Electrocatalytic dechlorination of chlorophenols on palladium/graphene-Nafion/titanium mesh electrode

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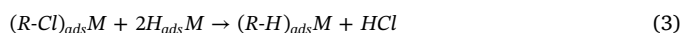
ABSTRACT

The electrocatalytic dechlorination of 3,5-dichlorophenol (3,5-DCP) and 2,3,5-trichlorophenol (2,3,5-TCP) on palladium/graphene-Nafion/titanium mesh electrode (Pd/rGO-Nafion/Ti electrode) was studied. The preparation conditions of Pd/rGO-Nafion/Ti electrode were investigated by electrochemical workstation, and the results showed that the addition of the graphene-Nafion middle layer could improve the electrocatalytic ability. The Pd/rGO-Nafion/Ti electrode was characterized by field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), inductively coupled plasma-atomic emission spectrometry (ICP-AES) and X-ray photoelectron spectroscopy (XPS). The influences of dechlorination current and initial pH value of reaction solution on the conversion efficiency and the current efficiency of dechlorination on Pd/rGO-Nafion/Ti electrode were investigated. Complete dechlorination of 3,5-DCP and 2,3,5-TCP could be achieved within 90 min under initial pH of 2.3 and current of 5 mA. The dechlorination intermediate products of 3,5-DCP and 2,3,5-TCP were detected and the dechlorination pathways were inferred. The kinetics results revealed that the dechlorination of 3,5-DCP and 2,3,5-TCP followed a two-stage mixed order kinetics.

1. Introduction

Chlorophenols (CPs), which are used as raw materials and intermediates in chemical industry, were detected in water and soil with wastewater discharge [1–3]. They have been listed as priority pollutants by the United States Environmental Protection Agency (USEPA) due to their high toxicity and refractory [4]. It is necessary to study the methods of chlorophenols degradation. Various methods including physical, biological and chemical methods have been developed to the degradation of chlorophenols. Physical adsorption [5], liquid membrane permeation [6] and membrane separation [7] have been studied to separate CPs from wastewater as conventional physical methods. Biodegradation, i.e., activated sludge process [8], biofilm technology [9] and anaerobic treatment [10] have been used to decompose CPs widely. The application of advanced oxidation processes in the degradation of CPs improves the removal efficiency [11–13], but may produce high toxicity byproducts [14]. Zero-valent metal reduction of CPs is an effective method to remove chlorine atoms from aromatic ring via chemical reduction [15,16]. However, it is difficult to recovery from the aqueous solution and produces secondary pollutants.

Recently, electrocatalytic reduction of CPs receives more and more attention owing to its high efficiency, non-secondary pollution, and easy control of reaction conditions [17–20]. CPs can be reduced via electrocatalytic hydrogenolysis (ECH) — chlorine atoms on aromatic ring are replaced by hydrogen atoms adsorbed on the electrode surface. The mechanism of ECH of CPs involves the steps described in Eqs. (1)–(4) [21–23].

$$2H_2O + 2e^- + M \rightarrow 2H_{ads}M + 2OH^- \quad (1)$$

$$R\text{-}Cl + M \rightarrow (R\text{-}Cl)_{ads}M \quad (2)$$

$$(R\text{-}Cl)_{ads}M + 2H_{ads}M \rightarrow (R\text{-}H)_{ads}M + HCl \quad (3)$$

$$(R\text{-}H)_{ads}M \rightarrow R\text{-}H + M \quad (4)$$

Where M is the electrode surface. At first, water is electrocatalytic reduced on the surface of electrode to produce adsorbed hydrogen (H_{ads}), which has much stronger reducibility than H_2 (Eq. (1)). Then, CPs (R-Cl) diffuse to the electrode surface (Eq. (2)) and react with H_{ads} to achieve the hydrogenolysis of CPs (Eq. (3)). At last, ECH product (R-H) desorbs from the electrode surface (Eq. (4)). In the ECH process, the hydrogen evolution reaction (HER) phenomenon often occurs concomitantly, which proceeds either via Heyrovsky reaction (electrochemical recombination, Eq. (5)) or via Tafel reaction (chemical recombination, Eq. (6)) [24,25]

$$2H_{ads}M + H_2O + e^- \rightarrow H_2 + OH^- + M \tag{5}$$

$$H_{ads}M + H_{ads}M \rightarrow H_2 + M \tag{6}$$
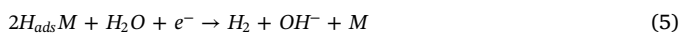
In the ECH process, the generation of H_{ads} is affected by the property of electrode and reaction conditions (such as pH value and current density). Among the effect factors, the nature of electrode material has the remarkable impact. Palladium (Pd), which is a noble metal, has the excellent property of the electrocatalytic reduction of H^+ or H_2O to produce H_{ads} [26] and the strong adsorption/ absorption ability for hydrogen [27,28]. It has been used for dehalogenation and exhibits high catalytic activity [29–32].

Nanocarbon is a carbon material with a dispersed phase size of less than 100 nm, which is widely used for catalysis due to its excellent pore structure, stable chemical property, and high electrical and thermal conductivity [33]. Carbon nanotubes (CNTs) and graphene are two types of nanocarbon materials. We have reported that the presence of CNTs could improve the electrocatalytic performance of the electrode [34]. Unlike carbon nanotubes, graphene is a two-dimensional (2D) carbon material composed of single-layer carbon atoms on a honeycomb structure. It is widely used in the field of electronic devices [35,36], energy storage devices [37], and optoelectronic devices [38] owing to its excellent mechanical, electrical, thermal, and optical properties (Young's modulus of 1.0 ± 0.1 TPa, tensile strength of 130 ± 10 GPa [39], electrical conductivity of 10^6 S cm^{-1} [40], and thermal conductivity of 3000–5000 Wm^{-1}K^{-1} [41], respectively). Moreover, graphene has a larger specific surface area (2630 m^2 g^{-1}) compared to carbon nanotubes (150–1315 m^2 g^{-1}) [42], which can be used as catalysts supports to increase the attachment site of the catalyst [43–46].

In this paper, graphene dispersed with Nafion-ethanol solution was used as a middle layer to prepare palladium/graphene-Nafion/titanium mesh electrode. The preparation condtions of the electrode on the modification of graphene-Nafion layer and the electro-deposition of Pd particles were investigated. The electrocatalytic dechlorination processes of 3,5-dichlorophenol (3,5-DCP) and 2,3,5-trichlorophenol (2,3,5-TCP) on the electrode were investigated in aqueous solution.

2. Experimental section

2.1. Materials and chemicals

Ti mesh was purchased from Anping Wire Screen Mesh Plant, China. Its aperture density and line diameter were 150 pores per inch (PPI) and 0.1 mm, respectively. Nafion (5 wt%) was obtained from Du Pont. Reduced graphene oxide (rGO, > 98 wt%) was supplied by Chengdu Organic Chemicals Co., Ltd., China. Palladium Chloride (PdCl$_2$) was purchased from Xi'An Catalyst Chemical Co., Ltd, China. Phenol, sodium sulfate (Na$_2$SO$_4$), sodium hydroxide (NaOH), sulfuric acid (H$_2$SO$_4$, ~98%), and cetyl trimethyl ammonium bromide (CTAB) were provided by Sinopharm Chemical Reagent Co., Ltd., China. Chlorophenols (3,5-DCP, 2,3,5-TCP and chlorophenolic intermediates) were purchased from Beijing Hengye Zhongyuan Chemical Co., Ltd., China. Deionized (DI) water (18.2 MΩ cm) obtained from Milli-Q water purification system were used for preparing solution.

2.2. Preparation of electrode

The substrate of Ti mesh (20 mm × 20 mm) was degreased in 0.1 mol L^{-1} Na$_2$CO$_3$ solution for 30 min at 65 °C and removed the surface oxides in 0.1 mol L^{-1} boiled oxalic acid solution for 30 min in sequence. The pretreated Ti mesh was rinsed with DI water and stored in ethanol.

rGO-Nafion suspension was obtained via dispersing rGO in 0.1 wt% Nafion-ethanol solution. The suspension was then sonicated for 30 min to ensure that it was homogeneous. A dip-coating method was used to loaded rGO on the pretreated Ti mesh. The pretreated Ti mesh was used
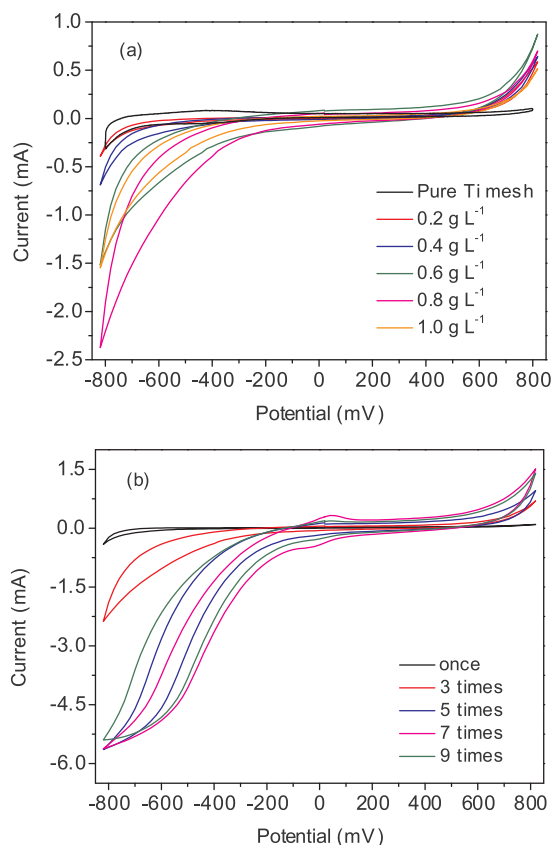

Fig. 1. CV curves of pure Ti mesh and rGO-Nafion/Ti supporting electrodes prepared at different rGO concentrations (a) and different times of dip-coating (b) (electrolyte: 0.5 mol L^{-1} H$_2$SO$_4$ solution, scan rates: 50 mV s^{-1}).

as substrate for dipping into the suspension for 15 s, withdrawn at a speed of 1 cm·s^{-1}, and then dried completely under ambient condition. After several repeated cycles, the rGO-Nafion/Ti supporting electrode was obtained. Then, the rGO-Nafion/Ti supporting electrode was used as cathode and a Pt foil was used as anode for Pd particles deposition under a constant current to prepare Pd/rGO-Nafion/Ti electrode. The plating solution was PdCl$_2$ solution containing surfactant CTAB (20 mol L^{-1}).

For comparison, a Pd/Ti electrode was synthesized by electro-deposition of Pd particles on Ti mesh under the same preparation conditions without modified with rGO-Nafion middle layer.

2.3. Dechlorination experiments

Electrochemical degradation of 3,5-DCP and 2,3,5-TCP was carried out at a two-compartment reactor separated by a Nafion-324 cation-exchange membrane with continuously stirring at 400 rpm. The cation-exchange membrane was used for avoiding generating chlorinated by-products on the anode. The catholyte was 0.05 mol L^{-1} Na$_2$SO$_4$ solution containing 3,5-DCP or 2,3,5-TCP. The anolyte was 0.05 mol L^{-1} Na$_2$SO$_4$ solution. The Pd/rGO-Nafion/Ti electrode and a Pt foil were used as cathode and anode for constant current degradation of 3,5-DCP and 2,3,5-TCP, respectively. Constant current for electrochemical dechlorination was provided by a U2722 A modular source measure unit (Keysight, USA).

2.4. Analysis and characterization

Electrochemical measurements (cyclic voltammetry, CV) of pure Ti mesh, rGO-Nafion/Ti supporting electrode, Pd/rGO-Nafion/Ti and Pd/Ti electrode were carried out by electrochemical workstation (Metrohm