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Dimethyl phthalate degradation at novel and efficient electro-Fenton cathode

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ABSTRACT

A novel three-dimensional porous carbon nanotube sponge (CNTS) with high electrical conductivity was prepared, characterized and investigated as the catalytic cathode for oxygen reduction and employed for an electro-Fenton process to degrade dimethyl phthalate (DMP) in aqueous solution. For comparison, the conventional electro-Fenton cathode, graphite gas diffusion electrode (GDE) and graphite electrode, was also tested. Experiments showed that the side reaction of H_2 evolution was avoided and the H_2O_2 accumulation concentration arrived at the maximal value at CNTS cathode as the cathode potential was set at −0.5 V (*vs.* SCE). The apparent rate constant for DMP degradation was 0.057 min^{-1} at CNTS cathode, much higher than 0.005 min^{-1} at graphite cathode and 0.011 min^{-1} at graphite GDE. Meanwhile, CNTS possessed desirable stability without performance decay after 20 times reaction. It was also found that more negative cathode potential than −0.5 V could cause the side reaction of H_2 evolution and thus leading to a deteriorated DMP degradation. Moreover, the initial DMP concentration affected the apparent rate constant of DMP degradation. Compared to the case of higher initial DMP concentration, DMP degraded faster in the case of lower initial DMP concentration. The pH value and initial Fe^{2+} concentration for DMP degradation at CNTS cathode were optimized to be 3.0 and 0.5 mmol L^{-1}, respectively. The CNTS is promising to be potentially used as the cathode for electro-Fenton system to remove organic pollutants in wastewater.

1. Introduction

Advanced oxidation processes (AOPs) are promising technology for effluent purification when the contaminants are difficult to remove by biological processes [1–4]. Among AOPs, the Fenton oxidation process [5–8], whose high performance is based on the high oxidation power and the non-selective oxidation ability of hydroxyl free radicals (•OH) generated from Fenton's reagents ($H_2O_2 + Fe^{2+}$), has received tremendous attention in recent years. The Fenton's reaction mechanism for the formation of •OH is complicated, while the main reaction can be described as follows:

$$Fe^{2+} + H_2O_2 \rightarrow \bullet OH + OH^- + Fe^{3+} \quad (1)$$

The high oxidative efficiency of Fenton oxidation process has been well established, while its application is limited by the storage and shipment of concentrated hydrogen peroxide (H_2O_2). To solve these problems, electro-Fenton process [9–13] is developed to eliminate or minimize this drawback. In electro-Fenton process, H_2O_2 can be in situ supplied electrochemically through oxygen reduction reaction (ORR), and ferrous ions (Fe^{2+}) can be regenerated at cathode in acidic aqueous solution. Therefore, H_2O_2 production from ORR at cathode is crucial to the electro-Fenton process [14].

It should be noted that ORR has two possible reaction pathways involving two or four electrons transfer, which can be expressed by Eqs. (2) and (3), respectively [15,16].

$$O_2 + 2H^+ + 2e \rightarrow H_2O_2 \quad 0.695\,V \ (vs.\ NHE) \quad (2)$$

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$$O_2 + 4H^+ + 4e \rightarrow 2H_2O \quad 1.229 \ \ V(vs.\ NHE) \qquad (3)$$

Obviously, the 4-electron process of ORR (Eq. (3)) should be avoided as much as possible so that sufficient H_2O_2 can be supplied for the electro-Fenton process. Whether ORR follows two or four-electron process depends strongly on the cathode materials [17,18]. Graphite electrode has been traditionally adopted as the cathode for electro-Fenton system before 2000, because of its high selectivity for 2-electron process of ORR and its low cost. However, due to the limited pore numbers and unsuited pore structure on its surface, their mass transfer characteristics and the electrochemical reaction areas are poor for H_2O_2 generation from ORR. Accordingly, the performance is in need of further improvement for electro-Fenton process, and any effort to identify novel cathode to develop electro-Fenton process should be encouraged [12].

Recently, some novel electro-Fenton cathodes have been investigated, such as carbon gas diffusion electrode (GDE) [12,17,19,20], graphite felt [21], carbon felt [22–24], carbon sponge [25] and so on. In these investigations, the electro-Fenton performance has been enhanced through improving the mass transfer characteristics of cathode. Considering these reports, the novel electro-Fenton electrode materials should possess several characteristics as follows: (1) high selectivity for 2-electron process of ORR, (2) good mass transfer performance, (3) high electrochemical active reaction area, and (4) high electrical conductivity. As reported, carbon nanotubes (CNTs) meet with the above properties. The organic contaminants in wastewater can be quickly destroyed through electro-Fenton process using CNTs electrode as the cathode [26–29].

On the other hand, CNTs generally have a strong tendency to agglomerate due to their nano-size and high surface energy. Therefore, their applications are limited due to the difficulty in dispersing them in a solvent (water or organic agent). Carbon nanotube sponge (CNTS) is a newly developed materials, which is a sponge-like bulk material consisting of self-assembled, interconnected CNT skeletons, a porosity of >99%, high structural flexibility and robustness, high electrical conductivity, and wettability to organics in pristine form [30–32].

Considering that the sponge-like bulk CNTS can be directly used as the cathode for electro-Fenton system, in the present study, CNTS was prepared and directly adopted as the electro-Fenton cathode. Dimethyl phthalate (DMP), widely employed as an indispensable additive of plastics to increase the flexibility, belongs to the family of endocrine disruptor compounds, whose ubiquity in the environment has brought a great concern to academia and public [33,34]. The world annual production of plastics is estimated to be around 100 million tons. DMP has been listed as one of the priority pollutants in some countries including China, and has been used in rapid performance assessment of some AOPs including electro-Fenton reaction [15,33,34]. Herein, it was used as a model substrate to evaluate the cathode performance [33,34,15]. It was found that this electro-Fenton system with CNTS cathode exhibited higher efficiency and desirably recycling stability for degrading DMP.

2. Experimental

2.1. Preparation and characterization of CNTS

CNTS was obtained through a chemical vapor deposition (CVD) process using ferrocene and 1,2-dichlorobenzene as the catalyst precursor and carbon source, respectively. The detailed preparation process has been previously reported [30–32]. In brief, Ferrocene powders were dissolved in dichlorobenzene to obtain a solution (0.06 g mL^{-1}), which was then continuously introduced into a quartz tube fixed in a high-temperature furnace by a syringe pump. The reaction temperature was set at 860 °C. A gas mixture of Ar and H_2, was supplied at a rate of 2000 mL min^{-1} and 300 mL min^{-1}, respectively. A rectangular quartz sheet (2.0 in. × 1.0 in.) was placed in the reaction zone as the growth substrate. After a growth period of 4 h, the sponge-like products were collected from the quartz substrate after CVD. The morphology of the CNTS was obtained by scanning electron microscopy (SEM) (LEO-1530VP, Germany). The X-ray diffraction (XRD) measurements were carried out on a D/Max-IIIA (Rigaku Co., Japan) using Cu Kα radiation (λ = 0.15406 nm), and operating at 40 kV and 40 mA and the scan rate was 10° min^{-1}. Raman spectra were obtained on a Raman spectrometer (Renishaw Corp., UK) using a He/Ne laser with the wavelength of 514.5 nm.

2.2. H_2O_2 generation and DMP degradation

The H_2O_2 generation and DMP degradation experiments were carried out in an undivided glass cell on a Metrohm Autolab PGSTAT302N instrument. The as-prepared CNTS (2.0 cm × 2.0 cm) was used as the cathode (working electrode), a Pt foil and a saturated calomel electrode (SCE) were used as the anode (counter electrode) and the reference electrode, respectively. In the case of H_2O_2 generation, 120 mL of 0.1 mol L^{-1} Na_2SO_4 solution at initial pH 3.0 was used as the electrolyte. In the DMP degradation experiment, Fe^{2+} and DMP with different concentrations were introduced into the above electrolyte. O_2 was fed onto the cathode surface at a flow rate of 400 mL min^{-1}. Without specification, the potentials applied in this study were referred to the SCE.

2.3. Analysis

Linear sweeping voltammetry (LSV) was adopted to investigate and identify the potential for ORR under specific conditions. H_2O_2 concentration was determined by the potassium titaniumoxalate method using a UV–VIS spectrophotometer (TU1810, Universal Analysis, Beijing, China) [33]. The DMP concentration was measured by HPLC (Techcomp, LC 2130, Shanghai, China) equipped with a reverse phase column (Waters, XT erra MS C-18, 5 μm) and a UV detector. The mobile phase was a mixed solution of 50% acetonitrile and 50% water (V/V), and the detection wavelength was set at 276 nm. The total organic carbon (TOC) concentration was determined using a TOC analyzer (Shimadzu 5000A).

3. Results and discussion

3.1. Characteristics of CNTS electrode

As can be clearly seen from Fig. 1A, the as-prepared CNTS appears as a macroscopic and monolithic sponge. The further amplifying observation through SEM (Figs. 1B and C) shows the porous morphology and overlapped carbon nanotubes (CNTs). Moreover, the sponge consists of CNTs self-assembled into a porous, interconnected, and three-dimensional framework. The corresponding diameter and length of multi-walled nanotubes are in the range of 30–50 nm and tens to hundreds of micrometers, indicating that there are multiple layers of CNTs existing in the bulk sponge.

The XRD patterns of the CNTS are shown in Fig. 2A. The characteristic diffraction peaks of graphite carbon at about 26 and 45°, corresponding to (0 0 2) and (1 0 0) face, respectively [35,36]. It indicates a high graphitization and thus a high electrical conductivity with a value of 6×10^{-3} Ω m obtained from a two-probe measurement. This behavior is quite beneficial as the cathode in the electro-Fenton system. The high graphitization can also be confirmed from the Raman spectra of CNTS as given in Fig. 2B. The peak at 1365 cm^{-1} is assigned to the disordered graphite (D-line). The peak at high frequency of 1591 cm^{-1} corresponds to a splitting of the E_{2g} stretching mode of graphite and reflects the structural