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Electrochemical hydrodechlorination of 4-chlorobiphenyl in aqueous solution with the optimization of palladium-loaded cathode materials

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Abstract

The electrochemical hydrodechlorination of 4-chlorobiphenyl (4-MCB) in aqueous solution containing methanol (MeOH), sodium acetate, acetic acid and bromide of hexadecyltrimethylammonium (CTAB) was investigated under constant current electrolysis at ambient temperature by using a membrane-separated flow-through cell operated in batch-recycle modes. The effects of catalyst type, cathode substrate, cathode recycle, and catalyst loading on the conversion of 1 mM 4-MCB were evaluated. Convention hydrogenation catalysts including Pd, Pt, and Ni and several types of cathode substrates such as metallic mesh/foam and activated carbon material, were tested. It was found that the palladium-loaded nickel foam was most suitable to be used as cathode for the treatment of 4-MCB due to its high performance and stability, which could rapidly dechlorinate 4-MCB to biphenyl with 94.3% conversion and 91.5% yield under constant current of 15 mA after 3 h electrolysis. During the electrolysis, the current efficiencies and energy consumptions were in range of 5.5–20% and 2.1–7.9 kWh kg^{-1}, respectively.

Keywords: Electrochemical hydrodechlorination (HDC); 4-Chlorobiphenyl; Palladium; Cathode materials; Nickel foam

1. Introduction

Chlorinated aromatic compounds caused great environmental challenges due to their widespread use in industrial processes, inherent toxicity and high resistance to degradation. Contamination of water and soil with chlorinated solvents, pesticides, and insulating fluids spurred an endeavour to develop efficient and cost-effective treatment. Among a variety of promising treatment methods, chemical and electrochemical catalytic HDC have proved to be the effective methods for the elimination of hazardous chlorinated aromatic compounds from organic wastes [1–4].

The main ways of chemical HDC applied in remediation have been explored based on zero-valent iron (ZVI) particles, which have shown extremely chemical reactive properties to reduce a wide range of chlororganics pollutants like chlorinated solvents. However, chemical HDC using iron alone suffered from slow reaction rates, especially for chlorinated aromatic compounds, under ambient temperature and pressure (e.g., nanosized ZVI dechlorinated PCBs with congener half-lives ranging from 40 days to 77 years) [2].

In addition to chemical HDC, bimetallic catalysis, along with the electrochemical method, provides more efficient dechlorination because of its ability to thoroughly remove a wide range of chlorinated compounds without leaving chlorinated side products (as is often the case for the use of ZVI alone). The frequently used catalysts include Pd, Pt, and Ni, which are supported on ZVI, activated carbon, or highly porous metallic oxides such as alumina. The catalytic systems have been successfully used to treat a number of chlorinated compounds such as chlorophenols, PCBs, and chlorinated aliphatic hydrocarbon [5–8].

Recently, the electrochemical HDC of chlorinated aromatic compounds has been developed as another means to improve the rate of HDC for the treatment of chlorinated organic wastes, as it involves the electrochemical reduction of a protic solvent to produce continuously adsorbed "nascent" hydrogen atoms that react chemically with an adsorbed organic substrate [9]. A further advantage of the electrochemical HDC is that the cathodic polarization of the catalyst appears to offer protection against the adsorption of catalyst poisons, thereby extending the catalyst's longevity. Actually, this method is often technically flexible, inexpensive, and ready for the dechlorination of the

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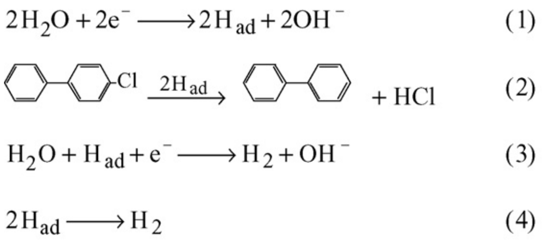

Scheme 1. Electrochemical HDC of 4-MCB.

conventional chlorinated aromatic compounds including a variety of chlorophenols and chlorobenzenes [10–14]. However, few studies in this area have investigated the more refractory chlororganics such as PCBs, which are listed in Stockholm Convention on Persistent Organic Pollutants (POPs) as priority chemicals for eventual elimination by 2025, and other chlorinated binuclear aromatics.

The only reported work of electrochemical HDC of PCBs was the dechlorination of monochlorobiphenyl by using a flow-through cell with palladized activated carbon felt cathode [15]. A conversion, up to 98% dechlorination, of 20.11 mM 4-MCB to biphenyl was achieved at constant current density in aqueous solution containing 40% MeOH (v/v), 0.5 M tetra-*n*-hexylammonium bromide and 0.5 M trifluoroacetic acid after 4 h electrolysis. However, the maximal current efficiency was only 9.1%; and the energy consumption was as high as 21.1 kWh kg^{-1} 4-MCB.

The purpose of our work was to explore an electrochemical system, especially in new efficient cathode material, for facilitating the electrochemical HDC of the persistent chlorinated binuclear aromatics in aqueous solutions. 4-MCB was selected as the objective since it is more difficult to be reduced than more heavily chlorinated PCB congeners for the electrochemical HDC and the ability to dechlorinate it to biphenyl implies the ability to dechlorinate the higher chlorinated PCB congeners as well. Relatively high concentration (mM) of 4-MCB containing surfactant in aqueous solution was prepared in order to simulate the soil washing solution of PCBs contaminated soil [16]. In addition, 4-MCB electrochemical HDC processes are described in Scheme 1.

2. Experimental

2.1. Materials, chemicals and solutions

Ni Foam (99.9%, S_{BET}: $1.2217 \pm 0.1296\ m^2\ g^{-1}$, PPI: 130) and Cu Foam (99.9%, S_{BET}: $1.3742 \pm 0.1074\ m^2\ g^{-1}$, PPI: 130) were obtained from Changsha Lyuan Material Co., China. Ti mini mesh (99.9%, mesh size 50, wire diameter 0.17 mm), stainless steel mesh (AISI 304L, mesh size 60, wire diameter 0.191 mm), Al mesh (99.5%, mesh size 28, wire diameter 0.274 mm), Cu–Zn alloy mesh (mesh size 50, wire diameter 0.15 mm), Ni mesh (99.9%, mesh size 60, wire diameter 0.12 mm) and Fe mesh (99%, mesh size 60, wire diameter 0.178 mm) were from Hebei Anping Wire Mesh Producing Factories, China. Activated carbon felt (ACF) and cloth (ACC) (S_{BET}: $1200 \pm 50\ m^2\ g^{-1}$) were purchased from Nantong Sutong Carbon Fiber Co., China. The above materials were all used as received.

$PdCl_2$ (99.5%) was from Changsha Asia Light Co., China. 4-MCB, biphenyl, and CTAB were from ACROS ORGANICS. Sodium acetate (NaAc), acetic acid (HAc), Na_2CO_3, $H_2PtCl_6{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, oxalic acid and H_2SO_4 were purchased from Beijing Chemical Reagents Co., China. Acetonitrile (HPLC-grade), MeOH, and acetone were from Fisher Chemical Co. Cation-exchange membrane used in the work was Nafion 324 (DuPont).

To prepare the catholyte of 1 mM 4-MCB, certain amount of CTAB, NaAc, and HAc (0.3 cm^3, pH buffer) were dissolved in 45 cm^3 of MeOH/H_2O solution to give 0.1 M concentration. Then 5 cm^3 of 10 mM 4-MCB dissolved in MeOH reservoir was added and the content of water was about 50% (v/v) in the catholyte. Anolyte, 50 cm^3, was prepared by diluting H_2SO_4 in water to pH 1. All solutions were prepared using water with a resistivity of 18.2 MΩ cm purified by a Millipore-Q system.

2.2. Apparatus and procedures

Several catalyzed electrodes, including these Pd-loaded metallic foams/meshes and carbon materials, were prepared by electrodeposition methods except Fe mesh. These palladized metal electrodes were prepared according to the following manner [17]. Firstly, these substrates were degreased and cleaned in acetone under ultrasonic vibration, and etched in dilute H_2SO_4 solution to remove surface native oxides except Ti mesh, which needed to be first rinsed with warm Na_2CO_3 solution and following etching with heated oxalic acid solution. Then they were put into 150 cm^3 N_2-saturated hot aqueous solution of $PdCl_2$ (0.21–2.1 mM) with magnetic stir and the deposition solution was buffered by 50 mM NaAc–HAc to pH 5.0. Finally, Pd was electrodeposited at a constant current of 15 mA to the foam substrates or 5 mA to the mesh substrates until the brown color of the $PdCl_2$ solution disappeared. The amount of Pd deposited on the metallic substrates surface was finally confirmed by comparing the substrate weights before and after deposition and was between 0.5 and 5 mg cm^{-2} geometric area. A number of electrodes were deposited under the same conditions to check reproducibility. As for Fe mesh, the electroless deposition of Pd on the cleaned Fe mesh was performed by immersion in a 20 cm^3 solution of 5 mM $PdCl_2$ and 50 mM NaCl similarly to Ref. [18]. The amount of Pd deposited on the Fe mesh was finally about 2 mg cm^{-2} geometric area for installation in the cell.

The carbon materials supported Pd through the next process. The carbon strips were completely immersed in 10% hydrochloric acid for 24 h and heated in boiling water for 30 min, washed with water to remove fine fibers and impurities, then dried at 200 °C for 2 h under N_2 protection ambience. Subsequently, electrodeposition was carried out and then preactivation as described in Ref. [19]. The carbon strips loaded finally 10% (w) Pd particles for next electrolysis.

Dechlorination of 4-MCB was carried out by constant current electrolysis, controlled by CHI 636B electrochemical worksta-