ISSN: 2414-1895 DOI: 10.6919/ICJE.202505_11(5).0038

Heterogeneous Catalytic Degradation of Methyl Orange by H_2O_2 with FeS Micro-flakes

Shaoming Zeng*

School of Physics and Optoeletronic Engineering, Guangdong university of technology, Guangzhou, Guangdong, 510006, China

*E-mail: zengshaom@126.com

Abstract

Organic dyes are common water pollutants that harm both the environment and human health. This study addressed this issue by synthesizing FeS as a heterogeneous catalyst, using methyl orange (MO) as the target pollutant and H_2O_2 as the oxidant. The degradation performance of FeS was examined. Experimental results demonstrated that, without pH adjustment and at 30 °C, the synergistic effect of 0.8 g/L FeS and 20 mM H_2O_2 achieved over 90% degradation of MO within 10 minutes and nearly complete removal of MO within 20 minutes. Moreover, high degradation efficiency was achieved over a wide pH range (2 ~ 7.5). This work offers a new and efficient approach for treating dye-containing wastewater.

Keywords

FeS Micro-flakes; Fenton Reaction; Degradation; MO.

1. Introduction

The issue of environmental pollution is one of the most significant and important ones in the world today. It is estimated that the textile industry produces about 1 million tons of dyes and pigments annually, but 10% of the colorants are lost during production and application, which undoubtedly causes continuous pollution to soil and water bodies[1]. Dark colored pollutants can block sunlight from penetrating water bodies, thereby affecting the photosynthesis of aquatic plants and severely impacting the food sources of aquatic organisms. At the same time, the discharge of dyes forms a thin layer on the surface of the water, reducing the dissolved oxygen in the water and affecting the respiration of aquatic animals[2].

At present, there are many methods for degrading textile wastewater, such as coagulation [3,4], adsorption [5], microbial degradation [6], advanced oxidation technology [7-11], etc. Advanced oxidation processes (AOPs) are efficient and environmentally friendly for removing organic pollutants from water [12]. In addition, AOPs also have the advantages of simple operation, fast reaction, good environmental compatibility, and wide pH range [13-16]. As one of the AOPs, Fenton method is considered the most powerful oxidation treatment tool and has been widely applied. However, the traditional Fenton method requires strict acidic conditions, while other activation methods require additional energy consumption and equipment requirements. In contrast, the non-homogeneous Fenton reaction method has relatively relaxed requirements for the reaction environment. Heterogeneous catalysts can effectively activate H_2O_2 and generate hydroxyl radicals (HO ·) for the degradation of organic pollutants. When degrading monoazo pigments, oxidative attack mainly occurs at the position of the azo bond, degrading the chromophore part of the molecule and leading to decolorization [17].

ISSN: 2414-1895 DOI: 10.6919/ICJE.202505_11(5).0038

At present, there are two types of heterogeneous catalysts, one is natural minerals [18-20], and the other is synthetic iron-based materials [21,22]. Based on the above situation, a FeS with micro-flakes structure was synthesized by hydrothermal method. The prepared FeS micro-flakes serve as heterogeneous Fenton catalysts for the degradation of methyl orange dye (MO). This research aims to explore the efficiency of degrading MO using FeS micro-flakes and the influence about pH on degradation efficiency

2. Experiment

2.1 Materials and Instruments

The simulated dye wastewater in the experiment was prepared using MO (Sigma Aldrich, 99.99%). Fe (Alfa Aesar, 99.5%) and $Na_2S·9H_2O$ (Aladdin, 99.99%) were used as raw materials for preparing FeS micro-flakes. In addition, NaOH (Aladdin, 98%) and HCl (ThermoFisher, 30%) were used to adjust the pH of the MO solution. The solvent used in the experiment is ultrapure water. The MO concentration of the experimental solution was indirectly measured by a UV Vis spectrophotometer (EVOLUTION 201, Thermo science), while the pH of the solution was measured using a PHS-3C precision pH meter. To ensure the accuracy of pH, the pH meter must be calibrated with a pre configured calibration solution before use.

2.2 Preparation

Based on our previous work [23], FeS micro-flakes were prepared using a hydrothermal method. Weigh 25 mg of MO and add it to the flask. Add an appropriate amount of ultrapure water and sonicate the mixture for 60 seconds to completely dissolve MO in water. Add the mixture into a 250 ml volumetric flask and fill it with ultrapure water to prepare a 100 ppm MO standard solution. Before the experiment begins, prepare solutions of different concentrations using the MO standard solution. By measuring the absorbance of different MO concentrations, establish a linear relationship between absorbance and MO concentration for subsequent degradation experiments to calculate MO concentration and removal efficiency.

2.3 Degradation Experiment

Prepare 100 ml of 50 ppm MO solution using the standard solution. First, measure the initial absorbance of the solution, then place the prepared solution on a magnetic stirrer and add FeS micro-flakes. After the FeS micro-flakes are uniformly stirred in the solution, H_2O_2 is rapidly added using a pipette to initiate the reaction. Collect samples and filter residual FeS micro-flakes at different degradation time. In order to reduce errors, the solution sample was immediately tested using a spectrophotometer after collection. Based on the previously established linear relationship between absorbance and MO concentration, the concentration is determined and the degradation efficiency is calculated by measuring the absorbance of the sample. The degradation efficiency is commonly used to evaluate the performance of FeS micro-flakes in degrading MO. In formula 1, the initial concentration (C_0) and instantaneous concentration (C) of MO are expressed in milligrams per liter (mg/L).

$$\text{degradation efficiency} = \frac{(C_0 - C)}{C_0} \quad (1)$$

3. Results and discussion

3.1 The plotting of scan spectra and standard curves.

Take a 10 ppm concentration of MO solution and use a spectrophotometer to scan the spectrum in the visible wavelength range to determine the optimum absorption wavelength. Fig.1 (a) shows the spectrum of absorption wavelengths within the visible light wavelength range and determines 463 nm as the optimal absorption wavelength for MO solution. Usually, low concentrations of MO can be directly measured using a spectrophotometer, while high concentrations of MO need to be diluted to

ISSN: 2414-1895 DOI: 10.6919/ICJE.202505_11(5).0038

low concentrations before measurement. Therefore, a linear relationship between MO concentration and absorbance was plotted using MO solutions of different concentrations (0, 2, 4, 6, 8, 10 ppm), with MO concentration on the x-axis and absorbance on the y-axis, as shown in Fig. 1 (b). Meanwhile, the functional relationship between absorbance and MO concentration is shown in Equation 2. The fitting coefficient is greater than 0.99. Among them, y is the adsorption coefficient, and x is the MO concentration (mg/L).

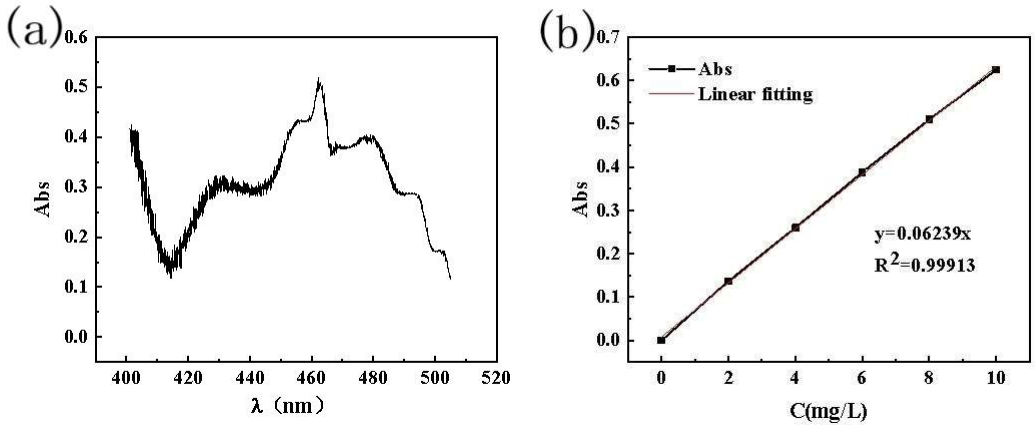

Fig. 1 (a) Scanning spectrum of 10 ppm MO solution. (b) Standard curve of absorbance-MO concentration.

$$y = 0.06239x \quad (2)$$

3.2 The Efficiency of FeS Catalytic Degradation of MO

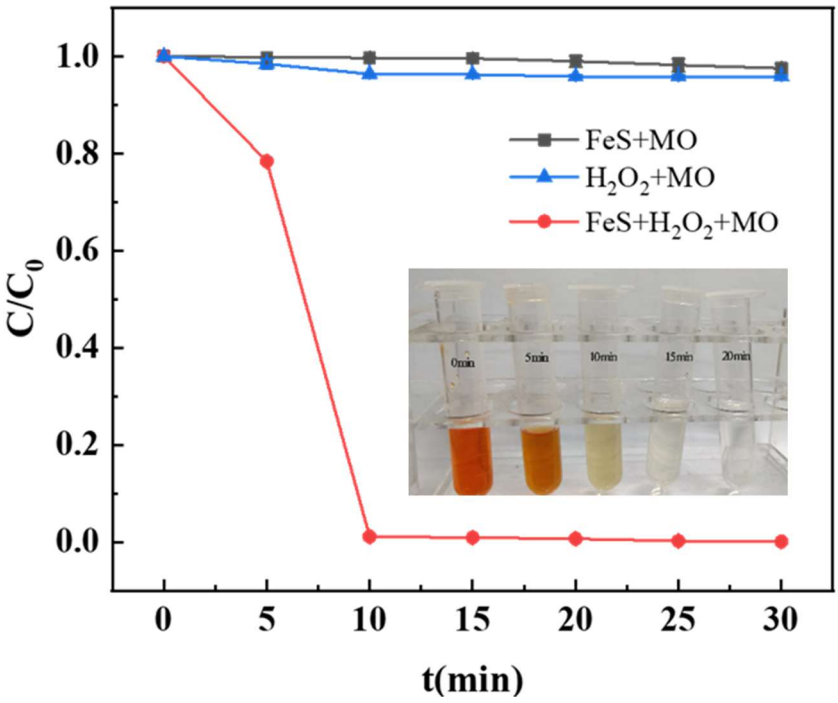

Fig. 2 MO degradation efficiency of different reaction systems (MO=50 ppm, FeS=0.8 g/L, H2O2=20 mM, temperature = 30°C; pH = 6.5). The illustration shows the color change of MO degraded with time in FeS/H_2O_2/MO system.

To investigate the performance of FeS micro-flakes in degrading MO, three experiments were conducted under the same experimental conditions. As shown in Fig. 2, under the same experimental

ISSN: 2414-1895 DOI: 10.6919/ICJE.202505_11(5).0038

conditions, when only 0.8 g/L FeS or 20 mM H_2O_2 is added, the color of MO hardly changes, and the concentration change of MO before and after the reaction detected by the instrument is very small. However, in the FeS/H_2O_2/MO system, the color transition process during MO degradation is: deep red → brown → light brown → colorless. After 30 minutes, the absorbance approached zero and the MO removal efficiency was calculated to be greater than 99%, indicating that the addition of FeS alone did no effect on the degradation of MO. It can be concluded that FeS alone cannot achieve efficient degradation of MO through its own reduction or adsorption properties, and H_2O_2 alone is difficult to degrade and generate free radicals on its own, and its oxidation performance is weak. When H_2O_2 and FeS micro-flakes were added simultaneously, it was evident that the MO solution was oxidized and discolored, confirming that FeS micro-flakes are an efficient catalyst that can rapidly activate H_2O_2 and degrade MO.

3.3 The Influence of pH on Degradation Efficiency

Take seven 100 ml MO soulution with the concentration of 50 ppm, adjust the pH to 2, 3, 4, 5, 6.5 (without pH adjustment), 7.5 and 8.5 in turn, then add 0.5 g/L FeS micro-flakes, stir evenly, add 20 mM H_2O_2 to start the reaction, and take samples at fixed times. The results are shown in Fig. 3.

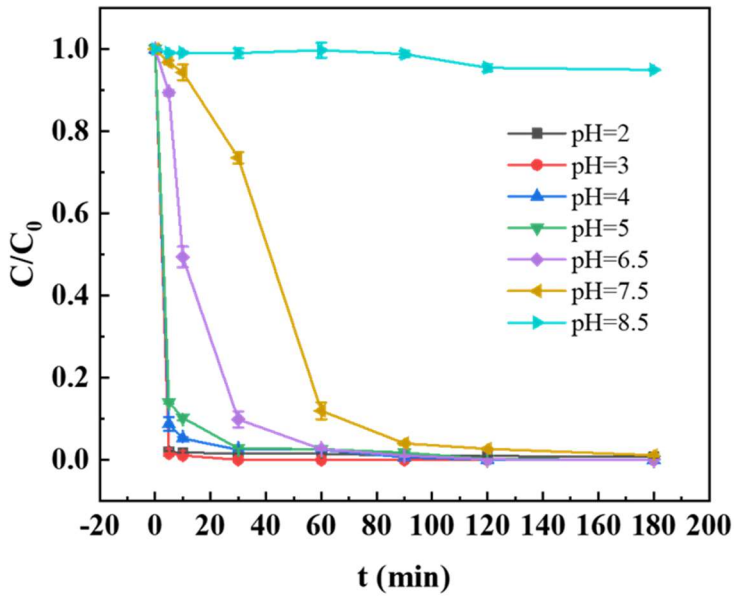

Fig. 3 Effect of initial pH on MO degradation (MO=50 ppm, FeS=0.5 g/L, H_2O_2=20 mM, temperature = 30℃; pH = 6.5).

It is known that Fe^{2+} can act as a heterogeneous catalyst to generate the • OH from H_2O_2 in acidic environments. • OH has a high oxidation-reduction potential, which can rapidly oxidize organic pollutants in wastewater without selectivity, thereby breaking down large organic molecules that are difficult to degrade in the medium into small organic molecules that are easily degraded by microorganisms, or completely mineralizing into CO_2 and H_2O [24,25]. In the pH range of 2 to 7.5, FeS micro-flakes can maintain a high removal efficiency, reaching over 99% within 3 hours, far higher than the classical Fenton reaction. What's more, FeS still maintains high removal efficiency in weakly alkaline environments, which indicating excellent applicability of the catalyst to pH. The reason may be that the presence of sulfur ions has a good buffering effect on the pH of wastewater. The best pH of MO degradation efficiency is pH=3, which may be due to the following reasons: (1) MO is more active and easier to degrade under acidic conditions. The basic structure of MO is azobenzene, which is relatively stable [26]; (2) Under strong alkaline conditions, the decomposition rate of free radicals accelerates, which is not conducive to further mineralization of MO.

ISSN: 2414-1895 DOI: 10.6919/ICJE.202505_11(5).0038

When the pH increased from 2 to 7.5, the degradation efficiency of MO significantly decreased. It can be explained that the self oxidation decomposition ability of H_2O_2 is enhanced, which inhibits the production of • OH. Fe^{2+} in the solution precipitates in the form of hydroxide, removing the catalytic ability, thus facilitating the removal of MO under acidic conditions. When the pH value is too low (pH⩽2), the concentration of H^+ is too high, which is not conducive to the formation of Fe^{2+} and the stability of • OH is poor, resulting in slow degradation of MO. When the pH ⩾ 8.5, some Fe^{2+} hydrolyzes to form the hydroxy complex Fe $(OH)^+$, which is easily oxidized by dissolved oxygen in water to form iron ion hydrates. This will inhibit the production of • OH and cause iron ions to precipitate in the form of hydroxides, reducing or losing oxidation. $Fe(OH)_2$ complex is easily adsorbed on the surface of FeS, forming an electronic barrier. In addition, excessively high pH values can lead to the self decomposition of H_2O_2.

4. Conclusion

In this study, FeS micro-flakes were prepared by hydrothermal method and applied to activate H_2O_2 for the degradation of MO. The experimental results show that the synergistic effect of 0.8 g/L FeS and 20 mM H_2O_2 can achieve over 90% degradation of MO within 10 minutes and nearly complete removal of MO within 20 minutes. In the pH range of 2 ~ 7.5, the removal efficiency of MO can also reach 99% within 3 hours. This demonstrate that FeS is an efficient catalyst for dye wastewater treatment.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (Grant Nos. 51702058).

References

[1] NIDHEESH P V, GANDHIMATHI R. Trends in electro-Fenton process for water and wastewater treatment: An overview [J]. Desalination, 2012, 299(1-15.

[2] DESAI C, KUMAR B D. Four and half decades of Indian Journal of Pharmacology [J]. Indian Journal of Pharmacology, 2014, 46(5): 473-4.

[3] KHOUNI I, MARROT B, MOULIN P, et al. Decolourization of the reconstituted textile effluent by different process treatments: Enzymatic catalysis, coagulation/flocculation and nanofiltration processes [J]. Desalination, 2011, 268(1-3): 27-37.

[4] RIERA-TORRES M, GUTIERREZ-BOUZAN C, CRESPI M. Combination of coagulation-flocculation and nanofiltration techniques for dye removal and water reuse in textile effluents [J]. Desalination, 2010, 252(1-3): 53-9.

[5] LIU Y, LIU Y. Biosorption isotherms, kinetics and thermodynamics [J]. Separation and Purification Technology, 2008, 61(3): 229-42.

[6] BRAS R, GOMES A, FERRA M I A, et al. Monoazo and diazo dye decolourisation studies in a methanogenic UASB reactor [J]. Journal of Biotechnology, 2005, 115(1): 57-66.

[7] BABUNA F G, CAMUR S, ALATON I A, et al. The application of ozonation for the detoxification and biodegradability improvement of a textile auxiliary: Naphtalene sulphonic acid [J]. Desalination, 2009, 249(2): 682-6.

[8] ROBINSON T, MCMULLAN G, MARCHANT R, et al. Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative [J]. Bioresource Technology, 2001, 77(3): 247-55.

ISSN: 2414-1895 DOI: 10.6919/ICJE.202505_11(5).0038

[9] DE A K, CHAUDHURI B, BHATTACHARJEE S, et al. Estimation of (OH)-O-center dot radical reaction rate constants for phenol and chlorinated phenols using UV/H2O2 photo-oxidation [J]. Journal of Hazardous Materials, 1999, 64(1): 91-104.

[10] GUADALUPE A, ROSALBA R M, EDITH M. Oxidation of halobenzenes by OH radical produced radiolytically in aqueous solution [J]. Radiation Physics and Chemistry, 2021, 187(

[11] YANG Z S, JIANG W J, ZHANG Y, et al. Inactivation of dinoflagellate Scripsiella trochoidea in synthetic ballast water by advanced oxidation processes [J]. Environmental Technology, 2015, 36(6): 750-9.

[12] JUSTINO C, MARQUES A G, RODRIGUES D, et al. Evaluation of tertiary treatment by fungi, enzymatic and photo-Fenton oxidation on the removal of phenols from a kraft pulp mill effluent: a comparative study [J]. Biodegradation, 2011, 22(2): 267-74.

[13] BEDOUI A, SIN K, BENSALAH N. Treatment of refractory organics contained in actual agro-industrial wastewaters by UV/H2O2 [J]. Clean-Soil Air Water, 2008, 36(4): 373-9.

[14] DWYER J, LANT P. Biodegradability of DOC and DON for UV/H2O2 pre-treated melanoidin based wastewater [J]. Biochemical Engineering Journal, 2008, 42(1): 47-54.

[15] WU J J, MURUGANANDHAM M, CHANG L T, et al. Oxidation of propylene glycol methyl ether acetate using ozone-based advanced oxidation processes [J]. Ozone-Science & Engineering, 2008, 30(5): 332-8.

[16] EDALATMANESH M, MEHRVAR M, DHIB R. Optimization of phenol degradation in a combined photochemical-biological wastewater treatment system [J]. Chemical Engineering Research & Design, 2008, 86(11A): 1243-52.

[17] ILHA C E G, DOS SANTOS A, SOUZADE J R. Degradation of Monoazo Pigments Red 53:1 and Red 48:2 by Fenton, Photo-Fenton and UV/Peroxide Reactions [J]. Clean-Soil Air Water, 2009, 37(10): 799-805.

[18] MATTA R, HANNA K, CHIRON S. Fenton-like oxidation of 2,4,6-trinitrotoluene using different iron minerals [J]. Science of the Total Environment, 2007, 385(1-3): 242-51.

[19] HUANG H H, LU M C, CHEN J N. Catalytic decomposition of hydrogen peroxide and 2-chlorophenol with iron oxides [J]. Water Research, 2001, 35(9): 2291-9.

[20] LU M C, CHEN J N, HUANG H H. Role of goethite dissolution in the oxidation of 2-chlorophenol with hydrogen peroxide [J]. Chemosphere, 2002, 46(1): 131-6.

[21] TIMOFEEVA M N, KHANKHASAEVA S T, BADMAEVA S V, et al. Synthesis, characterization and catalytic application for wet oxidation of phenol of iron-containing clays [J]. Applied Catalysis B-Environmental, 2005, 59(3-4): 243-8.

[22] LIU W J, QIAN T T, JIANG H. Bimetallic Fe nanoparticles: Recent advances in synthesis and application in catalytic elimination of environmental pollutants [J]. Chemical Engineering Journal, 2014, 236(448-63.

[23] LAI X F, ZHANG H, WANG Y Q, et al. Observation of Superconductivity in Tetragonal FeS [J]. Journal of the American Chemical Society, 2015, 137(32): 10148-51.

[24] AZBAR N, YONAR T, KESTIOGLU K. Comparison of various advanced oxidation processes and chemical treatment methods for COD and color removal from a polyester and acetate fiber dyeing effluent [J]. Chemosphere, 2004, 55(1): 35-43.

[25] CANIZARES P, PAZ R, SAEZ C, et al. Costs of the electrochemical oxidation of wastewaters: A comparison with ozonation and Fenton oxidation processes [J]. Journal of Environmental Management, 2009, 90(1): 410-20.

[26] DEVI L G, KUMAR S G, REDDY K M, et al. Photo degradation of Methyl Orange an azo dye by Advanced Fenton Process using zero valent metallic iron: Influence of various reaction parameters and its degradation mechanism [J]. Journal of Hazardous Materials, 2009, 164(2-3): 459-67.