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Enhanced electro-catalytic generation of hydrogen peroxide and hydroxyl radical for degradation of phenol wastewater using MnO_2/Nano-G|Foam-Ni/Pd composite cathode

Dong Li [a, b], Tianyi Sun [a, b, *], Lu Wang [a], Na Wang [b, c]

[a] State Key Laboratory of Urban Water Resource and Environment, School of Environment, Harbin Institute of Technology, Harbin 150090, China
[b] School of Chemistry, Chemical engineering and Materials, Department of Environmental Science and Engineering, Heilongjiang University, Harbin 150080, China
[c] National Engineering Research Center of Urban Water Resources, Harbin 150090, China

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ABSTRACT

To improve the electro-catalytic degradation efficiency of the cathode in electrochemical advanced oxidation processes, MnO_2 modified Nano-graphite (MnO_2/Nano-G) and Pd loaded Foam-Ni (Foam-Ni/Pd) composites were prepared by the chemical redox and electro-deposition methods, respectively, and a two-layer type MnO_2/Nano-G|Foam-Ni/Pd composite cathode was prepared with the chitosan as a binder. The composites were characterized by X-ray diffraction, scanning electrons microscopy and X-ray photoelectron spectroscopy. Results showed that the mix-crystal structural MnO_2 (α-MnO_2 and γ-MnO_2) nanorods with length of 80–200 nm and width of 20–50 nm were uniformly loaded on the Nano-G surface, and the three-dimensional Pd° metal trees/crystals were tightly deposited on the Foam-Ni substrate. The as-prepared cathode was applied to the electro-catalytic degradation of phenol wastewater, and the reaction parameters were optimized. Compared with MnO_2/Nano-G|Foam-Ni and Nano-G|Foam-Ni cathodes, the degradation efficiency of phenol by MnO_2/Nano-G|Foam-Ni/Pd cathode was significantly improved. The removal efficiencies of phenol and total organic carbon (TOC) by MnO_2/Nano-G|Foam-Ni/Pd cathode reached 98.7% and 85.3% after 120 min electrolysis under oxygen aeration condition, respectively. The optimal reaction parameters were current density of 39 mA cm^{-2}, electrolyte (Na_2SO_4) concentration of 0.1 mol L^{-1}, electrode distance of 4 cm and initial pH of 7. By determining the variations of H_2O_2 and •OH content in the cathode chamber, it was found that Pd metal crystals improved the reduction of O_2 to H_2O_2 and MnO_2 nanorods accelerated the dissociation of H_2O_2 to •OH, producing more H_2O_2 and •OH to oxidize phenol and eliminate TOC in wastewater. The results in this study provide useful information for the control of refractory organic pollutants with electrochemical advanced oxidation in wastewater treatment.

1. Introduction

Phenol is not only an essential raw and intermediate material but also a common by-product in various industries of chemical, plastic, leather, pharmaceutical and petroleum, etc [1–4]. The global demand of phenol has annually increased and is expected to exceed 11 million kilograms by 2020 [1]. However, phenol is a highly hazardous chemical, which has been listed as a priority pollutant by United States Environmental Protection Agency, due to its acute toxicity on living organisms and damage on ecological system even at low doses [1–3]. Phenol is a refractory pollutant in conventional treatment processes [5–7]. Conventional biological treatment is generally ineffective for the degradation of phenol wastewater with high concentration because of the inhibition or even inactivation effect of phenol on the activity of microorganisms [3,7]. Proposing an effective method for the treatment of phenol wastewater is important in wastewater treatment.

Electrochemical advanced oxidation processes have been demonstrated to be an effective technology for degradation and/or mineralization of refractory organic wastewater with high

* Corresponding author. State Key Laboratory of Urban Water Resource and Environment, School of Environment, Harbin Institute of Technology, Harbin 150090, China.
E-mail address: tianyi870328@163.com (T. Sun).

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concentration [8,9]. This technology has many advantages including high efficiency, simple operation, small occupation and environmental compatibility [10,11]. The degradation of organic pollutants is mainly depended on the production of the strong reactive oxygen species (•OH and H_2O_2) by electro-catalysis, which can oxidize a wide range of organics into CO_2, H_2O and/or small molecule products quickly and non-selectively [8,9,11–13]. The anode can oxidize H_2O to generate •OH [8,11]. The cathode can catalyze the conversion of dissolved O_2 to H_2O_2 by two-electron reduction, which can be dissociated to •OH [8,14–16]. Thus, the electrode is the most important factor for the generation of reactive oxygen species and electrochemical degradation efficiency. The degradation of organics are performed by using various anodes effectively, such as dimensionally stable anode (DSA), platinized titanium (Ti/Pt) anode, lead dioxide (PbO_2) anode, or boron-doped diamond (BDD) anode [17–20]. Some of these anodes have been developed and applied to the actual wastewater treatment. The cathodes used in electrochemical advanced oxidation processes have principally focused on the titanium mesh [21], stainless steel [22,23], and various carbon materials (such as porous carbon, carbon felt, activated carbon fiber, and graphite) electrodes for their conductivity and low cost [24–29].

Among these cathodes, the carbon materials electrodes with high yield of H_2O_2 are considered as the ideal cathodes [30]. The traditional graphite materials electrodes have been widely used as the cathode because of their chemical resistance [29,30]. As one of the graphite materials, the two-dimensional flake-like Nano-G, which is made up of ultrathin graphite sheet or even few-layer graphene, possesses not only the superior electrical conductivity and high chemical stability but also the large specific surface area and high surface energy [31]. Most importantly, Nano-G can be more easily and cheaply manufactured on a large scale compared with graphene [31]. Yu et al. [32] used ultrasound to disperse expanded graphite for producing the Nano-G and found that the electrochemical performances and electro-catalytic degradation efficiency of Nano-G cathode are superior to traditional graphite materials cathodes. To improve the electro-catalytic degradation efficiency, the cathode materials should be further explored. Typically, manganese oxide (MnO_x) and palladium (Pd) metal as the catalysts were successfully used for modifying carbon materials to enhance the electro-generation of H_2O_2 by O_2 reduction or dissociation of H_2O_2 to •OH. Wang et al. [33,34] used the Pd metal to modify the activated carbon electrode and indicated that the presence of the Pd metal can accelerate the two-electron reduction of O_2 to H_2O_2 for effective degrading chlorinated phenols in wastewater. Fathy et al. [35] reported that the MnO_2 modified multi-walled carbon nanotube nanocomposite catalyzes greatly the dissociation of H_2O_2 to •OH and shows high activity for the degradation of reactive blue 19 dye from wastewater. Furthermore, Roy et al. [36] and Goldestine et al. [37] also indicated that the MnO_x can effectively promote the dissociation of H_2O_2 to •OH. However, to our best knowledge, there is still lack of a study in regard to cathode modified with MnO_x and Pd metal for simultaneously enhancing the generation of H_2O_2 and •OH.

In recent years, the novel multi-layer composite cathodes were developed by researchers for wastewater treatment. Fan et al. [38] prepared a Fe-CHI/Foam-Ni|ACF|Fe-CHI/Foam-Ni sandwich cathode for electro-Fenton system, in which one piece of activated carbon fiber (ACF) was fixed between two pieces of Fe^{2+}-chitosan loaded nickel foam (Foam-Ni). This cathode was very stable and could efficiently degrade rhodamine B by in situ generating both H_2O_2 and iron ions. In our previous study [39], a two-layer type Nano-G|Foam-Ni (Nano-G film layer and Foam-Ni layer) cathode was successfully synthesized, and showed a better electro-catalytic degradation performance in comparison with monolayer Nano-G cathode and Foam-Ni|Nano-G|Foam-Ni sandwich cathode. Furthermore, the unique three-dimensional cross-linked grid structure of the Foam-Ni can provide high porosity and surface area, which can also support the catalysts for increasing the contact areas between catalysts and reactants [40]. Therefore, to utilize the catalytic property of the Pd metal, Pd deposited Foam-Ni electrode may exhibit the advantage for the generation of H_2O_2.

In this work, we prepared the MnO_2 modified Nano-G (MnO_2/Nano-G) and Pd loaded Foam-Ni (Foam-Ni/Pd) composites by the chemical redox method and electro-deposition method, respectively, and then used them to construct a two-layer type MnO_2/Nano-G|Foam-Ni/Pd composite cathode for the electro-catalytic degradation of phenol wastewater. The morphology, structure and element chemical state of the MnO_2/Nano-G and Pd/Foam-Ni composites were analyzed. The degradation efficiencies of phenol and TOC with MnO_2/Nano-G|Foam-Ni/Pd composite cathode were investigated, and the reaction parameters were optimized. Finally, the roles of the MnO_2 and Pd metal on the phenol degradation by MnO_2/Nano-G|Foam-Ni/Pd composite cathode and the cathodic catalysis mechanisms were revealed. As expected, the as-prepared MnO_2/Nano-G|Foam-Ni/Pd composite cathode exhibited high H_2O_2 and •OH yields and electro-catalytic degradation performance.

2. Experimental section

2.1. Materials and chemicals

Natural flake graphite was purchased from Heilongjiang Oyu Graphite Group Co., Ltd. Foam-Ni (99.9%) was purchased from Changsha Liyuan New Material Co., Ltd. Phenol, glutaraldehyde and palladium chloride were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Chitosan was purchased from Aladdin Reagent Co., Ltd. Potassium permanganate, manganese acetate and perchloric acid were purchased from Tianjin Xinyuan Chemical Co., Ltd., China. All chemicals used in our work were analytical grade. All solutions were prepared by using deionized water.

2.2. Preparation of MnO_2/Nano-G and Foam-Ni/Pd composites

The Nano-G was prepared according to our previous study [31]. The MnO_2/Nano-G composite was prepared by the chemical redox method. The concrete process was as follows. 1.5 g of Nano-G and 0.49 g of manganese acetate were orderly added into 20 mL of deionized water under continuous magnetic stirring. After mixed thoroughly, 13 mL of 0.1 mol L^{-1} potassium permanganate solution was slowly added into above solution. Subsequently, the mixed solution was heated up to the temperature of 353.15 K and maintained for 30 min. The turbid solution was then filtered and dried in a thermostatic vacuum oven at 373.15 K. At last, the mixture was calcinated at 623.15 K for 120 min in a muffle furnace to obtain the MnO_2/Nano-G composite.

The Foam-Ni/Pd composite was prepared by the electrodeposition method in an electrolytic cell with two electrode configurations, in which Ti/IrO_2/RuO_2 electrode and Foam-Ni were used as the anode and cathode, respectively. Prior to preparation, Foam-Ni was immersed into 5% hydrochloric acid solution for 2 min. Foam-Ni was then ultrasonically washed with acetone and ethanol for 10 min in turn. The electrodeposited process was conducted in an aqueous solution containing 3 mM NaCl and 1 mM $PdCl_2$ with a constant current of 10 mA at 313.15 K for 120 min.

2.3. Preparation of MnO_2/Nano-G|Foam-Ni/Pd composite cathode

The MnO_2/Nano-G film was prepared by the hot-pressing method. The stainless steel mesh was used as the support. 1.2 g of