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Short communication

High-efficient treatment of wastewater contained the carcinogen naphthylamine by electrochemical oxidation with γ-Al_2O_3 supported MnO_2 and Sb-doped SnO_2 catalyst

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HIGHLIGHTS

- A method for the electrochemical catalytic oxidation of 1-naphthylamine in synthetic wastewater is elucidated.
- The novel catalyst, Mn–Sb–Sn/γ-Al_2O_3, was prepared and characterized.
- A fairly satisfactory result (92.2% COD removal rate) was achieved in 20 min at pH 7 under mild conditions.
- The hypothetical mechanism of electrochemical catalytic oxidation degradation was also proposed.

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ABSTRACT

1-Naphthylamine wastewater causes severe environmental pollution because of its acute toxicity and carcinogenicity in humans, which makes it difficult to reuse by conventional technologies. In this study, we report an investigation of the electrochemical catalytic oxidation of 1-naphthylamine in synthetic wastewater in a 150 mL electrolytic batch reactor with Ti/Sb–SnO_2/PbO_2 as anode and steel plate as cathode, where the reaction was assisted by MnO_2 and $Sn_{1-x}Sb_xO_2$ composite materials as the catalyst and γ-Al_2O_3 as the carrier ($MnO_2–Sn_{1-x}Sb_xO_2/\gamma\text{-}Al_2O_3$). The catalyst was synthesized by impregnating process and was characterized by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The effects of pH and current density on the efficiency of the electrochemical degradation process were also studied. It was found that $MnO_2–Sn_{1-x}Sb_xO_2/\gamma\text{-}Al_2O_3$ exhibited excellent catalytic activity in the electrochemical degradation of 1-naphthylamine wastewater. The results showed that the refractory organics in wastewater can be effectively removed by this process, and a chemical oxygen demand (COD) removal efficiency of 92.2% was obtained in 20 min at pH 7.0 and current density was equal to 50 mA cm^{-2}. According to the experimental results, a hypothetical mechanism of electrochemical catalytic degradation was also proposed.

1. Introduction

The removal of hazardous organic pollutants from groundwater and wastewater is one of the most critical and urgent topics in environmental research. Naphthylamine, representatives of naphthalene compounds, is one of the top priority contaminants and also the most important substructures of potentially carcinogenic pollutants discharged from pharmaceutical, dyestuff, photographic, and agrochemical industries [1,2]. Therefore, the efficient removal of naphthylamine from waste streams has increasingly become a significant environmental concern.

In recent years, different techniques have been applied in the treatment process of the naphthylamine wastewater, e.g. extraction, adsorption and condensation method [3–7]. Adsorption process has a prominent advantage over the others in removing organic pollutants without producing any harmful byproducts. Especially, macroporous resin adsorbents was frequently used as an alterative to activated carbons in industrial applications for efficiently removing and recovering naphthylamine from waste streams. However, the macroporous resin adsorption process is only suitable for treating the high concentration wastewater from the production of naphthylamine. Moreover, they are toxic and carcinogenic even in the presence of low concentration. Therefore, how to treat effectively and economically the tail water of naphthylamine ($COD < 1200\ mg\ L^{-1}$) has got considerable attention.

Many advanced oxidation technologies and processes have been conventionally attempted for the tail water of naphthylamine, such as chemical oxidation [8], wet oxidation [9], ozone oxidation [10], photo-catalytic oxidation and oxidation in supercritical water

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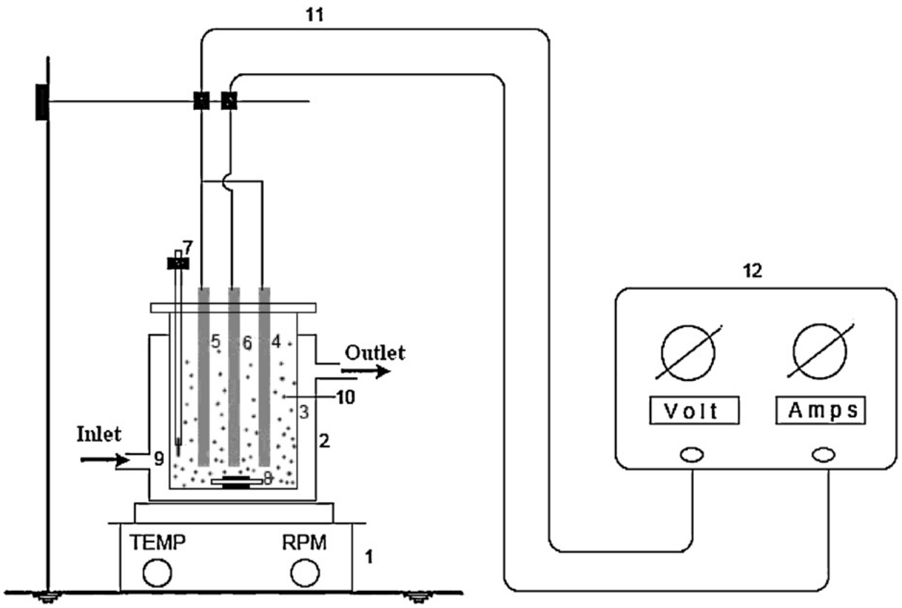

Fig. 1. Schematic diagram of experimental setup: (1) stirring apparatus; (2) water bath; (3) electrochemical reactor; (4) anode; (5) anode; (6) cathode; (7) thermometer; (8) magnetic bar stirrer; (9) ciculating water; (10) catalysts; (11) copper wire; (12) D.C. power.

[11,12]. But there are few suitable processes to deal with this high toxicity effluent [13]. Electrochemical method offers the prospect of relatively simple equipment, environmental friendliness, and the possibility of high-energy efficiency. Then, electrochemical oxidation method for removal of aromatic compounds has attracted a great deal of attention [14,15]. The oxidation of wastewater is principally depended on the hydroxyl radical generated on the surface of the electrodes. Therefore, the processes are called advanced electrochemical oxidation processes (AEOPs) [13]. Nowadays a single process alone may not be adequate for the treatment of organic compounds. In order to improve the efficiency of oxidation and accelerated the reaction rate, lots of solid catalysts have been investigated in the AEOPs processes.

Herein, we report that a AEOPs process for the tail water from the production of 1-naphthylamine assisted by $MnO_2–Sn_{1-x}Sb_xO_2/\gamma$-$Al_2O_3$ catalyst was investigated. The catalyst thus was prepared by impregnating process and was characterized by XRD and XPS technology, with Sb as a doping component, Sn and Mn related species as active components and γ-Al_2O_3 as a substrate. $MnO_2–Sn_{1-x}Sb_xO_2/\gamma$-$Al_2O_3$ exhibited excellent catalytic activity in the AEOPs process, the toxic and carcinogenic pollutants could be simply and effectively degraded, and a COD removal efficiency of 92.2% was obtained in 20 min at pH 7 at room temperature and atmospheric pressure. In this context, the effects of operating conditions, including current density and initial pH were described, and a possible mechanism of electrochemical catalytic degradation was also discussed.

2. Materials and methods

2.1. Materials

All chemicals in the experiment were of analytical grade and employed without any purification. γ-Al_2O_3, provided by Tianjin Chemical Research and Design Institute, China, is composed of aluminum oxide [surface area: $250\,m^2\,g^{-1}$ and pore volume: $0.4683\,cm^3\,g^{-1}$].

2.2. Catalyst preparation

The novel catalyst, $MnO_2–Sn_{1-x}Sb_xO_2/\gamma$-$Al_2O_3$, was prepared by impregnation method. Adding 11.3 g $MnCl_2{\cdot}4H_2O$, 10 g $SnCl_4{\cdot}5H_2O$ and 0.5 g $SbCl_3$ into 65 mL absolute ethanol, then 5 mL hydrochloric acid was added to dissolve the metal chloride. 50 g γ-Al_2O_3 carrier, which was sifted out, washed with distilled water for several times, dried at 383 K for 12 h and calcined at 523 K for 3 h, was impregnated into the above solution for another 12 h after the solution was stirred for 1 h under room temperature, then the sample was dried at 353 K for 10 h followed by dried at 383 K for 2 h. The dried samples were calcined at 773 K for 4 h in ambient air. Finally, this procedure was repeated for two or three times, and then the $MnO_2–Sn_{1-x}Sb_xO_2/\gamma$-$Al_2O_3$ catalyst was obtained.

2.3. Set-up of wastewater treatment

Fig. 1 shows the schematic diagram of the experimental apparatus. The experiments were conducted by batch process using undivided cell of 150 mL capacity under constant temperature conditions. Double-anode and single cathode were positioned vertically and parallel to each other with an inner gap of 1.0 cm. Two $Ti/Sb–SnO_2/PbO_2$ electrodes (supplied by Shenao Metal Material Company Limited, Shaanxi) were served as anode, and a steel plate was employed as cathode. The superficial surface of the working electrode (2.5 cm × 8.0 cm × 2) was $40\,cm^2$. The solution for treatment was prepared by dissolving 1-naphthylamine to $0.5\,g\,L^{-1}$ in distilled water, its conductivity was raised by adding Na_2SO_4 ($5\,g\,L^{-1}$), and its pH was adjusted by adding either diluted sodium hydroxide or diluted sulfuric acid. $30\,g\,dm^{-3}$ smashed catalyst was added into the system to form an oxidizing electrochemical reactor. The solution was constantly stirred at 200 rpm using a magnetic stirrer in order to maintain uniform concentration of the electrolyte solution. The electric power was supplied with regulated dc power supply, HY3003F-2, Hangzhou, China. The current and voltage were adjustable in the range of 0–3.0 A and 0–35 V, respectively.