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Simultaneous removal of methylene blue and copper(II) ions by photoelectron catalytic oxidation using stannic oxide modified iron(III) oxide composite electrodes

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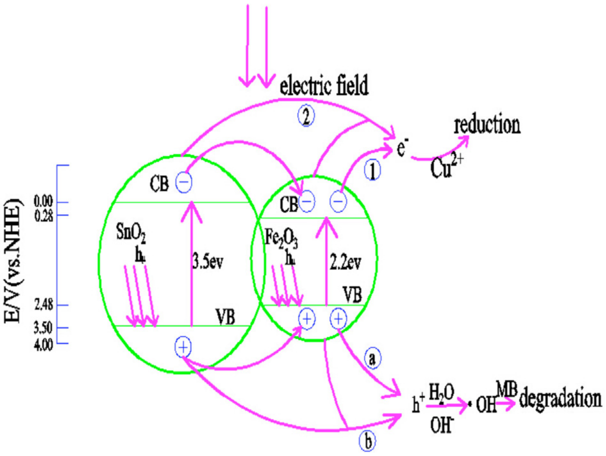
HIGHLIGHTS

- Photoelectron catalytic oxidation was used for methylene blue and Cu^{2+} removal.
- SnO_2/Fe_2O_3 was prepared and characterized for use as photoanodes and photocathodes.
- Optimal reaction conditions were determined for methylene blue and Cu^{2+} removal.
- Methylene blue removal followed the Langmuir–Freundlich–Hinshelwood kinetic model.
- Cu^{2+} removal followed the first-order rate model.

GRAPHICAL ABSTRACT



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ABSTRACT

Stannic oxide modified Fe(III) oxide composite electrodes (SnO_2/Fe_2O_3) were synthesized for simultaneously removing methylene blue (MB) and Cu(II) from wastewater using photoelectron catalytic oxidation (PEO). The SnO_2/Fe_2O_3 electrodes were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD), and photoelectrochemical techniques. The removal of MB and Cu(II) by PEO using the SnO_2/Fe_2O_3 composite electrodes was studied in terms of reaction time, electric current density, and pH of the electrolyte. The kinetics of the reactions were investigated using batch assays. The optimal reaction time, pH, and electric current density of the PEO process were determined to be 30 min, 6.0, and 10 mA/cm^2, respectively. The removal rates of MB from wastewater treated by PEO and electron catalytic oxidation process were 84.87% and 70.64%, respectively, while the recovery rates of Cu(II) were 91.75% and 96.78%, respectively. The results suggest that PEO is an effective method for the simultaneous removal of MB and Cu(II) from wastewater, and the PEO process exhibits a much higher removal rate for MB and Cu(II) compared to the electron catalytic oxidation process. Furthermore, the removal of MB was found to follow the Langmuir–Freundlich–Hinshelwood kinetic model, whereas the removal of Cu(II) fitted well to the first-order reaction model.

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1. Introduction

Dye effluents contain complex compounds and toxic synthetic substances. The presence of even trace amounts of dyes can reduce the oxygen solubility in water [1], which would be harmful to aquatic life in downstream environments [2,3]. Methylene blue (MB), which is one of the most widely applied dyes, is often used as a biological stain, cyanide antidote, oxidation indicator, and chemical analysis reagent, and is also widely used in various fields such as printing, dyeing, and monitoring [4,5]. Although MB is not strongly hazardous, its harmful effects such as carcinogenicity, mutagenicity, and toxic effects on aquatic organisms have been well documented [1,2]. In addition, during the printing and dyeing processes, copper salts are commonly used as mordants to optimize various properties of the dyeing and printing products [6,7]. The excess copper ions discharged along with the wastewater can damage the internal organs, cause metabolic disorders, and become a threat to aquatic life. Therefore, wastewater from the dyeing process must be properly treated before being discharged into the environment.

A variety of physical, chemical, and biological methods have been applied for the treatment of dye wastewater, which contains dyes and heavy metals. Such methods include adsorption [8], ion-exchange [9], membrane separation [10], coagulation [11], chemical oxidation [12], electrochemical processing [13], and aerobic and anaerobic microbial degradation [14]. However, achieving the combination of sufficient removal efficiencies, economic viability, and ecological protection is difficult with any of the above processes. In particular, sufficient chromaticity is usually difficult to achieve using the above methods. Additionally, most of these methods mainly focus on handling single contaminant species, and the simultaneous removal of a variety of pollutants is difficult to achieve. To date, some methods such as catalytic reduction [15], photocatalysis [16], electrochemical oxidation [13], adsorption [8], and advanced oxidation [17], have been proven as practical methods for removing MB from solutions. However, there is little information in the literature on the removal of heavy metal ions, which are often present in dyeing wastewater.

Electrochemistry-assisted photocatalytic reaction technology involves applying an external voltage on a system to promote the separation of photoelectrons from vacancies, thereby improving the efficiency of quantization. This process allows organic pollutants to mineralize at the anode, while heavy metal ions are reduced at the cathode. Therefore, photoelectron catalytic oxidation (PEO) may be a viable approach for the simultaneous removal of dyes and heavy metal ions from industrial wastewater [18,19].

In this study, a photoelectric catalysis system using a in-house SnO_2/Fe_2O_3 electrode was constructed. SnO_2 in the SnO_2/Fe_2O_3 electrode, which serves as a catalyst, can not only promote excellent catalytic performance of the Fe_2O_3 photocatalyst, but can also improve the stability of Fe_2O_3 in aqueous solutions [20–22]. By applying a certain electric-field intensity on the system in the presence of sunlight, the anode can produce hydroxyl radicals and vacancies, which can oxidatively degrade MB. At the same time, applying an electric-field can not only promote the separation of photoelectrons from vacancies, but can also cause the reduction of Cu^{2+} at the cathode.

The main purpose of this study was to investigate the simultaneous removal of MB and Cu^{2+} from dyeing effluents using PEO. A SnO_2/Fe_2O_3 electrode was designed and characterized in this study for using in the PEO system. Optimal treatment conditions including reaction time, pH, and electric current density, and the treatment kinetics of MB and Cu^{2+} were investigated using batch assays. The mechanism of MB and Cu^{2+} removal from solutions by PEO will also be discussed.

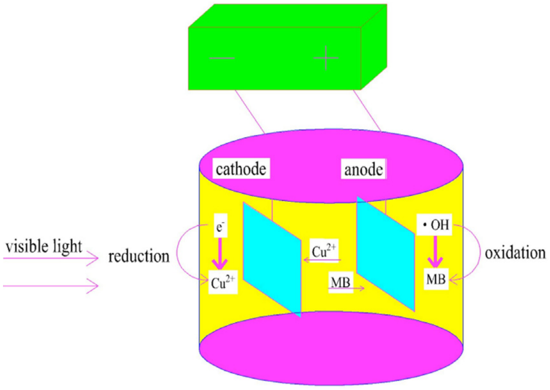

Fig. 1. Experimental setup.

2. Experimental

2.1. Preparation of iron sheets

Iron (Shanxi Shenglonghua magnetic material Co., Ltd) and titanium (Shanxi Baoji Jucheng Titanium Industry Co., Ltd) sheets (20 mm × 40 mm × 1.5 mm) were rubbed with sandpaper of various mesh sizes (80 mesh, 200 mesh, and 400 mesh), placed into 10% oxalic acid solution (Tianjin Basf Chemical Co., Ltd) and 18% hydrochloric acid, respectively, and boiled for 10 min to remove surface impurities. They were then washed with deionized water and dried. The electrolysis cell was assembled by using the treated iron and titanium sheets as anode and cathode, respectively, whereas 0.25% NH_4F (Shanghai Purple Mountain Chemical Technology Co.,Ltd) solution ($V_{ethyleneglycol(TianjinKaitongChemicalReagentCo.,Ltd)}/V_{deionizedwater} = 97:3$) served as the electrolyte. The cell voltage and temperature were adjusted to 30 V and 20 °C, respectively, and electrolysis was conducted for 2 h. After electrolysis, the iron sheets were ultrasonicated (Kunshan Ultrasonic Instruments Co., Ltd.) for 5 min, washed with deionized water, and burned on a muffle (Hefei Kejing Materials Technology Co. Ltd.).

2.2. Preparation of the SnO_2/Fe_2O_3 composite electrode

In this study, we adopted a hydrothermal method to prepare the SnO_2/Fe_2O_3 composite electrode. First, 0.203 g of $SnCl_4{\cdot}H_2O$ (Tianjin Basf Chemical Co., Ltd) and 0.623 g of NaOH (Tianjin Yong-largest Chemical Reagents Development Center) were dissolved in 35 mL of deionized water and ultrasonicated for 10 min. The mixture was then transferred into a 50 mL reaction still (Yantai Corry Chemical Equipment co., Ltd) along with the previously prepared iron sheets. The reaction still was then placed in a drying oven (Nantong Jia Cheng instrument co., Ltd) at 220 °C for 2 h. After 2 h, the reaction still was naturally cooled to the ambient temperature. Finally, the SnO_2/Fe_2O_3 composites were removed from the reaction still and placed in a drying oven at 60 °C for 1 h.

2.3. Experimental setup

Fig. 1 shows a schematic illustration of the experimental cell consisting of SnO_2/Fe_2O_3 composite electrodes with dimensions of 20 mm × 40 mm × 1.5 mm. The reactor volume was 500 mL and the distance between the two electrodes was adjustable. First, the SnO_2/Fe_2O_3 composite electrodes were connected to the negative and positive terminals of a direct current (DC) power supply. A xenon lamp (500 W) with optical filter to filter all source light below 420 nm was used to supply light, which mimicked sunlight to the photoelectric catalysis system. Next, equal volumes