on its catalytic activity are not clear at present.

In this study, the degradation property, reaction kinetics and reaction mechanism of the nano-Fe₃O₄/H₂O₂ was investigated at room temperature based on the nano-Fe₃O₄ prepared with the coprecipitation method, with the dinitrotoluene wastewater as the treatment object.

Materials and methods

Test reagents and instruments

Reagents included dinitrotoluene, hydrogen peroxide (30%), ferric chloride, ferrous chloride, ferric sulfate, sodium hydroxide and concentrated hydrochloric acid were all of analytical grade and purchased from Aladdin.

Instruments included UV-7504 (A) UV/VIS spectrophotometer, DELTA-320 pH meter, thermostatic magnetic stirring instrument, TOC Shimadzu analyzer, Hitachi S-4800 scanning electron microscope, D8 advance-type X-ray diffractometer.

Preparation of magnetic nano-Fe₃O₄

The nano-sized magnetic Fe₃O₄ was prepared by coprecipitation. The 5.4 g FeCl₃·6H₂O and 2.0 g FeCl₂·4H₂O were dissolved in 200 mL pre-deoxygenated deionized water, and then, 0.85 mL concentrated hydrochloric acid was added; with the protection of nitrogen, the solution was heated to 358 K in a water bath. Next, 20 mL ammonia water (25 wt%) was added with mechanical stirring, followed by 30 min of aging; and then the solution was cooled by ice-water bath; thereby nano-Fe₃O₄ particles were generated. Next, such nano-Fe₃O₄ particles were subject to the centrifugal separation and washed with the deoxygenated deionized water to be neutral; finally, they were dried in a vacuum oven at 40 °C for use (Zhang et al. 2011; Kim et al. 2001).

Characteristic of catalyst

The X-ray diffractometer (XRD) (Bruker AXS D8 Advance, Germany) was used for the material phase analysis on the characteristics of Fe₃O₄ based on the Cu-Kα radiation with 2θ range of 20° to 80° and the

number of steps of 0.01976; the scanning electronic microscope (Hitachi S-4800, Japan) was used to observe the microstructure of catalyst and perform the surface element analysis; and the vibrating sample magnetometer (VSM, 730 T, USA) was used for magnetic measurement of Fe₃O₄.

Test methods

The concentration of 2,4-dinitrotoluene was determined with the reducing-azo photometric method (Ministry of Environmental Protection of the People's Republic of China 1989); TOC with Shimadzu TOC analyzer, and pH value with DELTA-320-type pH meter.

Dinitrotoluene degradation test: A certain amount of nano-Fe₃O₄ catalyst was put into the self-prepared dinitrotoluene wastewater, and then a certain amount of H₂O₂ was added to start the decomposition reaction. Sampling and analysis were conducted based on a certain interval, in order to investigate the effects of such factors such as initial pH value, H₂O₂ dosage and the amount of catalyst on the degradation rate. The degradation rate η of dinitrotoluene was calculated with the formula $\eta = (C_0 - C_t)/C_0 \times 100\%$, where, C_0 is the initial concentration of dinitrotoluene, C_t is the concentration of dinitrotoluene when the reaction time is t .

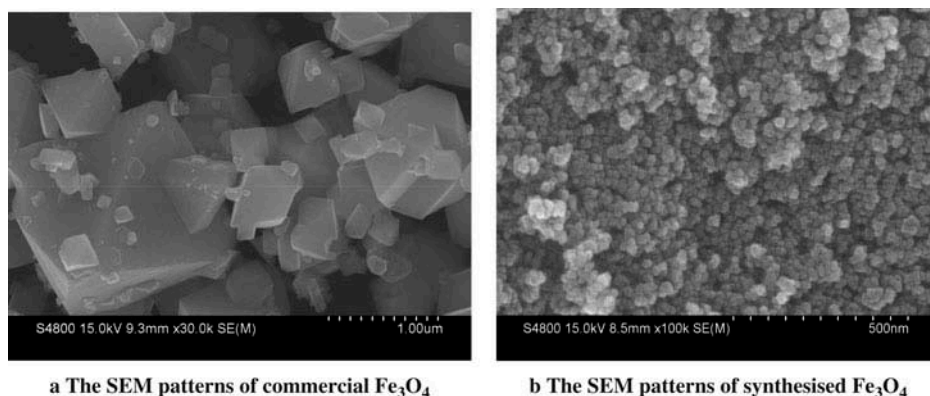
Kinetic study: The reaction kinetics study was conducted using a reaction equation $dC/dt = -K \cdot C$ namely $C_t = C_0 \exp(-kt)$. In the equation, k is the apparent rate constant and t is the reaction time.

Results and discussion

Characteristic of catalyst

Figure 1 shows the SEM images of the commercial Fe₃O₄ catalyst and the Fe₃O₄ catalyst self-prepared in the laboratory. From Figure 1 (a), it can be seen that the commercial Fe₃O₄ crystal is of pyramid shape with clear edges and non-uniform of distribution of particle size. The particle size ranges from 0.1 μm to 0.4 μm; according to Figure 1 (b); it can also be seen that the self-prepared Fe₃O₄ crystal is ball-like, with uniform distribution of particle size. The particle sizes range from 20 nm to 30 nm, which is smaller than that of commercial Fe₃O₄ crystal.

The XRD results of the commercial Fe₃O₄ and the Fe₃O₄ catalyst self-prepared were showed in Figure 2. Figure 2 indicates that the peaks in the XRD spectra of the commercial Fe₃O₄ catalyst and the Fe₃O₄ catalyst self-prepared in the laboratory are identical. Strong



a The SEM patterns of commercial Fe_3O_4

b The SEM patterns of synthesized Fe_3O_4

Figure 1. SEM images of synthesized Fe_3O_4 and commercial Fe_3O_4 .

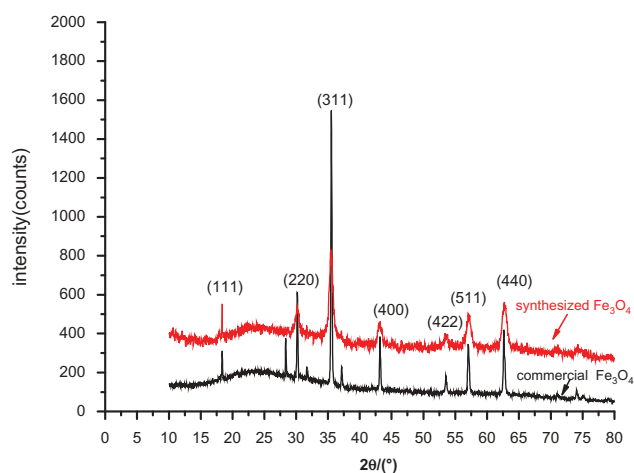


Figure 2. XRD patterns of synthesized Fe_3O_4 and commercial Fe_3O_4 .

characteristic diffraction peaks appear at the points where 2θ is 18.40° , 30.17° , 35.56° , 43.15° , 53.64° , 57.04° and 62.61° , respectively. Compared with the standard Fe_3O_4 diffraction card (JCPDS 19-629), they are respectively attributed to the diffraction of planes (111), (220), (311), (400), (422), (511) and (440) of cubic crystal Fe_3O_4 , which indicates both the commercial Fe_3O_4 catalyst and the Fe_3O_4 catalyst self-prepared in the laboratory have an inverse spinel crystal structure.

According to Figure 3, the saturation flux density of commercial Fe_3O_4 was 83.17 emug^{-1} and that of the Fe_3O_4 catalyst self-prepared in the laboratory was 65.26 emug^{-1} . Both are larger than 16.3 emug^{-1} , indicating that either Fe_3O_4 was easy to be separated from wastewater by magnetic separation. In the magnetic hysteresis loops, the residual magnetic flux density and the coercive force of the commercial Fe_3O_4 were small, close to zero, while the residual magnetic flux density and the coercive force of the Fe_3O_4 catalyst self-prepared in the laboratory were zero, indicating that

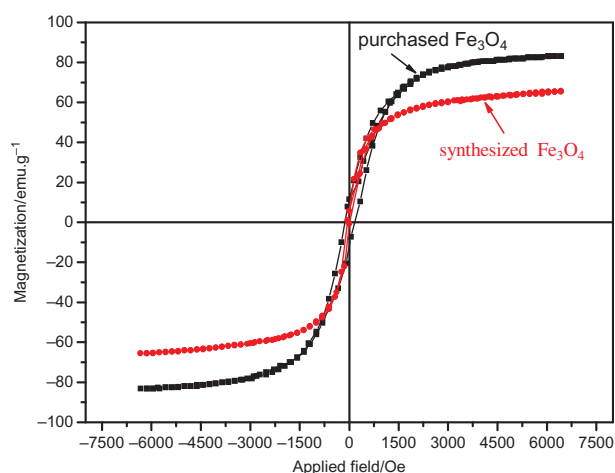


Figure 3. VSM curves of synthesized Fe_3O_4 and purchased Fe_3O_4 .

the self-prepared Fe_3O_4 catalyst had better paramagnetism than the commercial Fe_3O_4 , and it was better dispersed in the reaction system, which is conducive to reuse.

Effects of H_2O_2 concentration on degradation of dinitrotoluene wastewater

According to Figure 4a, when the H_2O_2 dosage was within the range of 0 to 0.8 mL/L, the degradation rate grew with the increase of the H_2O_2 dosage. In this case, the removal rate of dinitrotoluene rose to 97.6% from 15.7% within 120 min; when the H_2O_2 dosage was further increased to 1.0 mL/L, the removal rate of dinitrobenzene was almost unchanged. But when the H_2O_2 dosage was increased to 1.5 mL/L, the removal rate of dinitrobenzene decreased to 89.9%. Figure 5b shows that there was a good linear relationship between different $\ln(C/C_0)$ and time T, showing the characteristics of the first-order reaction kinetics; when the H_2O_2 dosage was

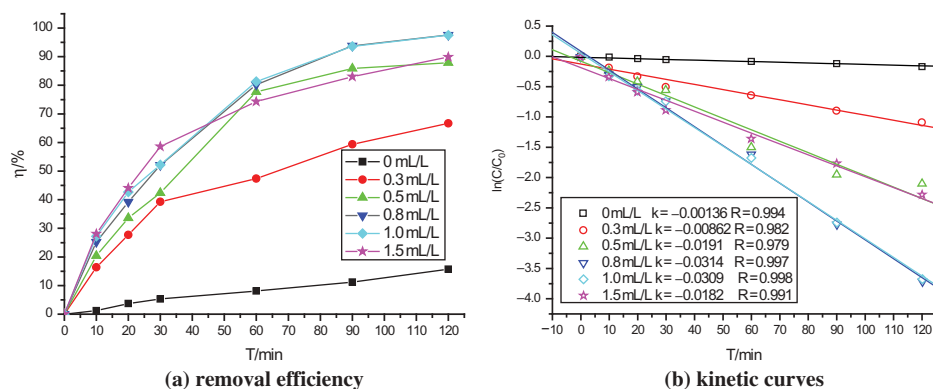


Figure 4. Effect of H_2O_2 concentration on removal of dinitrotoluene by Fe_3O_4 (catalyst dosage 1.0 g/L, initial pH 3.0, $T 25 \pm 1^\circ\text{C}$ and dinitrotoluene concentration 100 mg/L).

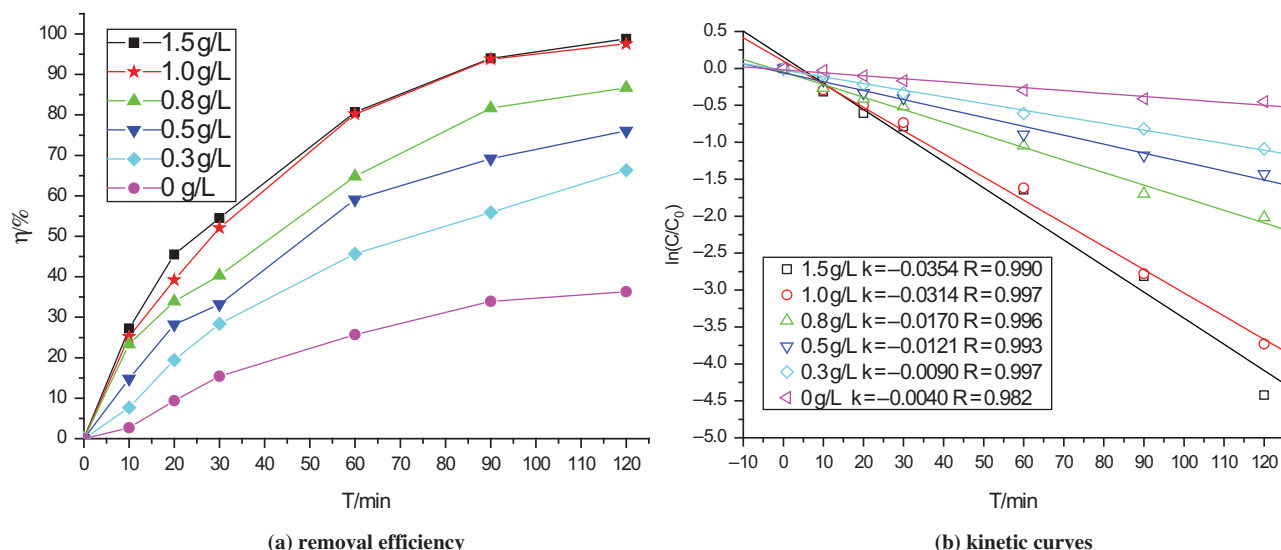


Figure 5. Effect of catalyst dosage on removal of dinitrotoluene by Fe_3O_4 (H_2O_2 concentration 0.8 mL/L, initial pH 3.0, $T 25 \pm 1^\circ\text{C}$ and dinitrotoluene concentration 100 mg/L).

increased to 0.8 mL/L from 0, the reaction rate of dinitrotoluene grew from 0.00136 min^{-1} to 0.0314 min^{-1} , when the H_2O_2 dosage was further increased, the reaction rate decreased, indicating that when the H_2O_2 dosage was between 0–1.0 mL/L, the more the H_2O_2 was added, the more $\cdot\text{OH}$ would be generated as the catalytic result of the catalyst and H_2O_2 , which was conducive to the degradation of dinitrotoluene; however, after the H_2O_2 dosage exceeded 1.0 mL/L, the excessive H_2O_2 reacted with $\cdot\text{OH}$ and generated $\text{HO}_2\cdot$ radicals with weaker oxidization ability, while $\text{HO}_2\cdot$ would continue to react with $\cdot\text{OH}$, generating water and oxygen to reduce the $\cdot\text{OH}$ involved in the oxidation of dinitrotoluene in the reaction system (Hassan and Hameed 2011; Zhang et al. 2014). Therefore, the optimal dosage of H_2O_2 was 0.8 mL/L under the conditions for this test.

Effects of catalyst dosage on degradation of dinitrotoluene wastewater

Figure 5a shows that when the catalyst dosages were, respectively 0, 0.3 g/L, 0.5 g/L, 0.8 g/L, 1.0 g/L and 1.5 g/L. After 120-min reaction, the degradation efficiencies of dinitrotoluene were, respectively, 36.3%, 66.3%, 76.1%, 86.7%, 97.6% and 98.8%, indicating the catalyst degradation efficiency of dinitrotoluene also grows with the increased catalyst dosage. When the dosage was increased to 1.0 g/L, the degradation efficiency did not significantly grow any longer with increased catalyst dosage. The main reason for this is that the increase of the catalyst dosage can improve the contact area between catalyst and hydrogen peroxide, thus generating more hydroxyl radicals, which can increase the degradation efficiency of the system (Hassan and Hameed 2011; Xu and Wang 2012).

However, the generation amount of hydroxyl radical will stop increasing when it reaches a certain extent.

Figure 5b shows that there is a good linear relationship between $\ln(C/C_0)$ and time T, indicating that the catalytic degradation of dinitrotoluene under different catalyst dosages is identical with the characteristics of the first-order reaction kinetics. The reaction rate grew with increase of the catalyst dosage, rising from 0.0040 min^{-1} to 0.0354 min^{-1} . The reaction of nano- Fe_3O_4 catalyzing H_2O_2 belongs to the heterogeneous reaction. In such reaction, the dinitrotoluene in the wastewater and H_2O_2 were required to be dispersed onto the catalyst surface, and then the H_2O_2 would react with the catalyst, generating hydroxyl radical. Next, the hydroxyl radical would have the oxidation reaction with pollutants. Finally, the oxidation products would be dispersed into the wastewater from the catalyst surface. With the increase of the catalyst dosage, the catalytic activity of the catalyst grew accordingly, thus improving the reaction rate of the Fenton-like reaction (Wang and Huang 2011).

Effects of initial pH value on degradation of dinitrotoluene wastewater

According to Figure 6a, the degradation efficiency of dinitrotoluene was 79% when the pH value was 1; the same was 97.6% when the pH value was 3; 93% when the pH value was 5; 69% when the pH value was 7; and 50% when the pH value was 9, which indicates that the Fe_3O_4 - H_2O_2 Fenton-like reaction has a good degradation efficiency when the pH value is within the interval of 3–5. When the pH value is within the intervals corresponding to strong acidity and weak alkaline, the

removal rate will greatly decrease. From Figure 6b, it is known that there is a good linear relationship between $\ln(C/C_0)$ and T, indicating that the reaction of dinitrotoluene with different initial pH values belongs to the first-order reaction; the catalytic reaction rate when the pH value is in the range of 3 to 5 is larger than those under other pH values.

The existing studies have found that the pH value of the solution may affect charge properties, adsorption behavior and electron transfer capability on the catalyst surface (Si et al. 2010). If the pH value is too low, for example, the pH value of the solution is below 3, the content of hydrogen ions will be too high, so that Fe^{3+} cannot be successfully converted to Fe^{2+} , and the excess H^+ will capture $\cdot\text{OH}$ to generate H_2O , resulting in the ineffective decomposition of $\cdot\text{OH}$; while the pH value is above 4, the nano Fe_3O_4 will form hydrated iron or hydrated ferrous complexes, resulting in the reduction of its catalytic degradation ability (Kim et al. 2012).

Catalytic effect comparison of self-prepared nano Fe_3O_4 and commercial Fe_3O_4

To investigate the effect that the self-prepared nano- Fe_3O_4 and the commercial nano- Fe_3O_4 catalyst and degraded dinitrotoluene, the dinitrotoluene wastewater with the initial concentration of 100 mg/L was degraded for research purposes under these conditions: catalyst dosage of 1.0 g/L, the H_2O_2 dosage of 0.8 mL/L, the pH value of 3, and the room temperature of $25 \pm 1 \text{ }^\circ\text{C}$, and the test results are shown in Figure 7. According to Figure 7, the removal rates of dinitrotoluene and TOC by the self-prepared Fe_3O_4 were both higher than those by the commercial Fe_3O_4 , indicating that the self-prepared Fe_3O_4 has a better effect

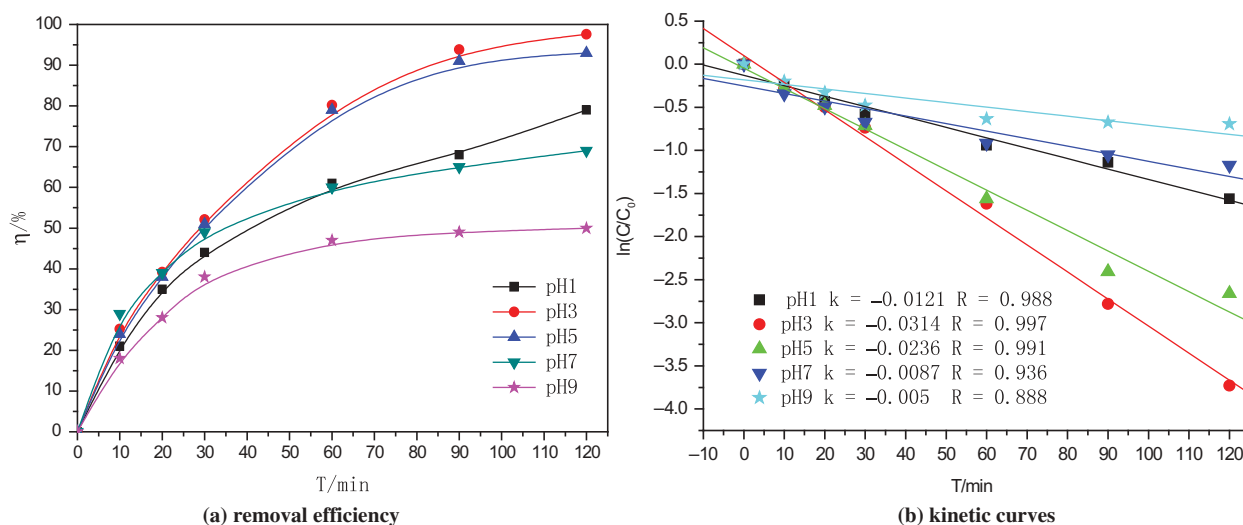


Figure 6. Effect of pH on removal of dinitrotoluene by Fe_3O_4 (H_2O_2 concentration 0.8 mL/L, catalyst dosage 1.0 g/L, $T 25 \pm 1 \text{ }^\circ\text{C}$ and dinitrotoluene concentration 100 mg/L).

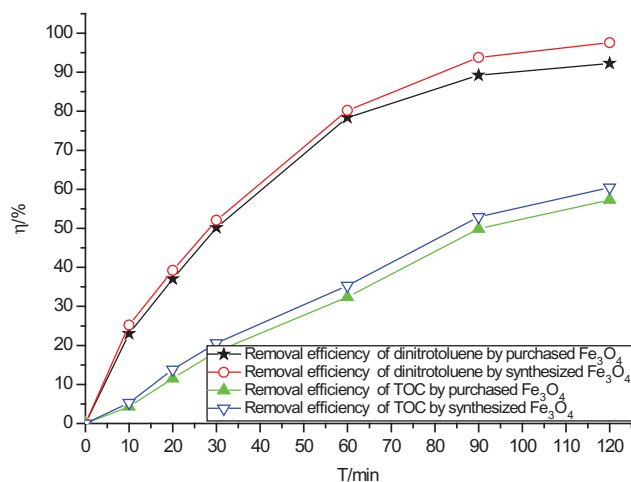


Figure 7. Comparison of the ability of synthesized Fe_3O_4 and purchased Fe_3O_4 to remove dinitrotoluene.

on the dinitrotoluene degradation than the Fe_3O_4 in the market. Besides, the test results suggest that the benzene ring structure of dinitrotoluene was destroyed and decomposed in the Fenton-like reaction system and further mineralized; after the completion of the reaction, the degradation rate of dinitrotoluene was greater than the removal rate of TOC, indicating that the dinitrotoluene was not completely mineralized to CO_2 , part of it was converted into other organic substances, such as alcohols, acetic acids (Lei et al. 2007).

Study of catalytic mechanism

Currently, the common view on the Fenton-like oxidation mechanism is the hydroxyl radical ($\bullet\text{OH}$) theory; the hydroxyl radical ($\bullet\text{OH}$) generated by catalyzing H_2O_2 in the Fenton-like oxidation reaction is the main active species (Zhou et al. 2013) used to degrade organic pollutants by oxidation. To verify whether the dinitrotoluene was degraded by the oxidation of hydroxyl radical ($\bullet\text{OH}$), one test group with the trapping agent of hydroxyl radical ($\bullet\text{OH}$) added was compared with the other test group without the trapping agent of hydroxyl radical ($\bullet\text{OH}$) added, and the test results are as shown in Figure 8.

Figure 8 shows that the adding of excessive tertiary butanol has a great interference with the removal efficiency of the catalytic reaction, indicating hydroxyl radical ($\bullet\text{OH}$) existed in the reaction system. After the hydroxyl radical ($\bullet\text{OH}$) was captured and removed by tertiary butanol, the oxidation degradation efficiency decreased significantly. However, it is also found that the reaction system still had a certain remove efficiency even after the hydroxyl radical ($\bullet\text{OH}$) was captured and removed, indicating that there may be oxidative activity species in the nano- $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ catalytic system except

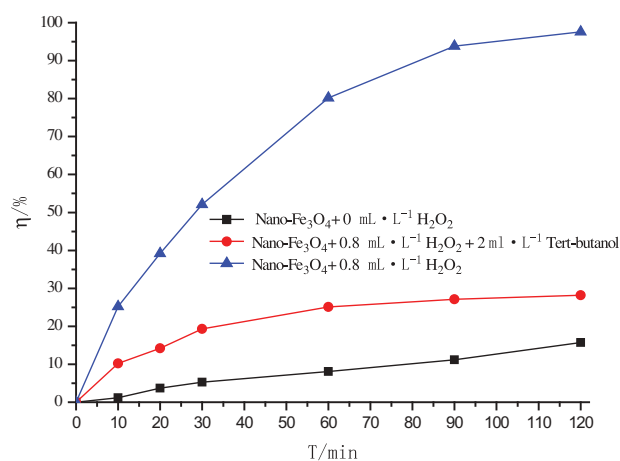


Figure 8. Effect of addition of tert-butanol on removal deficiency of dinitrotoluene.

for hydroxyl radical ($\bullet\text{OH}$), like superoxide radical ($\text{HO}_2\bullet$) (Luo et al. 2010; Xu et al. 2009).

For verification, the trapping agent of hydroxyl radical ($\bullet\text{OH}$) and superoxide radical ($\text{HO}_2\bullet$), i.e., benzoquinone were added to verify if there was superoxide radical in the reaction. The test results are as shown in Figure 9. Compared to Figure 8, we can see that the reaction system has a certain removal efficiency of dinitrotoluene equivalent to the removal rate during pure adsorption of nano- Fe_3O_4 , and this proves the theory that there is superoxide radical ($\text{HO}_2\bullet$) in the reaction system. Based on the preceding analysis, we hypothesized that the specific reaction mechanism of nano- $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ system is Equations (1)–(4):

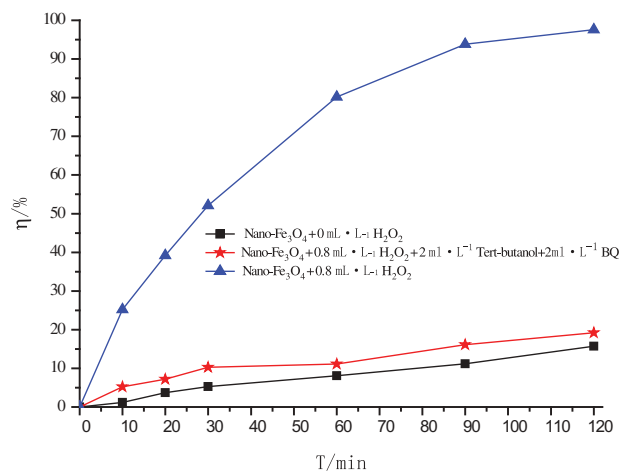
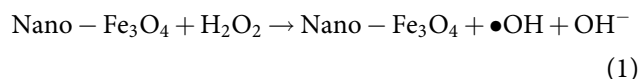
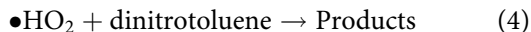
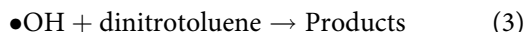
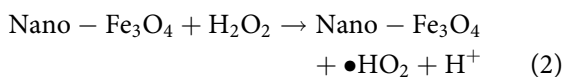


Figure 9. Effect of addition of benzoquinone on removal deficiency of dinitrotoluene.



Conclusions

- The Fe₃O₄ crystal self-prepared in the laboratory is ball-like, with uniform distribution of particle size ranging from 20 to 30 nm and superparamagnetism. Its catalytic degradation effect is better than that of the commercial micron-scale Fe₃O₄.
- The magnetic nano-Fe₃O₄-H₂O₂ system can effectively degrade dinitrotoluene within the pH value range from 1 to 9, and the optimal pH is 3; with the increase of catalyst dosage, the degradation efficiency and the catalytic reaction rate of dinitrotoluene will grow as well, and the optimal catalyst dosage is 1.0 g/L; when the H₂O₂ dosage is within the range of 0 to 0.8 mL/L, with the increase of H₂O₂ dosage, the degradation efficiency and the reaction rate will grow as well. However, with the further increase of the H₂O₂ dosage, the degradation efficiency and the reaction rate will decrease;
- The self-prepared nano-Fe₃O₄-H₂O₂ system can degrade dinitrotoluene better than the commercial micron-scale Fe₃O₄-H₂O₂ system. In the best conditions with the H₂O₂ dosage of 0.8 mL/L, the catalyst concentration of 1 g/L and the pH value of 3 at room temperature of 25°C, the degradation rate of the 100 mg/L dinitrotoluene in 120 min can reach 97.6%, and the reaction rate of the same will be 0.0314 min⁻¹; and,
- Through the use of the probe compounds n-butyl alcohol and benzoquinone, it is proved that the oxidation activity species in the nano-Fe₃O₄-H₂O₂ catalytic system are mainly hydroxyl radical (•OH) and superoxide radicals (HO₂•), based on which the reaction mechanism has been hypothesized.

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