Separation and Purification Technology 124 (2014) 224–230

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Preparation of palladium–nickel loaded titanium electrode with surfactant assistance and its application in pentachlorophenol reductive dechlorination

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ARTICLE INFO

Article history:
Received 26 June 2013
Received in revised form 21 December 2013
Accepted 17 January 2014
Available online 30 January 2014

Keywords:
Pentachlorophenol
Electrocatalytic dechlorination
Palladium–nickel bimetallic electrode
Electrodeposition
Surfactant

ABSTRACT

Palladium–nickel (Pd–Ni) bimetallic electrodes were prepared by electrodeposition method assisted with surfactants of cetyl trimethyl ammonium bromide (CTAB), sodium lauryl sulfonate (SLS) or sodium dodecyl sulfate (SDS). The prepared Pd–Ni electrodes were characterized in terms of cyclic voltammetry (CV), scanning electron microscope (SEM), X-ray diffraction (XRD), and inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The electrode prepared with CTAB assistance, Pd–Ni(CTAB)/Ti, with higher electrochemical activity, was applied to the dechlorination of pentachlorophenol (PCP) in aqueous solution. The influences of dechlorination current and initial pH value on the PCP removal were studied. Complete removal could be achieved at ambient temperature under the conditions of constant current of 3 mA and initial pH value of 2.1 on the Pd–Ni(CTAB)/Ti electrode within 90 min. Moreover, decay kinetics and apparent activation energy of PCP dechlorination were investigated.

1. Introduction

Chlorophenols (CPs) are used as pesticides or raw materials for pesticides due to one or more chlorine atoms and aromatic ring in their molecular structures. Pentachlorophenol (PCP) is one of such compounds and it has been widely used as wood preservative and pesticide [1]. Meanwhile, CPs including PCP have been identified as potential carcinogens and have been listed as priority pollutants by the United States Environmental Protection Agency (USEPA) [2]. Toxicity of CPs increases with the number of chlorine atom. Ecotoxicity of CPs, especially PCP, necessitates the development of rapid and reliable remediation techniques.

Electrochemical oxidation [3–7] and advanced chemical oxidation [8,9] of CPs have been profusely studied in the last decade. The two techniques require appropriate catalytic materials and may produce harmful byproducts. Chemically reductive dechlorination of CPs has been successfully utilized to dechlorinate chlorinated organics, e.g. by zero-valent metals [10–14] and bimetallic systems [15–19]. In these chemical reduction methods, molecular hydrogen was produced by anodic corrosion in water. Electrochemically reductive dechlorination is suggested as a promising method [20–22] due to its rapid reaction rate, low apparatus cost, mild reaction conditions, and absence of secondary contaminants [23,24]. The mechanism of electrochemically reductive dechlorination is known as electrocatalytic hydrogenolysis (ECH) [25–27]. Briefly, in the cathode compartment, water (or hydrogen ion) is electro-reduced on the electrode surface and adsorbed onto metal catalyst to form a metal hydride (M–H). Herein, the adsorbed hydrogen (H_{ads}) is activated with high reduction capacity and it reacts with CPs that adsorbed on the electrode surface through attacking the C–Cl bonds.

Palladium (Pd) is considered as the most ideal catalyst for ECH because it has a higher hydrogen evolution potential and unique ability for adsorption [28–30] and absorption of hydrogen to form hydride [31,32]. However, the pure Pd cathode has a particular disadvantage of high cost. Sound ways to limit the amount of Pd include electrodepositing Pd on a less expensive substrate material [33] and co-electrodepsiting Pd with other metals. High dispersity and large surface area of Pd particles are desirable for the electrochemically reductive dechlorination process. Therefore, the electrode supporting material plays an important role in ECH. Because of the penetrability and advantage for the mass transfer in dechlorination process, some permeable metallic materials were used as cathode substrates, such as meshed titanium (Ti) [34],

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http://dx.doi.org/10.1016/j.seppur.2014.01.022
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foam nickel (Ni) [35] and activated carbon fiber [36]. Surfactant, which has a long hydrophobic C–H chain and a hydrophilic head group, can adsorb at hydrophobic electrode and alter the properties of electrode/solution interface, influence the electrochemical process of electroactive species [37,38]. In this work, Pd–Ni bimetallic electrode was prepared by electrodepositing on meshed Ti substrate assisted with surfactant, and it was applied to PCP degradation in aqueous solution.

2. Experimental

2.1. Experimental chemicals and materials

Experimental chemicals including Pd chloride ($PdCl_2$) powder, hexahydrated nickel sulfate ($NiSO_4{\cdot}6H_2O$), ammonia, ammonium chloride (NH_4Cl), sulfuric acid (H_2SO_4) (98%), hydrochloric acid (HCl), oxalic acid ($H_2C_2O_4$), sodium carbonate (Na_2CO_3), sodium sulfate (Na_2SO_4), cetyl trimethyl ammonium bromide (CTAB), sodium lauryl sulfonate (SLS), sodium dodecyl sulfate (SDS) and PCP (99%) were analytic purity. Nafion-324 cation-exchange membrane (DuPont) was from Sigma–Aldrich Chemical Co. Meshed Ti was from Anping Wire Screen Mesh Plant, China. The aperture density and line diameter of meshed Ti were 150 PPI and 0.10 mm, respectively. All solutions were prepared with Millipore-Q water.

2.2. Preparation of Pd–Ni bimetallic electrode

Before electrodeposition, the meshed Ti substrate was pretreated first. It was placed in 0.3 mol L^{-1} Na_2CO_3 solution for 30 min at 363 K to remove the surface grease, in 0.1 mol L^{-1} boiling oxalic acid for 30 min to remove the surface oxides. Then, it was rinsed thoroughly with Millipore-Q water and was soaked in ethanol for later use.

Pd–Ni bimetallic microparticles were electrodeposited in an undivided electrolytic cell with constant current of 30 mA for 50 min. A platinum foil was used as anode and the pretreated meshed Ti with a geometric area of 8 cm^2 was used as cathode. The electrolyte was composed of 5 mmol L^{-1} Pd (II) and 14 mmol L^{-1} Ni (II) and 0.2 mol L^{-1} NH_4Cl was used as the supporting electrolyte. The solution pH was adjusted to 6.5 by addition of concentrated ammonia. Concentrations of CTAB, SLS and SDS were 3.0, 0.1 and 0.1 g L^{-1}, separately, which were selected results under the same electrodepositing parameters. The preparation processes of the three electrodes were described in Supplementary Materials. Pd–Ni loaded Ti bimetallic electrodes were prepared with assistance of the three surfactants, namely Pd–Ni(CTAB)/Ti electrode, Pd–Ni(SLS)/Ti electrode and Pd–Ni(SDS)/Ti electrode, respectively.

2.3. Characterization of electrode

The electrochemical analyses (cyclic voltammetry, CV) for prepared electrode were carried out by CHI 660C Potentiostat/Galvanostat with a conventional three electrode system. A platinum foil was used as the counter electrode and an Hg/Hg_2SO_4-saturated K_2SO_4 was used as the reference electrode. The as-prepared Pd–Ni bimetallic electrode was the working electrode. The electrolyte for CV measurement was 0.5 mol L^{-1} H_2SO_4 solution, which was purged with pure nitrogen for at least 20 min to remove oxygen before CV test.

The electrodes were characterized in terms of composition, crystal structure and morphology. The crystal structures of the electrodeposits were analyzed with a X-ray diffraction (XRD, Bruker/AXS D8 Advance, Germany) using Cu Ka radiation with k = 1.5405 Å. The loading levels of Pd and Ni particles were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES, RIS Intrepid ER/S, Thermo Elemental, USA). Surface morphologies of the electrodes were observed with a scanning electron microscope (SEM, Hitachi S4700, Japan) at 20.0 kV.

2.4. Dechlorination of PCP

PCP dechlorination experiments on selected electrode in aqueous solution were conducted in a two-compartment cell separated by a cation-exchange membrane Nafion-324, which was used for preventing the dechlorination products from re-chlorinating (shown in Fig. S1). The catholyte was 30 mL 0.05 mol L^{-1} Na_2SO_4 solution containing 10 mg L^{-1} PCP. The anolyte was 30 mL 0.05 mol L^{-1} Na_2SO_4 solution and different amount of H_2SO_4. Prepared Pd–Ni bimetallic electrode was used as cathode and a platinum foil (1 cm × 4 cm) was used as anode. The distance of the two electrodes was 8 cm. The catholyte was stirred magnetically with 400 rpm to eliminate the concentration polarization. The experiments of PCP degradation were carried out at the ambient temperature (298 ± 1 K) except when the influence of temperature was discussed. The concentration of PCP was analyzed by high performance liquid chromatography (HPLC, Waters, USA), which consists of a waters 1525 binary HPLC pump and a waters 2487 dual λ absorbance detector with a Kromasil reverse phase C18 column (5 μm particle size and 250 × 4.6 mm). The mobile phase was 15% water (containing 2% acetic acid) and 85% methanol with flow rate of 1.0 mL min^{-1}. Detection wavelength was set at 305 nm. The intermediate products were identified by gas chromatography–mass spectrometry system (GC–MS/MS, SCION TQ, Bruker Daltonics, USA).

3. Results and discussion

3.1. Electrode characterization

3.1.1. CV test

The CV curves of the three Pd–Ni bimetallic electrodes are plotted in Fig. 1. Curve (a) shows the CV test of the Pd–Ni(CTAB)/Ti electrode and its hydrogen adsorption current was up to −128 mA at about −650 mV. Curve (b) and curve (c) correspond to Pd–Ni(SLS)/Ti electrode and Pd–Ni(SDS)/Ti electrode with hydrogen adsorption currents of −81 mA and −77 mA, separately. According to the literature [39], the higher hydrogen adsorption current is in the voltammogram, the larger quantity of hydrogen atoms adsorb on the electrode. Consequently, electrodes with higher hydrogen adsorption current will be more effective for

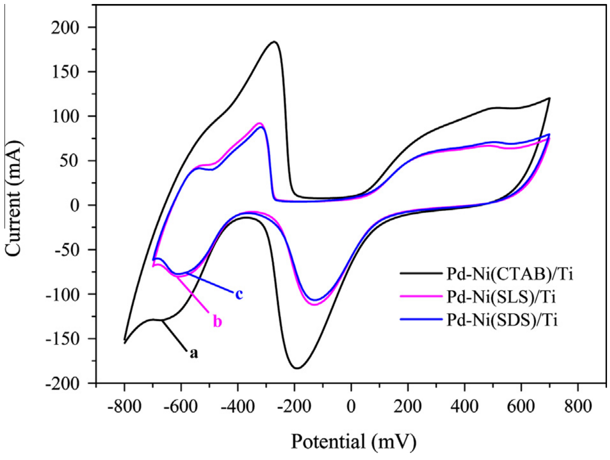

Fig. 1. CV curves of electrodes synthesized with different surfactants. Scan rate: 50 mV s^{-1}. Electrolyte: 0.5 mol L^{-1} H_2SO_4 solution.