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Copper Tannic Acid-Polyethyleneimine Encapsulated Melamine Sponge for Fenton-Like Degradation of Dyes

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Abstract: This study introduces the synthesis of an innovative heterogeneous Fenton-like catalyst, Copper Tannic Acid-Polyethyleneimine Encapsulated Melamine Sponge (MS-P-Cu-TA NPs), for the efficient degradation of dye wastewater. Through a simple impregnation and in-situ reduction method, copper tannic acid (Cu-TA) and polyethyleneimine (PEI) were uniformly coated onto the surface of a melamine sponge (MS), forming a stable catalytic system. The catalyst leverages the high porosity and surface activity of the melamine sponge, combined with the efficient catalytic properties of the CuTA-PEI complex, to activate hydrogen peroxide (H_2O_2) over a wide pH range, generating hydroxyl radicals (·OH) for the effective degradation of various dyes, such as methylene blue, rhodamine B, malachite green, methyl orange. Experimental results demonstrate that MS-P-Cu-TA NPs exhibits excellent catalytic activity under near-neutral conditions, the degradation rate of methylene blue can reach 98.4% within 24 hours. It also demonstrates good degradation efficiency for other dyes. This research provides a new approach for designing efficient and environmentally friendly heterogeneous Fenton-like catalysts.

Keywords: Copper tannic acid; Polyethyleneimine; Melamine sponge; Heterogeneous Fenton-like reaction; Dye degradation.

1. Introduction

The composition of textile dyeing wastewater is highly complex, making it a type of refractory organic wastewater. How to achieve its harmless treatment has always been a focus of researchers' attention [1]. In recent years, the Fenton reaction, as an important technology in advanced oxidation processes, has been widely applied in wastewater treatment, particularly for refractory organic pollutants such as dye wastewater and pharmaceutical wastewater. However, the classical Fenton reaction still suffers from limitations such as a narrow applicable pH range [2], sluggish Fe(III) reduction resulting in substantial iron sludge formation [3-4], and difficulties in catalyst recovery. To address these issues, Fenton-like technologies have emerged. For example, Liu [5] et al. investigated heterogeneous Fenton processes, replacing the Fe^{2+} catalyst in homogeneous Fenton systems with solid catalysts containing active components. This allows the Fenton catalytic reaction to occur at the active sites on the surface of the solid catalyst, preventing iron ion leaching, extending the working pH range, and reducing iron sludge production. However, achieving ideal high-performance adsorbent materials through low-cost, simple, environmentally friendly, and scalable manufacturing methods remains challenging.

A melamine sponge composed of melamine-formaldehyde (MF) is recognized as a highly promising material for addressing water pollution issues, owing to their affordability, lightweight nature, high porosity, exceptional flexibility, and straightforward modification potential [6-8]. Tannic acid (TA), a naturally occurring polyphenolic substance, is rich in phenolic hydroxyl groups and demonstrates a robust capacity to chelate with a wide range of metal ions [9-10]. By coordinating with metal ions such as Cu^{2+}, TA can form stable metal-polyphenol network structures. Combining the porous three-dimensional structure of MS enhances the loading of metal-TA conjugated polymers and exposes more active catalytic sites, enabling the composite to demonstrate excellent adsorption performance and dye degradation capabilities. Additionally, polyethyleneimine (PEI), a polymer rich in amino groups, can further enhance the material's adsorption and catalytic performance through synergistic effects with TA. Based on this, this study uses melamine sponge

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(MS) as a solid catalyst substrate, coating it with TA and PEI through immersion, followed by loading copper-based coordination polymers on its surface. This develops a heterogeneous Fenton-like catalyst based on copper tannic acid-polyethyleneimine encapsulated melamine sponge (MS-P-Cu-TA NPs), which extends the working pH range and demonstrates excellent degradation effects on methylene blue (MB), rhodamine B (Rh B), malachite green (MG), and methyl orange (MO).

2. Materials and Methods

2.1 Chemicals and Characterization

$CuCl_2 \cdot 2H_2O$ (Macklin), Tannic acid (Tianjing Hengxing, analytical regent), malachite green (Macklin, analytical regent), methylene blue (Yuanye), Rhodamine B (Adamas), methyl orange (Adamas), polyethyleneimine (Adamas), (3-aminopropyl) triethoxysilane (Alfa Aesar), Melamine Sponge (Shijia Shenqi).

The scanning electron microscopy (SEM) images were captured using a ZEISS Sigma 300 microscope, which was outfitted with an EDX system (Oxford Xplore 30). The UV-vis absorption spectra were measured using a SHIMADZU UV-1780 spectrophotometer.

2.2 Synthesis of MS-P-Cu-TA NPs

In 72 mL of tris-HCl buffer (pH 8.5) and 18 mL of anhydrous ethanol, 0.18 g of TA and 0.18 g of (3-aminopropyl) triethoxysilane (APTES) were added and completely dissolved. Then, 18 pieces of MS were added into the mixture, which was then agitated at 25 ℃ for a duration of 12 hours. Following this, the MS pieces were washed, and allowed to dry. These MS were thereafter submerged in 100 mL of a PEI solution (10 mg/mL) and subjected to stirring at 25 ℃ for a period of 6 hours. Afterward, the MS pieces were washed and dried. Finally, they were immersed in a solution containing 12.039 mL of $CuCl_2 \cdot 2H_2O$ (10 mg/mL) and 100 mL of tris-HCl buffer. The polymer products (MS-P-Cu-TA NPs) were collected by washing and drying.

2.3 Degradation Procedures

2.3.1 Degradation of MB at different pH levels

The degradation process was conducted in a 15 mL PET bottle. Three melamine sponges (MS-P-Cu-TA NPs) were added to a solution containing 0.1 mL of MB solution (1 mg/mL) and 9.89 mL of Phosphate-Buffered Saline (PBS) at different pH levels (pH 5.0, 6.0, 7.4, 9.0). The degradation reaction was initiated by adding 10 μL of H_2O_2 solution to the suspension in the buffer solutions of varying pH. After shaking on a shaker for 3 hours, the absorbance at a wavelength of 664 nm was measured. Each experiment was repeated three times, and the average value derived from the three measurements was utilized for data reporting. The efficiency of dye degradation was determined by applying the following equations:

$$\text{Degradationef ficiency}(\%) = (C_0 - C)/C_0 \times 100\% \quad (1)$$

C_0 and C were the concentration of the dye solution at 0 and t min, respectively.

2.3.2 Degradation of MB at different time points

The degradation process was carried out in a 15 mL PET bottle. Three melamine sponges (MS-P-Cu-TA NPs) were added to a mixture of 0.1 mL MB solution (1 mg/mL), 9.89 mL PBS buffer, and 10 μL H_2O_2 solution. The mixture was shaken on a shaker, and samples of 1 mL were taken after 30 min, 1 h, 3 h, 6 h, 12 h, and 24 h, after which the absorbance at a wavelength of 664 nm was measured. The control group consisted of the same volume of solution without the sponges. Each time, 1 mL of the test solution was taken out and replaced with PBS buffer of a specific pH. Each experiment was repeated three times, and the average value derived from the three measurements was utilized for data reporting.

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2.3.3 Degradation of other dyes

To investigate the degradation efficiency of MS-P-Cu-TA NPs on other dyes, the experimental procedure was the same as described above. The mixture was shaken on a shaker for 24 hours, and the degradation effects on other dyes (MO, Rh B and MG) were measured at wavelengths of 463 nm, 554 nm, and 618 nm, respectively.

3. Results and Discussion

3.1 Characterization of MS-P-Cu-TA NPs

Through scanning electron microscopy (SEM) technology, it can be observed that MS-Cu-TA NPs and MS-P-Cu-TA NPs possess identical inherent 3D and porous structures, confirming that the PEI coating process preserved the intrinsic structure of MS without detrimental effects. (Fig. 1a, b). Furthermore, it is evident that the surface of MS-P-Cu-TA NPs is rougher and has a greater amount of material loaded onto it (Fig. 1c, d).

The percentage of free copper ions in the solution relative to the composite sponge balls was detected using inductively coupled plasma (ICP) technology. In the MS-P-Cu-TA solution, free copper ions accounted for 28.67%, while in the MS-Cu-TA solution, they accounted for 49.57% (Fig. 2a). The amount of copper ions in the MS-P-Cu-TA solution was significantly lower than that in the MS-Cu-TA solution.

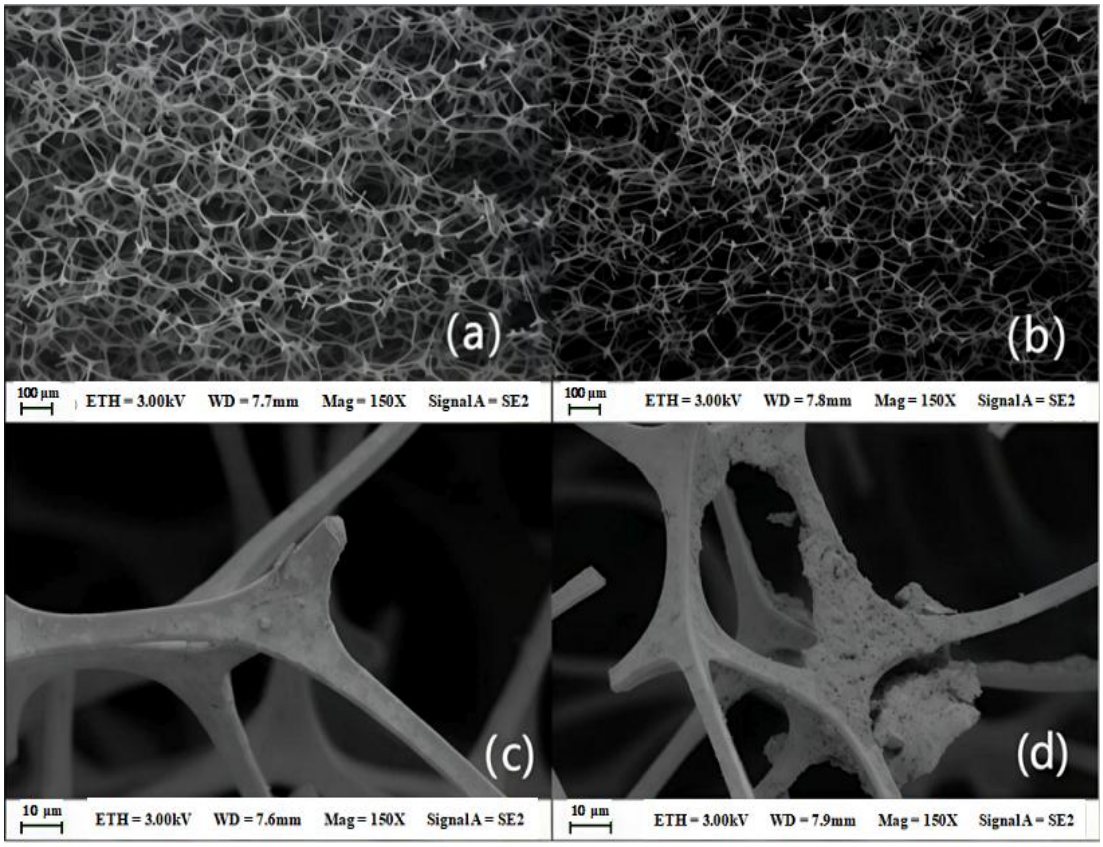

Fig. 1 (a) and (c) are the SEM images of MS-Cu-TA,
(b) and (d) are the SEM images of MS-P-Cu-TA.

3.2 Dyes Degradation

In the aforementioned Fenton-like studies, under varying pH conditions, the degradation rate of MB by MS-P-Cu-TA NPs was consistently around 60% (Fig. 2b). This suggests that the copper-based catalyzed Fenton-like reaction is applicable over a broad pH range, addressing the pH sensitivity issue associated with iron-catalyzed Fenton reactions. Given that national wastewater

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discharge standards require the pH of effluent to be controlled between 6 and 9 [11], this study takes the condition at pH 6 as an example.

Using MB as a representative dye, the degradation situation at different times was investigated. As shown in Fig. 2c, it exhibits excellent degradation effects under the action of H_2O_2, with the degradation rate reaching 98.4% after 24 hours.

When extending the degradation to other dyes (Rh B, MG and MO), similarly effective degradation results were observed under the action of H_2O_2 (Fig. 2d).

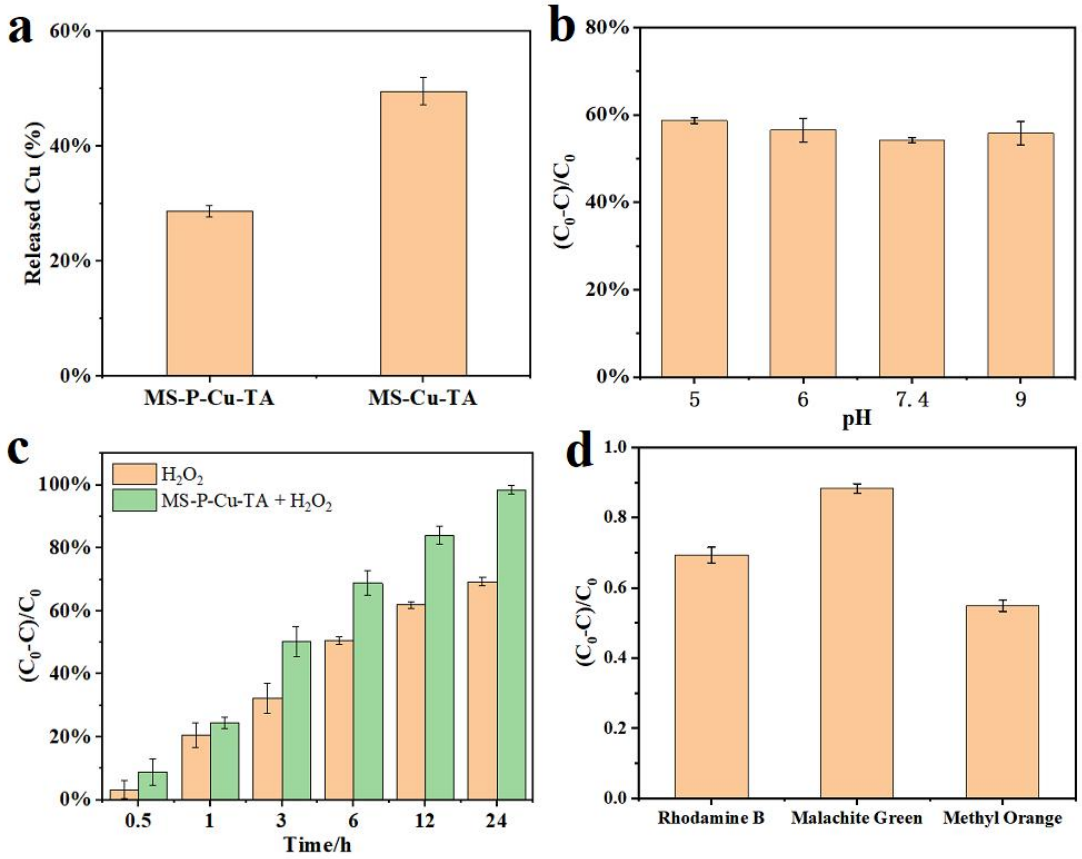

Fig. 2. a The percentage of free [Cu] in the solution relative to the composite sponge balls. b The degradation efficiency of MS-P-Cu-TA NPs on MB under different pH conditions. c The degradation of MB by MS-P-Cu-TA NPs and H2O2 at different time points under pH = 6.0. d The degradation of three different dyes by MS-P-Cu-TA NPs under pH = 6.0.

4. Summary

This study utilized melamine sponge as a substrate to prepare MS-P-Cu-TA NPs, which enhanced the loading of copper ions, reduced secondary environmental pollution, and expanded the working pH range. The degradation efficiency of methylene blue reached 98.4% after 24 hours. Extending the degradation to other dyes such as Rh B, MG and MO also demonstrated excellent degradation effects under the action of H_2O_2. The Fenton-like reaction system designed and synthesized in this study can effectively degrade dye pollutants and holds promise for application in the field of dye wastewater treatment.

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