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Electrocatalytic reduction of low-concentration thiamphenicol and florfenicol in wastewater with multi-walled carbon nanotubes modified electrode

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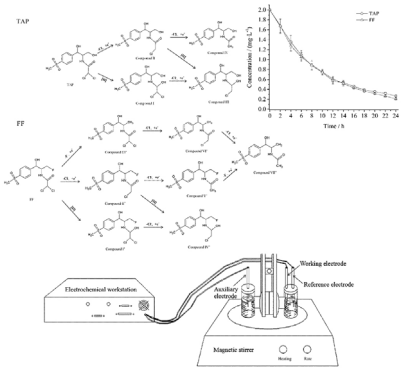
HIGHLIGHTS

- Thiamphenicol and florfenicol can be effectively removed with the MWCNTs modified electrode.
- The removal process of the two antibiotics could be described by pseudo first-order kinetic model.
- Electrocatalytic reduction is promising to remove low-concentration antibiotics in wastewater.
- The reduction pathways of the two antibiotics may include dehalogenation and carbonyl reduction.

GRAPHICAL ABSTRACT

Low-concentration thiamphenicol and florfenicol can be efficiently removed by electrocatalytic reduction through dehalogenation and carbonyl reduction.



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ABSTRACT

The electrocatalytic reduction of thiamphenicol (TAP) and florfenicol (FF) was investigated with multi-walled carbon nanotubes (MWCNTs) modified electrode. MWCNTs was dispersed in pure water with the assistance of dihexadecyl phosphate (DHP), and then modified on glassy carbon electrode (GCE). The electrocatalytic reduction conditions, such as bias voltage, supporting electrolyte and its initial pH, and the initial concentrations of TAP and FF, were also optimized. The experimental results indicated that the removal efficiencies of 2 mg L^{-1} TAP and FF in 0.1 M $NH_3{\cdot}H_2O$-NH_4Cl solution (pH 7.0) reached 87% and 89% at a bias voltage of −1.2 V after 24 h electrocatalytic reduction, respectively. The removal process could be described by pseudo first-order kinetic model, and the removal rate constants of TAP and FF were obtained as 0.0837 and 0.0915 h^{-1}, respectively. The electrocatalytic reduction products of TAP and FF were identified by liquid chromatography-tandem mass spectrometry (LC–MS/MS), and the possible reduction mechanisms

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were preliminarily analyzed. Electrocatalytic reduction is promising to remove low-concentration TAP and FF in wastewater with the MWCNTs modified electrode, and may cut down their toxicity through dehalogenation and carbonyl reduction.

1. Introduction

Antibiotics have been widely used to prevent and control human and animal diseases since 1940s' because of their broad-spectrum antimicrobial activity. The annual use of antibiotics reached 100,000–200,000 t around the world in the early 21 century [1], and has a significant increase in the last decade [2]. Among the antibiotic pharmaceuticals, chloramphenicols have played an important role in the prevention and treatment of animal diseases [3]. After chloramphenicol (CAP) was listed in the prohibited drugs due to its serious side effect [4], its derivatives, thiamphenicol (TAP) and florfenicol (FF) have been widely used in animal husbandry [5,6]. However, with the wide application and the increasing attention, TAP and FF were found to have hematotoxicity, embryotoxicity and strong immunosuppressive action, and even influence on physiological function of animals, plants and micro-organisms [7–9]. TAP and FF can enter in soil and water environment through animal metabolism, rainfall runoff and wastewater discharge, and be accumulated by food chain to produce toxic effects on the ecological environment and human body. As the emerging contaminants, TAP and FF have been frequently detected in wastewater and surface water [10–14]. Therefore, TAP and FF residues in water environment attract much attention in the recent years, and it is necessary to develop simple and effective method to remove them in wastewater.

The removal methods of antibiotics in water mainly include adsorption [15], photolysis [16], irradiation [17], ozonation [18], Fenton oxidation [19], membrane separation [20], and microbial degradation [21,22]. However, these techniques need special materials, more energy and complex operation procedures, and have been mainly used to treat 20 mg L^{-1} or higher antibiotics. In fact, antibiotics widely exist in wastewater with μg L^{-1} level [23], it is urgent to develop treatment technology for low-concentration antibiotics. In recent years, electrochemical methods display certain potential to effectively degrade chloramphenicol [24], nitrobenzene [25], and disinfection byproducts [26], and have advantages of low cost, simple operation and environmental friendly [27]. Compared with other electrode materials, carbon nanotubes (CNTs) have large specific surface area, strong stability and quantum effect, and good electrical conductivity, and also been used to prepare the modified electrodes to oxidize ceftazidime [28] and pyridine [29], and reduce chloramphenicol [30]. To the best of our knowledge, no report on the electrochemical removal of TAP and FF with CNTs modified electrode can be found. In this study, multi-walled carbon nanotubes (MWCNTs) were dispersed in pure water with the assistance of surfactant, and the prepared MWCNTs modified electrode was used to examine the removal efficiencies of TAP and FF in simulated wastewater, and the possible electrocatalytic reduction mechanisms were preliminarily analyzed through monitoring reduction products. This work is promising to develop effective treatment technology for low-concentration antibiotics in wastewater, and protect aquatic ecological environment.

2. Material and methods

2.1. Regents and materials

Thiamphenicol (TAP) and florfenicol (FF) standards (≥98.5%) were purchased from Dr. Ehrenstorfer GmbH, Germany. TAP (>96%) and FF (>98%) were used to prepare the simulated wastewaters, and provided by Hefei Bomei Biotechnology Co., Ltd., China. Methanol and acetonitrile (HPLC grade) were purchased from Fisher Scientific Inc., USA. Dihexadecyl phosphate (DHP) was purchased from Shanghai Jianglai Biochemical Reagent Co., and other reagents (analytical reagent) from Chengdu Kelong Chemical Reagent Co., China.

Stock solutions of TAP and FF (1000 mg L^{-1}) were prepared in deionized water with a small amount of methanol assisted dissolution, and stored at 4 °C in dark. Working solutions of TAP and FF (1, 2, 5 and 10 mg L^{-1}) were freshly prepared from the stock solutions by dilution with different electrolyte solutions (0.1 M HAc-NaAc, Na_2SO_4, $NH_3{\cdot}H_2O$-NH_4Cl, Na_2HPO_4-NaH_2PO_4).

Multi-walled carbon nanotubes (MWCNTs, >95%, 8–15 nm in tube diameter and 0.5–2 μm in length) functionalized with carboxylic group were purchased from Nanjing XFNANO Materials Tech Co., Ltd., China.

2.2. Preparation of the MWCNTs modified electrode

Glassy carbon electrode (GCE, 3 mm in diameter, Tianjin Aidahengsheng Tech Co., Ltd., China) was polished to mirror surface with 0.3-μm alumina powder, and successively cleaned with sonication in ultra-pure water, ethanol, and ultra-pure water for 5 min to remove any adhesive substances on the electrode surface. MWCNTs (25 mg) and DHP (25 mg) were ultrasonically dispersed in 25 mL of ultra-pure water for 20 min, and then a homogeneous dispersion of MWCNTs (1 mg mL^{-1}) was obtained, sealed and stored at 4 °C. The MWCNTs dispersion was taken out with micro-syringe, and coated onto GCE surface, and then dried at room temperature.

2.3. Electrocatalytic reduction of thiamphenicol and florfenicol

Electrocatalytic reduction device (Fig. 1) was constructed by an H-type glass cell (1.5 cm in diameter, 4 cm in height), which was separated into cathode chamber and anode chamber by Nafion 117 cation exchange membrane. The MWCNTs modified electrode (working electrode) and a saturated calomel electrode (SCE, reference electrode) were inserted into the cathode chamber, and a platinum electrode (auxiliary electrode) into the anode chamber. The three electrodes were fixed by punched Teflon cap, and connected with CHI 660E electrochemical workstation (Chenhua Instruments Co., Shanghai, China).

The simulated wastewater (8 mL) containing TAP or FF were added in the cathode chamber and covered with aluminum foil, while 8 mL of electrolyte solution were added in the anode chamber. Afterwards, the reduction device was placed on a magnetic stirrer with gentle stirring, and the electrocatalytic reduction of TAP or FF was carried out in time-current mode at room temperature for 24 h. The reaction solution (1 mL) was taken out from