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Electrochemical degradation of *m*-cresol using porous carbon-nanotube-containing cathode and Ti/SnO_2–Sb_2O_5–IrO_2 anode: Kinetics, byproducts and biodegradability

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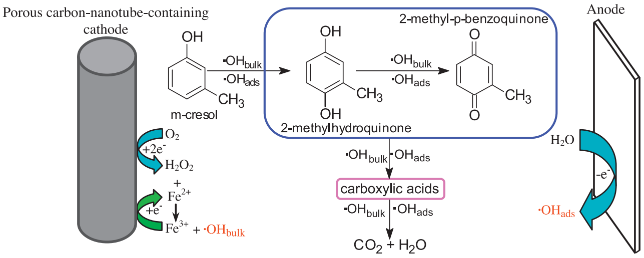
HIGHLIGHTS

- The porous carbon-nanotube-containing cathode used for electro-Fenton oxidation.
- The porous carbon-nanotube-containing cathode can reduce Fe^{3+} effectively.
- The byproducts and the reaction pathway of *m*-cresol degradation were presented.
- The electrochemical process is able to evidently enhance the biodegradability.

GRAPHICAL ABSTRACT



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ABSTRACT

The degradation of *m*-cresol solution was studied using an electrochemical oxidation system with Ti/SnO_2–Sb_2O_5–IrO_2 anode for anodic oxidation and porous carbon-nanotube-containing cathode for H_2O_2 electrogeneration along with Fe^{3+} reduction. Organic pollutants were oxidized by hydroxyl radical ($^\bullet OH$) formed simultaneously in the medium from electro-Fenton reaction in the presence of Fe^{2+} and at the anode surface from water oxidation. The porous cathode made of graphite, carbon nanotube (CNT) and polytetrafluoroethene (PTFE) exhibited a higher catalytic activity toward O_2 reduction producing H_2O_2 and Fe^{3+} reduction for Fe^{2+} regeneration, favoring organics degradation by electro-Fenton oxidation. The degradation kinetics results revealed that the reaction of *m*-cresol cleavage with hydroxyl radicals could be described by pseudo first-order kinetics. The progress of organics mineralization demonstrated some byproducts were formed during *m*-cresol degradation. Based on the byproducts identified by GC–MS and HPLC, the sequential process of *m*-cresol degradation was proposed. Furthermore, the aerobic biological treatment showed that the electrochemical treatment was able to evidently enhance the biodegradability of *m*-cresol solution.

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1. Introduction

Cresols are toxic organic compounds widely used in the manufacture of pesticides, biocides, antioxidants and other chemicals, which are commonly found in many industrial wastewaters [1,2]. These compounds resist biodegradation and have potential toxicity toward humans and animals [3,4]. Nowadays, many government agencies prescribe the legal limits for hazardous materials in the wastewater released from industries. For example, in China the discharge standard limit for *m*-cresol is 0.10 mg/L. For above reasons, there is an increasing interest in the development of environmentally clean technologies to destroy such phenolic compounds, and several methods have been investigated for the removal of cresols including Fenton oxidation [5], photocatalytic oxidation [6],

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photoelectro-Fenton oxidation [7], electrochemical indirect oxidation [8–10] and ozone oxidation [11].

It has been widely accepted that electrochemical oxidation is a promising technique for the degradation of toxic and bio-refractory organics [12–14]. Most of the electrochemical oxidation technologies mainly rely either on electro-Fenton process characterized by H_2O_2 electro-generation via O_2 reduction and using Fe^{2+} as catalyst generating $^{\bullet}OH$ [15–17], or upon anodic oxidation characterized by the generation of $^{\bullet}OH$ via water oxidation at the surface of anode [18,19]. In recent years, the novel electrochemical process employing electro-Fenton oxidation and anodic oxidation simultaneously for organics degradation was attracting more and more attention because of its high current efficiency. However, until now, literature was lacking in deal with the degradation of cresols by this new electrochemical process. Although Flox et al. achieved an excellent degradation of cresols by solar photoelectro-Fenton process, the high price of boron-doped diamond anode and the cost of pure oxygen limited its extensive industrial application [7]. Therefore, further efforts to investigate the degradation of cresols by the low-cost electrochemical process united electro-Fenton oxidation and anodic oxidation using new electrode materials is still necessary. Additionally, using electrochemical oxidation to enhance the biodegradability of phenol-containing wastewater instead of obtaining complete mineralization is also worth studying. The electrochemical pretreatment followed by biological treatment may be the promising alternative to deal with bio-refractory organic wastewater.

It is well known that the oxidation power of electro-Fenton system is mainly related to the efficiency of a cathode material for its H_2O_2 production. Therefore, the cathode materials which have high H_2O_2 production ability are very important for the effective destruction of organic pollutants. In the past two decades, the use of various cathodes such as mercury [20], graphite [21], carbon-polytetraflouoroethylene (Carbon-PTFE) [22], carbon felt (CF) [23], activated carbon fiber (ACF) [24] and carbon sponge [25] has been reported. The use of mercury has long been disregarded owing to its potential toxicity. Among the various carbon cathodes, carbon-PTFE has a porous structure leading to fast reduction of O_2 and presents the highest H_2O_2 production ability.

As a new member of carbon materials, carbon nanotube is characterized by light mass, high strength, large surface area, moderate catalytic activity and unique electric conductivity [26]. Recently, some attention has been paid to the application of carbon nanotube cathode in generating H_2O_2 by the electrochemical reduction of O_2 for electro-Fenton oxidation process [27,28]. However, Further investigation on the performance of this kind cathode for H_2O_2 generation and Fe^{3+} reduction should be conducted. Further more, to the best of our knowledge, the degradation of organic pollutants by the electro-Fenton oxidation system employing the composite porous cathode made of carbon nanotube, graphite and PTFE has not been reported.

The present study investigated the performance of the electrochemical oxidation system for the removal of *m*-cresol from water, using $Ti/SnO_2–Sb_2O_5–IrO_2$ anode and the composite porous cathode made of graphite, carbon nanotube and PTFE. The effect of Fe^{2+} and initial *m*-cresol concentration on the decay kinetics of *m*-cresol was surveyed. The mineralization of all solutions was assessed from the abatement of total organic carbon (TOC). On the base of identifying cyclic byproducts and aliphatic carboxylic acids formed during the degradation of *m*-cresol, a detailed oxidation pathway was proposed. The effect of electrochemical treatment on the biodegradability of *m*-cresol solution was evaluated by biological treatment experiments.

2. Materials and methods

2.1. Preparation of the porous cathode

Graphite powder (99.5% purity, China), multi-wall carbon nanotube (MCNT) (>99.7% purity, China) and PTFE emulsion (>60% solid content, China) were mixed according to a mass ratio of 10:1:5 (W_{carbon}: $W_{carbon\ nanotube}$: W_{PTFE}), followed by the addition of a small amount of ethanol and NH_4HCO_3. After the mixture was well mixed by ultrasonic equipment, it was shaped into the cylinder with a diameter of 24 mm using an extruder, and then was dried at 330 °C for 60 min in a muffle furnace. After that, the prepared material was dipped into acetone for 24 h. Finally, it was dried at 100 °C for 60 min, and then was washed by deionized water. The above procedures were also applied for preparing another porous cathode except for the absence of MCNT.

2.2. Electrolytic system

The electrolytic experiments were performed in an open and undivided tank reactor containing 200 mL of solution stirred with a magnetic bar at 300 rpm. The potential of work electrodes was controlled by a CHI760D electrochemical workstation (Shanghai Chenhua instrument Co. Ltd., China). The solution temperature was regulated at 25 ± 1 °C by circulating external thermostated water through the double-jacket. The $Ti/SnO_2–Sb_2O_5–IrO_2$ anode was prepared by thermal decomposition method [29]. The cathodes were fed with an air flow rate of 25 mL/s to continuously electro-generate H_2O_2. The geometric area in contact with the solution was 38 cm^2 for the anode and 32 cm^2 for the cathodes. The distance between anode and cathode was 15 mm. In all electrolytic experiments, a saturated calomel electrode (SCE) was used as a reference electrode.

2.3. Electrochemical generation of H_2O_2

The experiments were performed under potentiostatic condition using 200 mL of the solution containing 0.10 mol/L Na_2SO_4 and 100 mg/L *m*-cresol at pH 3.0. During the course of electrolysis, the samples were drawn at desired time to determine H_2O_2 concentration.

2.4. Electrochemical reduction of Fe^{3+}

The experiments were performed under potentiostatic condition using 200 mL of the solution containing 0.10 mol/L Na_2SO_4 and 100 mg/L $Fe_2(SO_4)_3$ at pH 3.0 with a stirring of 400 rpm. During the course of electrolysis, the samples were drawn at desired time to determine Fe^{2+} concentration.

2.5. Electrochemical degradation of *m*-cresol

For each run, 200 mL of the solution containing *m*-cresol and 0.10 mol/L Na_2SO_4 (pH 3.0) was poured into the reactor. $FeSO_4{\bullet}7H_2O$ was added into the solution before starting the electrolysis. At appropriate time intervals, samples were taken from the reactor for chemical analysis. Prior to each experiment, the cathode was subjected to a hot treatment at 330 °C for 60 min, and then washed by deionized water. All experiments were performed twice at least.

2.6. Biological treatment

TOC decay caused by aerobic biological treatment was employed to evaluate the biodegradability of *m*-cresol solutions before and after the electrochemical treatment. The pre-treatment of 250 mg/L

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