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Recycling granular iron dust to effectively activate peroxymonosulfate for degradation of methylene blue

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Abstract:

Iron dust is a byproduct generated during the machining of cast iron workpieces in industrial production. Its recovery and appropriate utilization contribute to resource recycling and the mitigation of environmental pollution from industrial activities. Herein, the low-price granular iron dust (denoted GFD) was reused as a catalyst of peroxymonosulfate (PMS) for the efficient oxidation of methylene blue (MB) in water. At first, several properties of GFD, such as crystal structure and chemical composition, have been measured. Subsequently, the performance of GFD towards PMS activation was examined, where GFD/PMS system could effectively degrade MB within a short time frame. Under experimental conditions with an initial substrate concentration of 10 mg/L, PMS dosage of 1 mM, and GFD dosage of 1 g/L, the 98.4% MB could be eliminated in 10 min. In contrast, the removal efficiencies of MB in the PMS and GFD systems were only 13.0% and 6.3%, respectively. Additionally, the following quenching experiments reveal that the $^{\bullet}OH/SO_4^{\bullet-}$ as the dominant reactive oxygen species (ROS) is responsible for MB oxidation. This work provides insight into constructing cost-effective persulfate activation system for water decontamination.

Keywords: granular iron dust; peroxymonosulfate; methylene blue; radicals

1. Introduction

Methylene blue (MB) is an azo dye that has been widely utilized for a long time. In the medical field, among the earliest synthesized antimalarial drugs was MB, which was tested at the end of the nineteenth century. It was also used in combination with other drugs and reported to be effective for diseases like falciparum malaria [1]. In recent years, a lot of research on synthetic dye compounds have contributed to the widespread application of MB. The rapid increase in the discharge of wastewater containing such dyes has resulted in the release of substantial amounts of organics that are challenging to biodegrade, leading to serious water pollution. Dye wastewater possesses complex composition, high concentrations of organic matter, and elevated chromaticity, making it resistant to biological degradation. Specifically, MB wastewater exhibits high toxicity, significant residual effects, as well as carcinogenic, teratogenic, and mutagenic properties, posing severe risks to aquatic organisms and human health [2]. Once a certain dose of MB is ingested, it becomes a serious threat to human health and has been known to cause damage to organs and ailments such as breathing difficulties. Therefore, it is urgent to develop efficient strategies to remove such hazardous pollutants from the water bodies [3].

Currently, the traditional methods for treating MB wastewater include biodegradation, coagulation, adsorption, and traditional chemical oxidation. Biodegradation methods are commonly employed in wastewater treatment, but they are influenced by factors such as pH and temperature [4]. This means that a series of additional treatments is still required, which escalates both costs and time, making it unsuitable for practical large-scale application. Besides, research indicates that wastewater generated from dyes such as azo dyes exhibits limited biodegradability, rendering biodegradation methods ineffective for the removal of MB [5]. The adsorption technique has a lot of advantages such as ease of application, moderate cost, and high efficiency, particularly in the removal of organic pollutants. However, this method is generally not effective for the degradation of pollutants. This process mainly depends on the transfer of them onto the adsorbent. Moreover, during the recovery and regeneration of the adsorbents, there is a risk that the adsorbed pollutants could leak into the surroundings, resulting in secondary contamination [6]. Stringent control on the dosages and pH is required in the coagulation process, and unfavorable conditions would lead to a decline in removal rates [7]. Chemical treatment has advantages like high-efficiency and short remediation time, however, many of which are costly and labor-intensive. Moreover, improper operation can lead to secondary pollution, such as the exacerbation of soil functionality [8]. Advanced oxidation processes (AOPs) have emerged in recent years as an appealing method for the oxidative removal of refractory organic contaminants. Sulfate radical-based AOPs have been widely applied in the remediation of polluted soils and wastewater, owing to their high degradation efficiency and adaptability. Sulfate radical ($SO_4^{\bullet-}$) is a powerful oxidant with high oxidation potential (2.5-3.1 V) which can be generated by scission of peroxo bond (O─O) of either PMS or PDS during their activation [9]. Peroxydisulfate (PDS, $S_2O_8^{2-}$) and peroxymonosulfates (PMS, HSO_5^-) are known as the strong oxidants, but their direct reaction with the majority of the pollutants is very slow so that the further activation is required. They can be activated through thermal, ultraviolet light, activated carbon, transition metal (such as Fe^0 and Cu^{2+}), ultrasound, etc. to generate $SO_4^{\bullet-}$, which are capable of effectively degrading contaminants. For heat activation, the energy input by the high temperature (>50°C) can cause the fission of O─O bond to form the sulfate radicals via Eq. (1) [10]. Although PMS could be activated under higher temperature conditions, its efficiency is quite low [11]. The activation of PDS and PMS through ultrasonic means involves two mechanisms. In both cases, the cavitation bubbles generated by the ultrasonic initiate the activation of PDS and PMS. The first mechanism involves the local high temperature (5000 K) resulting from the collapse of these cavitation bubbles, which activates PDS and PMS. The second mechanism entails the decomposition of water molecules into hydroxyl radicals and hydrogen radicals by the cavitation bubbles, which further activates PDS and PMS. Among the two, PMS has an asymmetric molecular structure and is more suitable for the production of $SO_4^{\bullet-}$. Notably, sulfate radicals-based AOPs have advantages over radical $^{\bullet}OH$-based methods, including a higher oxidation potential and a wider pH range. For the activation by carbonaceous-based materials, the mechanism could be the electron conduction, in which the electrons are withdrawn from carbonaceous-based materials such as aromatic graphene structures. Carbonaceous-based materials can thus donate an electron to PDS or PMS to form the reactive radicals. However, carbonaceous materials can adsorb a portion of pollutants, which require further treatment. Additionally, after a period of use, these materials may lose their activation capacity due to surface deactivation. For the activation of PMS by metal ions and metal oxide, following a redox reaction via Eq. (1), among them, iron-based oxides show good activation efficiency and stability [10].

$$HSO_5^- + M^n \rightarrow M^{n+1} + SO_4^{\bullet-} + OH^- \qquad (1)$$

Benefiting from the advantages of low prices, environmental friendliness, and excellent catalytic performance, iron-based transition metal catalysts are widely utilized in PDS activation [12]. For example, Liang and Lai evaluated the feasibility of using Fe^0 as a source of Fe^{2+} for the activation of persulfate (PDS) in the degradation of trichloroethylene (TCE) [13]. Moreover, studies have demonstrated that catalysts for AOPs constructed with special structures using materials such as Fe can effectively activate PMS [14]. Zero-valent iron activation offers advantages such as low toxicity, cost-effectiveness, ease of operation, and negligible secondary pollution to the environment. The use of a zero-valent iron-based reaction system minimizes the loss of catalyst, reduces operational costs, and prevents secondary pollution because of its

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magnetic properties. Iron dust, as a byproduct of metal processing in industrial production, is known for with high yield and low cost, making it suitable for use as an activator in practical wastewater treatment. Furthermore, in the steel industry, the production process is often accompanied by the generation of significant solid waste, such as iron dust, which can account for approximately 15% of steel output [15]. The volume of slag generated has been increasing annually, yet its overall utilization rate remains very low. In 2015, the total production of slag in China exceeded 1 billion tons, with an overall utilization rate of only 10% [16]. The disposal of discarded Fe dusts not only leads to environmental pollution but also increases operational costs for enterprises. If Fe dust can be effectively recycled and utilized for wastewater treatment, it would bring beneficial waste management outcomes and promote the cyclical use of waste materials. This study uses granular iron dust (GFD) to activate PMS for the degradation of MB in wastewater, exploring the feasibility of its activation for the degradation of MB and analyzing the underlying activation mechanisms.

2. Materials and Methods

2.1 Materials and Reagents

The granular iron dust was procured from Zhengzhou JinDeShuo Metal Materials Co., Ltd. The image of GFD is depicted in Figure 1. Potassium monopersulfate triple salt was acquired from Shanghai Macklin Biochemical Technology Co., Ltd. MB was sourced from Guangzhou Howei Pharma Tech Co., Ltd. Sodium thiosulfate pentahydrate was purchased from Sinopharm Chemical Reagent Co., Ltd. Methanol was obtained from Tianjin Hengxing Chemical Preparation Manufacturing Co., Ltd. And the purified water (Hangzhou Wahaha Group Co., Ltd.) was throughout used in all experiments.

2.2 Experimental Methods

The degradation experiments for the catalytic oxidation of MB were carried out in a glass beaker at room temperature, and the solution was homogeneously mixed through a constant magnetic stirring. In all experiments, a reaction volume of 200 mL was used. The specified concentrations of MB, GFD, and PMS were added sequentially to initiate each experiment. At given reaction time intervals, samples were withdrawn from the flask, and excess thiosulfate pentahydrate was added as the reaction terminator into the samples for further analysis. In the quenching experiment, a specific amount of Methanol was added to the stirred MB solution, followed by the sequential addition of GFD and PMS. The subsequent sampling and analysis steps were identical to those conducted in previous experiments.

2.3 Analysis Methods

The crystal structure of the GFD was characterized using X-ray diffraction (XRD, D8 ADVANCE BRUKER) with Cu Kα radiation at a speed of 5°/min. The surface morphology of GFD is obtained through a scanning electron microscope (SEM, Helios 5 PFIB CXe Thermo Fisher Scientific). The absorbance of the MB solution was measured using a UV/Vis spectrophotometer (HY-721, Shanghai Yoke Instrument Co., LTD.) at a wavelength of 665 nm. Based on the Langmuir-Beer law, the variations in absorbance of the solution could be utilized as a substitute for concentration to calculate the removal efficiency. The removal efficiency of MB at different reaction times *t* could be calculated via Equation (2).

$$Q = \frac{A_0 - A_t}{A_0} \times 1\,00\% \tag{2}$$

In the equation, A_0 represents the initial absorbance value, A_t denotes the absorbance value of MB at the reaction time t and Q indicates the removal efficiency of MB.

3. Results and Discussion

3.1 Characterization of GFD

From Figure 1, it is evident that GFD is macroscopically a type of black particle with irregular shapes and similar sizes, with lengths with millimeter dimensions. The surface texture is rough and exhibits a certain metallic luster. Moreover, there is a noticeable tendency to move towards magnetic materials when approaching them, indicating that GFD possesses magnetic characteristics.

Fig.1 The image of GFD

XRD (X-ray Diffraction) is a rapid, accurate, and efficient non-destructive testing technique for materials. As a method for characterizing crystal structures and their variations, it is primarily utilized for phase analysis, crystal texture analysis, and stress testing. The XRD characterization results are depicted in Figure 2. A comparison with the Fe standard card (PDF#06-0696) reveals that the strong peaks at diffraction angles of 2θ=44.7° and 65.0° correspond to the Fe (229) plane. Besides, the peaks belonging to other species are not observed, indicating that the impurity content in GFD is minimal or nonexistent. Therefore, it can be preliminarily concluded that the primary component of GFD is Fe.

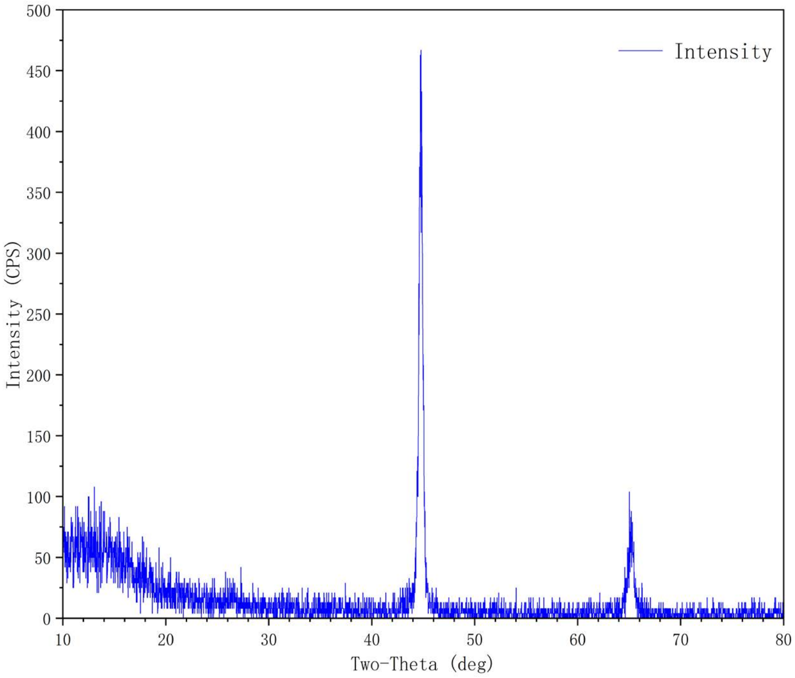

Fig.2 XRD pattern of GFD

SEM-EDS is a hybrid analytical device that combines a scanning electron microscope (SEM) and energy dispersive spectrometer (EDS) to analyze the composition of materials such as herbal substances. The Scanning Electron Microscope utilizes a focused, high-energy electron beam to scan specimens. Through the interaction between the beam and the material, it excites various physical information, which is then collected, amplified, and re-imaged to characterize the material’s microscopic morphology. The primary advantage of electron microscopy over optical microscopy is its superior image resolution [17]. SEM is utilized to characterize the surface morphology of GFD, as illustrated in Figure 3. The image magnified at 200x reveals that the GFD exhibits irregular and uneven morphology, and its length is approximately around 1 mm. with a loose and rough surface texture and blurred edges. From the locally enlarged images, it is evident that the surface of the GFD is not smooth, which enhances their contact with the reactant to a certain extent. Meanwhile, through the energy spectrum analysis provided by the SEM instrument, EDS allows for the identification and quantification of elements in the GFD. The results, as shown in Figure 4, indicate that GFD primarily comprises elements such as C, O, Si, and Fe, with corresponding atomic ratios of 25.28%, 1.75%, 2.94%, and 70.04% respectively. Considering that some GFD may be oxidized by oxygen in the air and that trace impurities might be introduced during production and testing, we can conclude that the GFD is primarily composed of carbon and iron after excluding the elements with very low atomic ratios, such as oxygen and silicon.

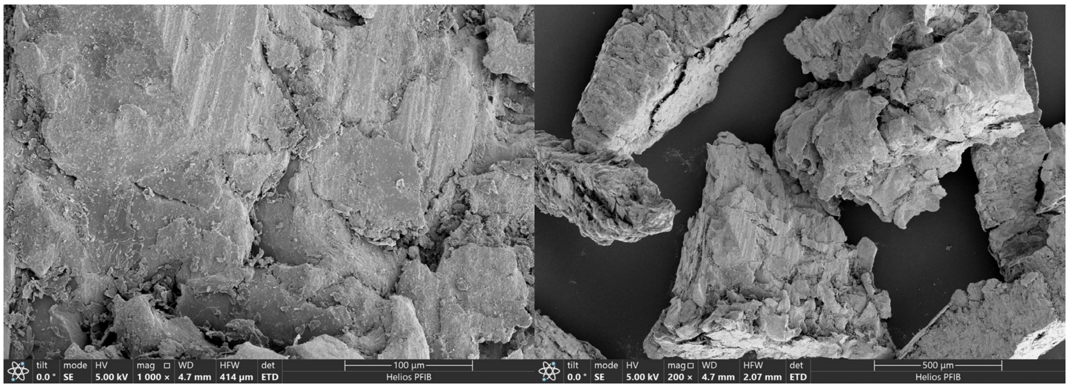

Fig.3 SEM image of GFD

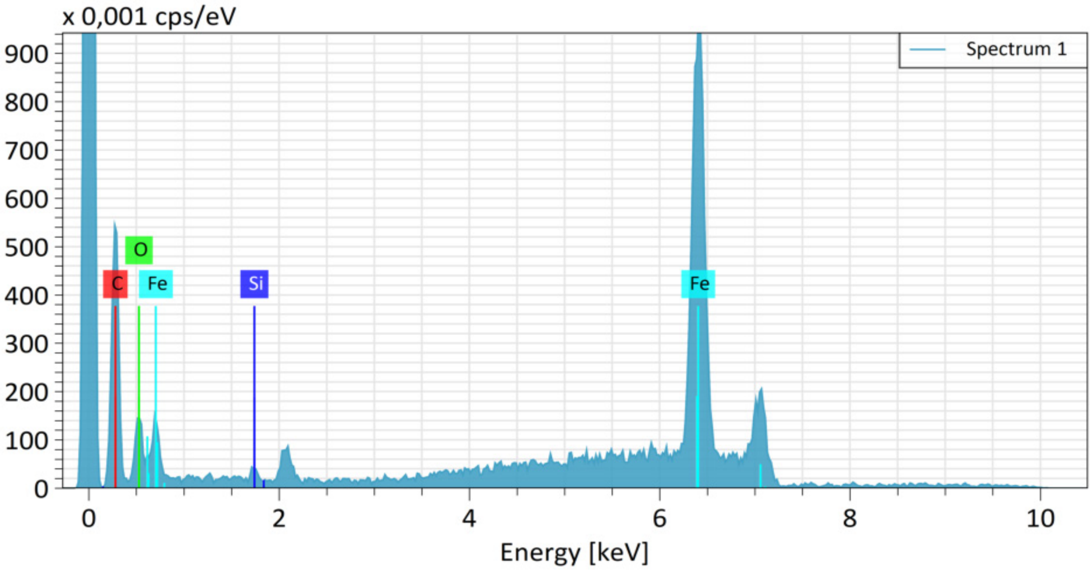

Fig.4 EDS diagram of GFD

3.2 Performance of GFD towards PMS activation

In order to evaluate the activity of GFD on activating PMS for pollutant removal, this experiment will involve a specific dosage of PMS with GFD, using MB as the substrate. The feasibility of GFD activating PMS will be validated by analyzing the removal of MB. Figure 5 illustrates the variation in the removal efficiency of MB over time under three systems (PMS/GFD, PMS alone, and GFD systems). As seen, it is evident that when 1 g/L of GFD is used alone, the removal efficiency of MB is only 6.3% within 10 min. Given that the GFD may have some adsorption ability, it can be concluded that GFD itself cannot degrade MB. When 1 mM of PMS is utilized alone, the removal efficiency of MB within 10 min is merely 13.0%. Without the participation of additional activation means, PMS hardly generates radicals and primarily achieves a degree of removal through direct oxidation reactions with MB, although the reaction rate is relatively slow. Under conditions where PMS concentration is 1 mM and the amount of Fe powder is 1 g/L, MB is almost completely degraded in about 10 min, showing a superior removal effect compared to when each component is used independently. The experimental results indicate that GFD can effectively activate PMS, facilitating the rapid removal of MB.

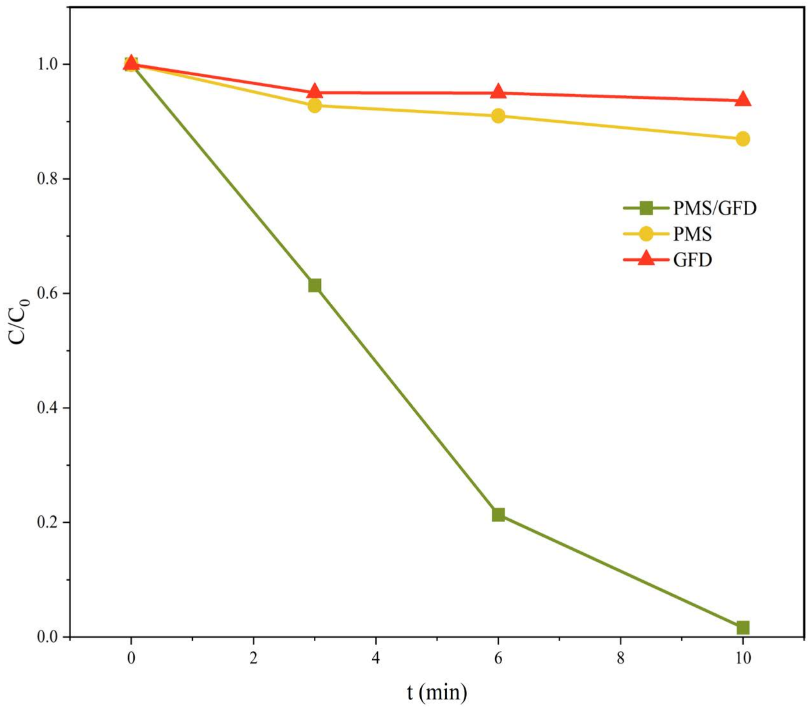

Fig.5 The degradation of MB under different systems ($[PMS]_0$=1 mM, GFD=1 g/L, $[MB]_0$=10mg/L).

3.3 Reaction Mechanisms

Research indicates that PMS activation can be triggered through radical and non-radical mechanisms, in which the hydroxyl radicals and sulfate radicals have been commonly probed during the activation process. Methanol is a commonly used radical quencher due to its α-H, which can easily react with hydroxyl radicals ($^{\bullet}OH$) and sulfate radicals ($SO_4^{\bullet-}$) [18].

In the radical quenching experiments, methanol (MeOH) was added to the MB solution before the introduction of PMS and GFD, with all other experimental conditions the same as those of the PMS/GFD system. Samples were taken at set time points, and the experimental results, shown in Figure 6, indicate that in the system with 500 mM MeOH, the MB removal efficiency dropped from 98.4% to 30.2% within 10 min, compared to the PMS/GFD system. In the system with 1000 mM MeOH, the MB removal efficiency decreased from 98.4% to 26.9% within 10 min. Considering that the quenching system with 1000mM MeOH involved an additional 4.045 mL of MeOH, it can be inferred that the MB removal efficiencies of the two quenching systems are nearly equal. This demonstrates that the radical mechanism plays a predominant role in the degradation of MB, with approximately 70% of the degradation achieved through radical mechanisms, while the remaining removal is accomplished through non-radical processes.

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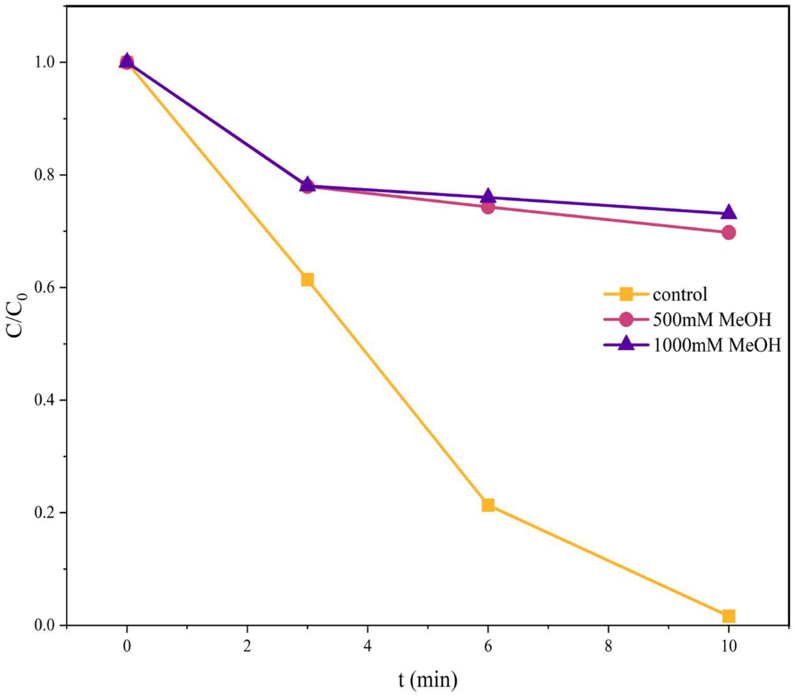

Fig.6 Quenching experiments on the GFD/PMS system (Conditions : $[PMS]_0$=1 mM, GFD=1 g/L, $[MB]_0$=10mg/L).

4. Summary

Considering the widespread use of iron-based catalysts in AOPs, this experiment employs the cost-effective and high-yield GFD for the catalytic degradation of MB. Based on the analysis of GFD, it can be inferred that it is a mixture primarily composed of iron and a small amount of carbon. Compared to other catalysts, it exhibits excellent recyclability due to its magnetic properties. Experimental evidence demonstrates that it can effectively activate PMS mainly through the $^{\bullet}OH/SO_4^{\bullet-}$ as the ROS to degrade MB, achieving a removal efficiency of 98.4% within 10 min, which indicates that GFD has the potential to be employed for the activation of PMS in the degradation of MB to reduce the damage brought by dye wastewater and achieve the goals of recycling abandoned metal and utilizing waste to treat waste.

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