



Research Article

The Catalytic Degradation Performance of α -FeOOH Doped with Silicon on Methyl Orange

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Abstract

In order to improve the catalytic degradation property of α -FeOOH, α -FeOOH was doped with sodium silicate. The α -FeOOH doped with silicon was used as catalyst to catalyze the degradation of methyl orange. The XRD spectra showed that the crystalline phase of α -FeOOH doped with silicon was same as that of α -FeOOH. The catalytic degradation property of α -FeOOH doped with silicon was 21.7% higher than that of α -FeOOH. The results showed that catalytic degradation of methyl orange was almost degraded thoroughly at the conditions that the concentration of α -FeOOH doped with silicon in the solution was 0.73 g/L, the concentration of H₂O₂ was 0.231 mmol/L. The pH value was between 2 and 3, and the degradation reaction was carried out at 60 °C for at least 20 min. Copyright © 2016 BCREC GROUP. All rights reserved

Keywords: α -FeOOH doped with silicon; catalytic degradation; methyl orange

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1. Introduction

α -FeOOH is not only a kind of common yellow inorganic pigments, but also can be used as precursor of magnetic recording medium γ -Fe₂O₃. Furthermore, α -FeOOH has a large specific surface area, small particles structure and strong adsorption ability. So it is emphasized to apply on environmental engineering [1]. For instance, it can be used as a removal agent of heavy metal in wastewater and gas desulfurization agent etc. [2-3]. In recent years many workers developed more applications of α -FeOOH on environmental engineering, especially application to the catalytic degradation of

organic materials. At the same time, some reports focused on increasing the catalytic degradation property of α -FeOOH by doping with other elements, such as manganese, aluminum and silicon elements, etc. [4-6]. In several papers, α -FeOOH and α -FeOOH doped with other elements have been employed to degrade the poisonous and refractory aromatic pollutants, such as phenol, perfluorooctane compounds, benzoic acid, and phthalic acid [7-9]. The results showed that they had a great effect on the degradation of these materials.

In this paper, the α -FeOOH was doped with silicon to endow α -FeOOH particles more reactive centers to improve its catalytic degradation property. Methyl orange was employed to test the catalytic degradation ability of α -FeOOH before and after modification. The optimal catalytic degradation conditions on methyl

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orange was studied. The results showed the catalytic degradation ability of α -FeOOH doped with silicon increased a lot.

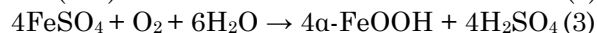
2. Materials and Methods

2.1. Materials

Ferrous sulfate reagent (AR), sulfuric acid (AR), sodium hydroxide (AR), methyl orange were produced from Chengdu Chemical agent Company, China, and sodium silicate (AR) and hydrogen peroxide solution (AR) from Chongqing Chemical Reagent Factory, China. Deionized water was prepared in our laboratory and was used for the experiments and tests.

2.2. The synthesis of α -FeOOH doped with silicon

The sodium silicate solution (0.36 g/L) was mixed with sodium hydroxide solution (1.0 mol/L), then the mixed solution was dropped into the ferrous sulfate (0.16 g/L) solution with continuous stirring at 60 °C for 2 h. Ultimately the synthesis of α -FeOOH doped with silicon was gained after suction filtration, drying and milling. The chemical reactions about preparation nanoparticles of α -FeOOH were displayed in Equations (1-3).



2.3. XRD spectra of α -FeOOH

The XRD spectra of α -FeOOH before and after doped with silicon were analyzed by using a Rigaku XD-3 (Beijing Purkinje General Instrument Co. Ltd., Beijing, China) at room temperature, at the scattering angles from 5° to 80°.

2.4. The catalytic degradation of methyl orange.

α -FeOOH and H_2O_2 were added to methyl orange solution (20 mg/L, 20 ml), and reacted for some time at different temperature and pH. After degradation treatment, the absorption value of methyl orange solution was measured by the TU-1810 ultraviolet and visible spectrophotometer instrument (Beijing Purkinje General Instrument Co. Ltd., Beijing, China). Based on the relationship between concentration of methyl orange (MO) in the solution and standard curve, the degradation rate could be obtained by the change of the concentrations of

methyl orange in solution after degradation treatment, and degradation rate calculation formula was presented in Equation (4).

$$\text{Degradation rate of MO} = (C_0 - C_t)/C_0 \times 100\% \quad (4)$$

where C_0 was the original concentration of methyl orange, and C_t was the concentration of methyl orange after degradation treatment.

3. Results and Discussion

3.1. Characterization of α -FeOOH doped with silicon

The XRD spectra of α -FeOOH before and after doped with silicon are shown in Figure 1. From Figure 1, both of the spectra of α -FeOOH before and after doped with silicon exhibited the characteristic diffraction peaks at 21.25°, 33.33°, 34.77°, 36.74°, 40.01°, 41.21°, 53.22°, 59.06°, 61.45°, 64.10° and 71.74°, respectively. There were basically no impurity peaks. The results suggested that the lattice of α -FeOOH particles was complete, and the α -FeOOH crystalline phase did not change.

3.2. Degradation rate at different dosages of α -FeOOH doped with silicon

Figure 2 shows the catalytic degradation rates of methyl orange at the different dosages of α -FeOOH doped with silicon at 60 °C, pH 2.5 and H_2O_2 1 ml. From Figure 2, when the reaction time was 10 min, the catalytic degradation rate of methyl orange raised greatly with the increasing of α -FeOOH dosage doped with silicon. While the time was up to 20 min, 97.6% methyl orange was degraded on the dosage of α -FeOOH doped with silicon (1.33 and 0.73

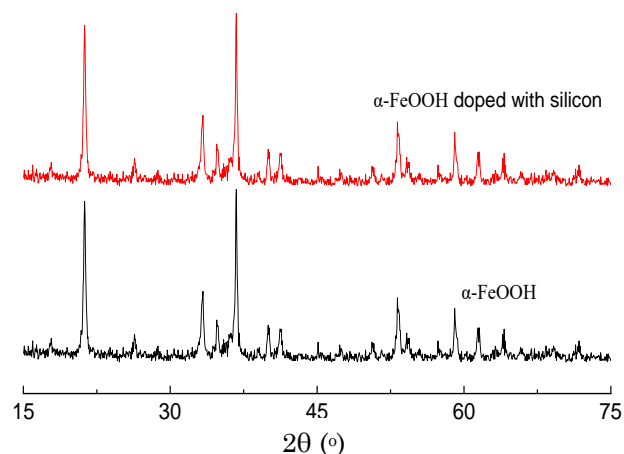


Figure 1. XRD spectra of α -FeOOH before and after doping with silicon

g/L), and for 30 min, the 0.33 g/L α -FeOOH with silicon could also catalyze to degrade methyl orange in same effect. The catalytic mechanism is that the hydrogen peroxide and organic molecules have been absorbed by the active center of catalytic as soon as they spread to the surface. Then the generated hydroxyl radical can oxidize the organic molecules. According to Figure 2, the following text selected 0.73 g/L as the best concentration of α -FeOOH doped with silicon to degrade the methyl orange.

3.3. Degradation rate at different dosages of H₂O₂

Figure 3 shows the catalytic degradation rate of methyl orange at the dosage of H₂O₂. When the degradation time was 10 min, the degradation rate increased obviously with the increase of H₂O₂ concentration. But when the H₂O₂ concentration was higher than 0.231 mmol/L, high H₂O₂ concentration did not cause high degradation rate, even the degradation rate decreased slightly. This is because in the degradation process, hydrogen peroxide is a strong oxidizer, which could produce a lot of hydroxyl free radicals under the catalysis of α -FeOOH, and then the organic compounds were degraded quickly in the initial time. But if there is excessive hydroxyl radicals in the system, the hydroxyl radicals will react themselves, and then the degradation effect decreases slightly. So the best concentration of 0.231 mmol/L was chosen.

3.4. Degradation rate at different temperature

The effect of catalytic degradation at different temperatures is shown in Figure 4. From

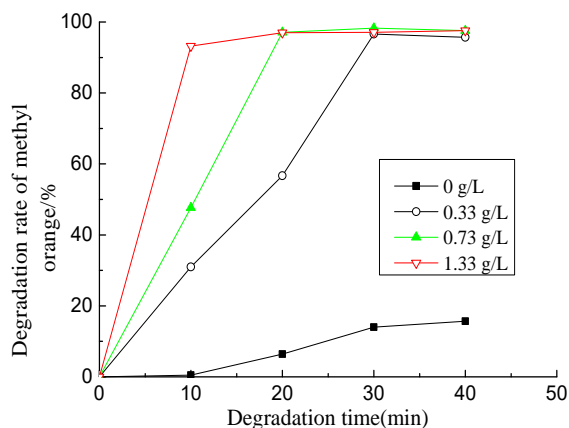


Figure 2. Effect of silicon dosage on catalytic degradation rate of methyl orange on α -FeOOH

Figure 4, the higher the temperature was, the higher the degradation rates were. When the temperature was above 45 °C, and the reaction time was longer than 30 min, all the degradation rates could be higher than 96.2%. Actually, there are several processes of catalytic degradation with α -FeOOH as catalyst, including the adsorption of target materials on the surface of α -FeOOH; the catalytic reaction on the surface of α -FeOOH; desorption of products after reaction from the surface of α -FeOOH and the procedure of diffusion into the solution. All the adsorption, catalytic reaction and desorption processes were accelerated by temperature. The molecular diffusion rate increased greatly with the continuous increasing temperature, which contributed to each stage of the reaction. From Figure 4, the temperature of 60 °C was considered as the ideal temperature-dependent parameter.

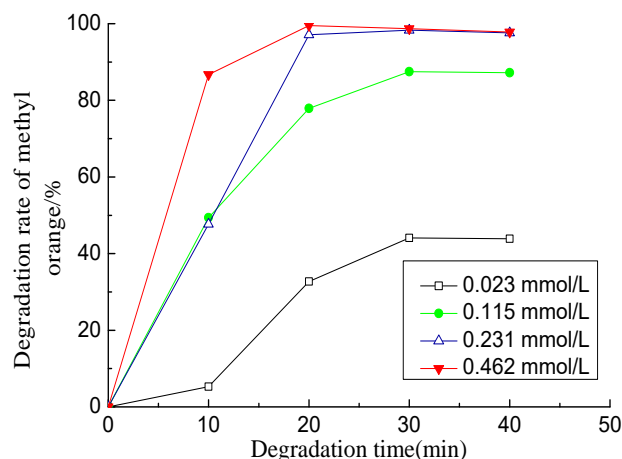


Figure 3. Effect of H₂O₂ concentration on catalytic degradation rate of methyl orange

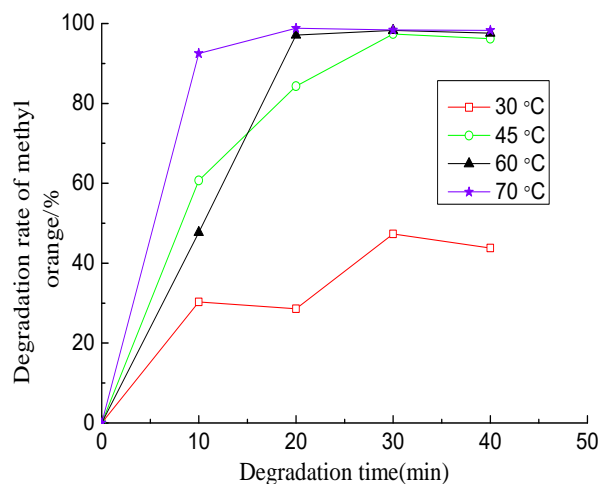


Figure 4. Effect of temperature on catalytic degradation rate of methyl orange

3.5. The degradation rate at different pH

At the optimum conditions of temperature, dosage of α -FeOOH and H_2O_2 , respectively, the effect of catalytic degradation of methyl orange at different pH is shown in Table 1. In this series of tests, with the augmentation of alkaline concentration, the degradation effect of methyl orange decreased greatly. By comparison, when the pH of the solution was 2.39, the methyl orange was degraded most thoroughly. This is because H_2O_2 is easier to decompose in alkaline solution than that of H_2O_2 in acid solution. So the pH value should be controlled between 2 and 3.

3.6. The catalytic degradation property of α -FeOOH before and after doping with silicon.

At the optimum conditions that were obtained above, the effect of catalytic degradation rate of methyl orange on before and after doping with silicon is shown in Figure 5. From Figure 5, there was an obvious difference before and after the α -FeOOH doped with silicon. When the reaction time was 40 min, the degradation of methyl orange on α -FeOOH doped with silicon was 97.6%, while the untreated α -FeOOH was 75.9%. This is because the α -FeOOH doped with silicon has more reactive centers than that of untreated α -FeOOH, the degradation reaction was completed at one and

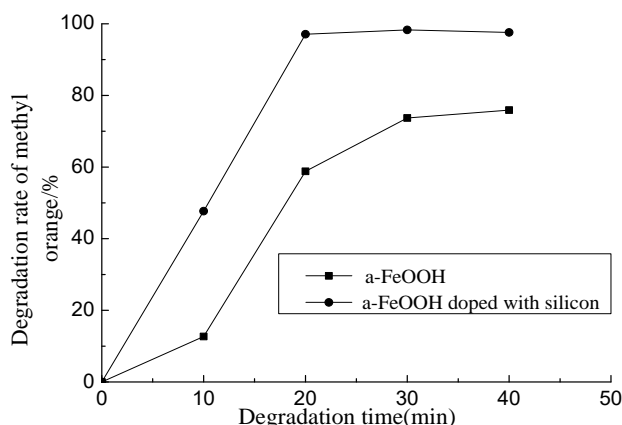


Figure 5. Effect of α -FeOOH before and after doped with silicon on catalytic degradation rate of methyl orange

two dimensional boundary crisscross where there were no enough atoms to form perfect lattice sequence and full valence. Because of such defect, there were many area to form more catalytic center. The addition of silicon would lead to part of the generation of Fe^{2+} , thus enhanced the catalytic activity of α -FeOOH, and then the degradation rate of methyl orange increased obviously.

4. Conclusions

The catalytic degradation ability of α -FeOOH could be improved efficiently by doping with silicon. The catalytic degradation property of modified α -FeOOH was 21.7% higher than that of original α -FeOOH. The results indicated that when the pH value of solution was between 2 and 3, the surrounding temperature was 60 °C, the degradation time was at least 20 minutes and the dosage of α -FeOOH doped with silicon and H_2O_2 were 1.33 g/L and 0.231 mmol/L, respectively, the methyl orange sample had almost been degraded thoroughly. The XRD spectra indicated that the crystalline phase of α -FeOOH doped with silicon was same as that of α -FeOOH. This showed the doping silicon is an effective method to increase the catalytic degradation ability of α -FeOOH.

Acknowledgments

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Table 1. Effect of catalytic degradation of methyl orange at different pH of the solution

pH value	2.39 (2~3)	5.00 (4~6)	6.71 (\approx 7)	10.46 (>8)
Absorption	0.018	0.772	0.805	0.804

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