Study on the Degradation of Methyl Orange in Wastewater by 3D-CuO Photocatalytic Activation of Sodium Bisulfite

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***Abstract*—3D-CuO is a new type of semiconductor nanomaterial. The uneven surface provides a larger specific surface area with more reaction sites, which leads to good electrical and optical properties. In the paper, 3D-CuO semiconductor nanomaterials were synthesized by the solvothermal method. The synthesized 3D-CuO for the photocatalytic activation of sulfites in order to degrade the organic dye wastewater under visible light was investigated. The results showed that 3D-CuO /$NaHSO_3$ in neutral conditions performed the best photocatalytic degradation effects of methyl orange. Under the visible light, 3D-CuO tends to produce more photogenerated electrons and holes, and HSO_3^- is oxidized by the photogenerated holes in the system and finally transformed into $SO_4{\bullet}^-$ free radicals. A new advanced oxidation method based on $SO_4{\bullet}^-$ was developed for the treatment of organic dye wastewater.**

***Keywords*—3D-CuO, $NaHSO_3$, degradation, dye wastewater**

I. Introduction

With the rapid development of the social economy, the environmental pollution problem caused thereby has become increasingly serious. Environmental pollution mainly includes air pollution, water pollution and soil pollution, among which air pollution and water pollution are the most serious. These environmental pollution phenomena are mainly caused by human social activities. For instance, orange-yellow II is a typical azo dye, widely used in textile dyeing and leather processing. If wastewater containing orange-yellow II is discharged into the environment without treatment, it will affect the growth of aquatic organisms and pose a serious threat to human health [1]. Bisphenol A is an important industrial raw material, widely used in the production of materials such as polycarbonate plastics and epoxy resins. After being discarded after use, it will gradually degrade in the natural environment and release bisphenol A. It is a typical endocrine disruptor with low concentration and high toxicity, posing potential hazards to the ecological environment and human health [2]. Brominated Flame Retardants (BFRs) are a type of chemical containing bromine atoms in their molecules and having excellent flame-retardant properties. They are widely used in electronic appliances, building materials, and mechanical equipment. Due to the characteristics of brominated flame retardants such as difficult degradation, long-distance transport, and bioaccumulation, they can enter water bodies through multiple pathways, thereby endangering the water environment and water safety [3]. Oxytetracycline hydrochloride is often used to treat diseases in livestock and poultry, but it cannot be completely metabolized by them. The residual oxytetracycline hydrochloride enters water bodies and endangers the health of the water environment [4]. Glyphosate is a broad-spectrum herbicide. Its residues can easily spread through soil and water bodies, causing environmental pollution and affecting ecological balance [5]. Carbamazepine is a typical antiepileptic drug and one of the most common new organic pollutants in water environments [6]. Organic substances in dyes, plastics, flame retardants, veterinary drugs, pesticides and pharmaceuticals have entered the soil or water bodies due to their extensive use, posing a threat to the environment.

Methyl Orange (MO), as a kind of azo dye, is widely used in dyeing clothes and making pigments. Methyl orange is one of the main components in printing and dyeing wastewater, which is weakly alkaline. If it is discharged directly into the environment without treatment, it will lead to reduced water visibility and ecological imbalance, affecting the growth of plants and animals in the water. At present, the main treatment methods of methyl orange in wastewater include physical adsorption method [7], chemical oxidation-reduction method [8], electrochemical method [9], and photocatalytic degradation method [10].

3D structural substances are composed of nanoparticles that are self-assembled into porous regular structures with certain morphological characteristics, such as spherical, hollow, and flower-like, etc. Metal oxides are commonly used materials in the field of industrial chemistry. At present, in order to improve the physical and chemical properties of metals, 3D-metal oxide are very common in various fields. The main synthesized methods of 3D-metal oxides include hydrothermal method [11], solvothermal method [12], and co-precipitation method [13]. The 3D-metal oxide is nanoscale, and the uneven surface can provide a larger specific surface area and more reaction sites in the application. The characteristics determine that it can play a role in a variety of fields, such as electrodes, sensors, and environmental protection fields, etc.

In recent years, the treatment of printing and dyeing wastewater by advanced oxidation process has become a research hotspot. It destroys the stable chemical structure of dyes by generating free radicals such as $OH{\bullet}$ and $SO_4{\bullet}^-$ [14]. $SO_4{\bullet}^-$ was produced by PS or PMS in dyeing wastewater and some nanomaterials were added to activate them to improve the degradation efficiency [15–16]. At present, some researchers try to add both sodium sulfite and photocatalytic activated nanomaterials in the dyeing wastewater to produce $SO_4{\bullet}^-$ [17]. In this experiment, we successfully prepared 3D-CuO by reacting copper acetate with urea in ethylene glycol with hot solvent method, which is used for photocatalytic activation of sulfite to degrade the MO under visible light. It has not been reported in other literature previously. 3D-CuO and $NaHSO_3$ are easy to obtain, low cost, non-toxic and environmental protection.

The study is of great significance for the treatment of dye wastewater in the environment.

II. Experimental Procedure

A. Reagents and Apparatus

Copper acetate, urea, ethylene glycol, anhydrous ethanol, methyl orange, sodium bisulfite, hydrochloric acid and sodium hydroxide were purchased from Sinopharm Chemical Reagent Company. All reagents were of analytical grade and used without further purification. All solutions were prepared with super pure water during the experiment. Photochemical reactor was purchased from Guangzhou Star Chuang Electronics Limited Company. The samples after photocatalytic degradation were analyzed by Ultraviolet and Visible Spectrophotometer of UV1200 from Shanghai Auyi Instruments Limited Company.

B. Synthesis and Characterization of 3D-CuO

3D-CuO was synthesized by the hot solvent-calcination method [18]. Accurately weigh copper acetate and urea by the molar ratio of 1:3. Dissolve them with 40mL glycol in a 100mL beaker, and at 80°C stir using a magnetic stirrer until the solid is completely dissolved to form a blue homogeneous solution. The solution was transferred to a high-pressure reactor and placed in a drying oven at 140°C for 12 hours. After the reactor was lowered to room temperature, the mixture was removed and centrifuged to get the deep yellow solid substance. The 3D-CuO precursor was obtained by washing with ultra-pure water and anhydrous ethanol several times respectively. The precursor was moved to the crucible and dried in a drying oven at 60°C for 12 hours. After drying, the solid is evenly ground using an agate mortar and transferred to a crucible. Placed the crucible in a box-type resistance furnace, and reacted at 400°C for 3 hours. After the box resistance furnace is lowered to room temperature, the black solid is removed and 3D-CuO is obtained after being evenly ground with an agate mortar.

C. Catalytic Degradation Experiment

Add a certain amount of catalyst to a test tube containing 50 mL of 20 ppm methyl orange solution, followed by the addition of a specific quantity of sodium bisulfite. Adjust the pH value of the mixed solution to enhance degradation efficiency by changing the conditions of the system. Subsequently, place the test tube in a photoreactor and initiate magnetic stirring. After stirring to achieve air saturation and adsorption equilibrium, proceed to activate a 500W xenon lamp to simulate solar light irradiation for experimental purposes. Extract 3 mL samples at a certain time interval, filter with a filter membrane immediately, and measure the absorbance of the supernatant at 465 nm with an ultraviolet spectrophotometer. It is known that the maximum absorbance of methyl orange aqueous solution is at 465 nm.

III. Results and Discussion

A. Effect of Different Photocatalysts on the Degradation of MO

The degradation effects of different catalysts on MO were compared under optimal experimental conditions, and the results are shown in Fig. 1. When $NaHSO_3$, 3D-CuO and 3D-CuO/$NaHSO_3$ mixtures were used as catalysts, the degradation rates of MO were 5.64%, 3.66% and 54.47%, respectively. In the experimental system, the degradation effect is the best with the 3D-CuO/$NaHSO_3$ mixture as photocatalyst. Therefore, the following experiments mainly discuss the factors, which affected the degradation of MO solution with 3D-CuO/$NaHSO_3$ in solar light irradiation.

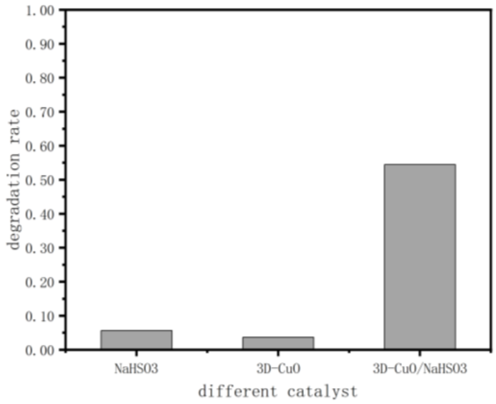

Fig. 1. The degradation effects of MO with the different catalysts under the optimized experimental conditions.

B. Effect of PH Value on the Degradation of MO

We discussed the effect of pH value on the catalytic degradation of MO in 3D-CuO/ $NaHSO_3$ system, and adjusted the pH value of the system by adding 1mol/L HCl and 1mol/L NaOH solution, as shown in Fig. 2. When the pH of the reaction systems was 3, 7 and 11, the degradation rates of MO was 17.28%, 74.60% and 12.23%, respectively. The results showed that the degradation effect of MO was the best under neutral conditions after radiating in visible light for 30 minutes. It may be due to the fact that 3D-CuO promotes $NaHSO_3$ to produce sulfate free radicals and hydroxyl radical under neutral conditions, and they are both very good decolorizing active substances, which react quickly with MO in the solution to achieve the purpose of degrading the MO.

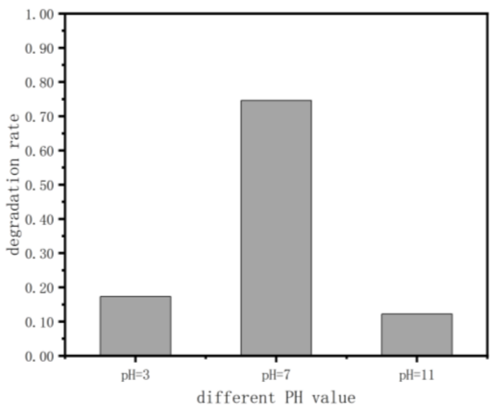

Fig. 2. Effect of pH value on the degradation rate of MO in 3D-CuO / $NaHSO_3$ system.

C. Degradation Kinetics of the Degradation of MO

We studied the degradation kinetic process of MO with 3D-CuO/$NaHSO_3$ in the neutral system, and under the optimal experimental conditions the experimental results were shown in Fig. 3. 1/C is almost in a direct proportional relationship with degradation time, as Eq. (1).

$$y=0.0102+0.9705x \quad (1)$$

According to the Langmur-Hinshelwood model, the second-order degradation kinetic equation is as follows:

$$1/C-1/C_0=2kt \qquad (2)$$

It can be inferred that the degradation of MO with 3D-CuO/ $NaHSO_3$ in neutral system is almost a second-order degradation kinetic process, and the degradation rate constant of MO is 0.4853min^{-1} under the optimal experimental conditions.

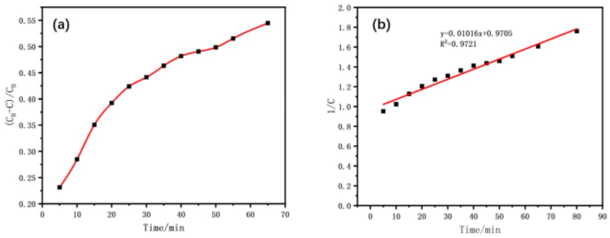

Fig. 3. (a)The degradation curve of MO under the optimized condition; (b)Ln(C/C0)-irradiation time curve.

D. Degradation Mechanism of the Degradation of MO

Combined with previous reports [19], it can be inferred that HSO_3^- was oxidized into HSO_4^- by O_2, as

$$HSO_3^- + O_2 \rightarrow HSO_4^- \qquad (3)$$

HSO_4^- is oxidized into $SO_4\bullet^-$ free radicals by photogenic holes in the system, as

$$HSO_4^- + M^{n+} \rightarrow SO_4\bullet^- + M^{(n-1)+} \qquad (4)$$

HSO_3^- was catalyzed into $SO_3\bullet^-$ by metal ion, as

$$HSO_3^- + M^{n+} \rightarrow SO_3\bullet^- + M^{(n-1)+} \qquad (5)$$

OH^- was catalyzed into $OH\bullet$ by metal ion, as

$$OH^- + M^{n+} \rightarrow OH\bullet + M^{(n-1)+} \qquad (6)$$

All free radicals of $SO_3\bullet^-$, $SO_4\bullet^-$ and $OH\bullet$ are important active species in dye degradation system. 3D-CuO is helpful to produce more photogenerated electrons and holes under the visible light, and further increases the active species in the degradation system. As reported by researcher Yifan Yao [1], in advanced oxidation reactions based on $NaHSO_3$ activation, sulfate radicals ($SO_4\bullet^-$) and hydroxyl radicals ($OH\bullet$) are reactive oxygen species that are often detected and capable of oxidizing organic pollutants. Tertbutanol (TBA) can quench hydroxyl radicals, while methanol (MeOH) is able to simultaneously quench hydroxyl radicals and sulfate radicals, which enable the detection of these two types of radicals through free radical scavenging experiments. The experiments illustrate that in the reaction system, not only the role of $OH\bullet$ exists, but also the role of $SO_4\bullet^-$ exists. In the other report [2], the research proposed, In acid solutions, HSO_3 is more likely to combine with Fe^{3+} to form $SO_3\bullet^-$ and Fe^{2+}, among which $SO_3\bullet^-$ can serve as a precursor for other ROS with stronger oxidizing properties.

E. Degradation Products of the Degradation of MO

In in the neutral system with the catalyst of 3D-CuO/$NaHSO_3$ the MO tends to be degraded to the smaller molecular weight of benzene compounds (e.g., m/z = 156), and a small account of small molecules such as CH_3COO^-, $HCOO^-$, NO_3^-, SO_4^{2-} as showed in Fig. 4 reported in the previous literature [19]. However, the removal rate of the Total Organic Carbon (TOC) is very low, and the dye is difficult to mineralize in this system. In the experiment, the degradation process is divided into two steps. In the first step, the carbon-nitrogen bond of MO is easily broken, and the MO is degraded into benzene compounds with smaller molecular weight, which causes the degradation products to become colorless. But the benzene ring is difficult to be destroyed. In the second step, a small account of the benzene compounds are oxidized by $SO_4\bullet^-$ into small organic acids and inorganic ions. More detailed degradation mechanisms are needed for further study. The findings of this study provide a promising advanced oxidation method for the degradation of organic pollutants through sulfite activation.

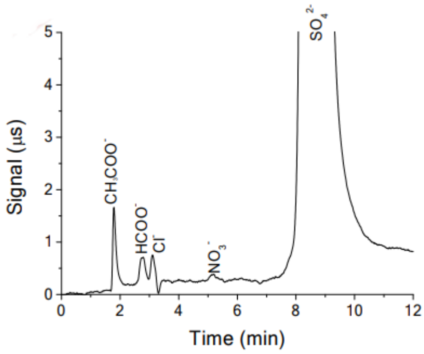

Fig. 4. The degradation products of MO by the ion chromatography.

IV. Conclusion

In the paper, the photocatalytic degradation effects on MO with different catalysts in different systems were studied. It was found that photocatalytic degradation of MO in 3D-CuO /$NaHSO_3$ system was the best. Under the visible light, 3D-CuO is much easier to produce more photogenerated electrons and holes, and HSO_3^- is oxidized by the photogenerated holes in the system and finally transformed into $SO_4\bullet^-$ free radicals. $SO_4\bullet^-$ free radicals is an important active species in the system of dye degradation. In addition, we also studied the effect of pH value on the degradation of MO by 3D-CuO /$NaHSO_3$, and the degradation effect of MO was the best in neutral solution. MO exists widely in organic dye wastewater, the work in the experiment is of great significance to guide people to treat organic dye wastewater. In the future, we will target the inorganic salts and their complexes of common metals such as Fe^{2+}, Fe^{3+}, Cu^{2+}, and Mn^{2+} to explore environmentally friendly sulfite active catalysts and establish the corresponding catalytic degradation system for environmental pollutants. The degradation effects of environmental pollutants such as dyes, plastics, flame retardants, veterinary drugs, pesticides and medicines are explored. The specific research ideas are shown in Fig. 5.

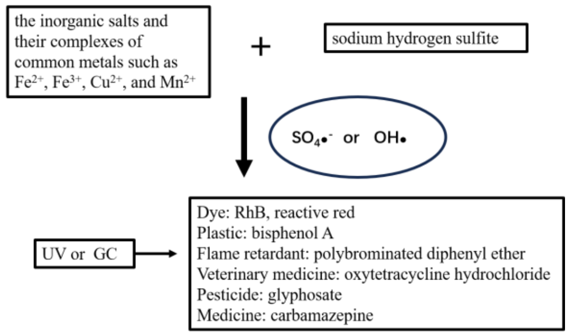

Fig. 5. The specific research ideas with the degradation effect by M^+ / $NaHSO_3$ system.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest.

AUTHOR CONTRIBUTIONS

Jinai Ma was responsible to design the research, analyze the experimental data and write the manuscript; Yongchao Liu, Yang Hu, and Junjie Wang performed the research; Junhao You was concentrated on the analytical test with Ultraviolet and Visible Spectrophotometer of UV1200 from Shanghai Auyi Instruments Limited Company; Yao Ning had given some efficient suggestions on the study; all authors had approved the final version.

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