Electrochemical dechlorination of chloroform in neutral aqueous solution on palladium/foam-nickel and palladium/polymeric pyrrole film/foam-nickel electrodes

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Abstract

Electrochemical dechlorination of chloroform in neutral aqueous solution was investigated using palladium-loaded electrodes at ambient temperature. Palladium/foam-nickel (Pd/foam-Ni) and palladium/polymeric pyrrole film/foam-nickel (Pd/PPy/foam-Ni) composite electrodes which provided catalytic surface for reductive dechlorination of chloroform in aqueous solution were prepared using an electrodeposition method. Scanning electron microscope (SEM) micrographs showed that polymeric pyrrole film modified the electrode-surface characteristics and resulted in the uniform dispersion of needle-shaped palladium particles on foam-Ni supporting electrode. The experimental results of dechlorination indicated that the removal efficiency of chloroform and current efficiency in neutral aqueous solution on Pd/PPy/foam-Ni electrode could be up to 36.8% and 33.0% at dechlorination current of 0.1 mA and dechlorination time of 180 min, which is much higher than that of Pd/foam-Ni electrode.

Key words: chloroform; electrochemical dechlorination; removal efficiency; Pd/foam-Ni electrode; Pd/PPy/foam-Ni electrode

Introduction

Chlorinated organic compounds, including chloroform, are widespread contaminants in surface water and groundwater (Canosa et al., 2006, Mukca et al., 2003). In recent years, it has been found that these chlorinated organic compounds are harmful to human health (Nagano et al., 2006). Consequently, a number of special methods such as activated carbon adsorption, membrane separation technology, and photochemical methods have been studied to remove chlorinated organic compounds from water. However, these methods are limited in application in the case of advanced water treatment due to their high cost or secondary contaminants that are difficult to treat. Electrochemically reductive dechlorination (Lin and Tseng, 1999; Gregory et al., 2001; Chen et al., 2004) is suggested as a promising method for its several merits, such as rapid reaction rate, low apparatus cost, mild reaction conditions, and absence of recalcitrant secondary contaminants. The mechanism of electrochemical reductive dechlorination (Cheng et al., 2004) is known as electrocatalytic hydrogenolysis (ECH), a process in which chemisorbed hydrogens are generated at the electrode surface by electrolysis of water and then exchange with chlorine atoms. The mechanism of ECH involves several steps as described in Reactions (1)–(4) (Kulikov et al., 1996).

\[
\begin{align*}
2\text{H}_2\text{O} + 2\text{e}^- + \text{M} & \rightarrow 2(\text{H})_{\text{ads}}\text{M} + 2\text{OH}^- \quad (1)
\end{align*}
\]

\[
\begin{align*}
\text{R–Cl}_{\text{ads}} + \text{M} & \rightarrow (\text{R–Cl})_{\text{ads}}\text{M} \quad (2)
\end{align*}
\]

\[
\begin{align*}
(\text{R–Cl})_{\text{ads}}\text{M} + 2(\text{H})_{\text{ads}}\text{M} & \rightarrow (\text{R–H})_{\text{ads}}\text{M} + \text{HCl} \quad (3)
\end{align*}
\]

\[
\begin{align*}
(\text{R–H})_{\text{ads}}\text{M} & \rightarrow \text{R–H} + \text{M} \quad (4)
\end{align*}
\]

The two prominent steps in the dechlorination process of original molecules are: (1) the chemisorptions of original molecules and H_{ads} on the metal surface forming metal chloride; (2) the exchange between H_{ads} and chlorine atoms. Palladium is a favorable catalyst in the ECH process because of its good chemisorption capacity for H_{ads}.

However, many studies on the electrochemically reductive dechlorination focused on reaction mechanisms. Dechlorination efficiency is low and electrode capability is unstable. In addition, most of the previous studies on dechlorination of chlorinated organic compounds are conducted in acidic solution. The pH of surface water or groundwater is close to neutral. Therefore, it is more important to study the dechlorination of halogenated compounds in neutral aqueous solution than in acidic solution.

In this article, electrochemically reductive dechlorination was studied in neutral aqueous solution using palladium/foam-nickel (Pd/foam-Ni) and palladium/polymeric pyrrole film/foam-nickel (Pd/PPy/foam-Ni) electrodes. Chloroform was chosen as a model compound
because it is a common chlorinated disinfection by-product in water.

1 Experimental

1.1 Chemicals and materials

Experimental chemicals included acetone, alumina powder, palladium powder, sulfuric acid (98%), chloroform, pyrrole (Py), and foam-Ni. PPy film formed on the electrodes can modify the electrode surface to be more lacunaris, making the distribution of Pd microparticles more uniform and dispersive. Foam-Ni is a novel metal material that provides lacunaris surface. The aperture and surface density of foam-Ni are 90 PPI (point per inch) and 400±30 g/cm², respectively. All chemicals are analytically pure and are supplied by Beijing Reagent Co., China. Foam-Ni was provided by Shenzhen Ronglianxing Power-Material Co. Ltd., Guangdong Province, China. Solutions were prepared using Millipore-Q water with a resistivity of 18.2 MΩ.

1.2 Methods

1.2.1 Electrode pretreatment

Foam-Ni electrode was pretreated as follows: a foam-Ni plate was placed in 0.5 mol/L sulfuric acid solutions for 1 min. Then, it was placed under ultrasonic conditions in acetone and Millipore-Q water (18.2 MΩ) for 10 min each. PPy film was formed on the surface of foam-Ni plate by electrodeposition at a constant current (5.0 mA) for 20 min in 100 ml of 0.05 mol/L sulfuric acid solution containing 1 ml distilled pyrrole.

1.2.2 Electrode preparation

Pd microparticles dispersed on foam-Ni and PPy/foam-Ni supporting electrodes were prepared by electrodeposition in palladium chloride solution with a concentration of 4.0 g/L. Constant electrode surface (0.8 cm × 1.0 cm × 0.15 cm, total geometrical surface 2.0 cm² calculated using the geometrical surface) was used in the electrodeposition process. Electrodeposition current and time on foam-Ni electrode ranged from approximately 5 to 12.5 mA and from 5 to 50 min, respectively.

1.2.3 Dechlorination

Dechlorination experiments were carried out in a two-compartment cell separated by a cation-exchange membrane (Nafion-324 E.I., DuPont de Nemours & Co., USA), which was used to prevent re-chlorination of reaction products by Cl₂ generated on the anode. The catholyte was 100 ml of 0.05 mol/L sodium sulfate solution containing 2.0 mg/L chloroform solution. And the anolyte was 100 ml of 0.05 mol/L sodium sulfate solution. Pd/foam-Ni and Pd/PPy/foam-Ni electrodes were separately used as cathodes and a platinum foil was used as anode. Electrochemically reductive dechlorination current and time ranged from 0.1 to 20.0 mA and from 30 to 180 min, respectively.

1.3 Analysis methods

Electrochemical characterization of Pd/foam-Ni and Pd/PPy/foam-Ni electrodes was performed in sulfuric acid solutions by cyclic voltammetry (CV) using a Model 273A Potentiostat/Galvanostat controlled by M270 software. Working electrode was a Pd/foam-Ni plate or a Pd/PPy/foam-Ni plate (working surface 2.0 cm²). A platinum foil was used as the counter electrode and an Hg/Hg₂SO₄ saturated K₂SO₄ electrode was used as the reference electrode. The morphology of the films on electrodes was studied by scanning electron microscope (SEM) technique. The concentration of chloroform was determined by Gas chromatography (Model GC7890II, TianMei Apparatus Co. Ltd., ShangHai, China) with an FID detector, equipped with a capillary column (SE-54, 30 m × 0.25 mm × 0.25 μm, Thames Restek U.K. Ltd., UK).

2 Results and discussion

2.1 Electrode characterization

Measurements of Pd/foam-Ni electrode characteristics were carried out in sulfuric acid solution by cyclic voltammetry (CV). It is found that sulfuric acid solution turns light green or green, and some black precipitates appear in certain cases. This may be caused by the dissolution of foam-Ni or the shedding of composite Pd plate during CV scanning. When the surface coverage of the Pd microparticles is low, foam-Ni may dissolve in water. When the surface coverage of the Pd microparticles is high, the composite Pd plate may shed into water. Table 1 shows the color change of H₂SO₄ solution in CV scans for the Pd/foam-Ni electrode at different electrodepositing currents and time. It is found that H₂SO₄ solution does not change color under four conditions: 5 mA and 40 min, 7.5 mA and 40 min, 10 mA and 40 min, and 12.5 mA and 30 min. It implies that the Pd microparticles covered the foam-Ni electrode completely and firmly. Fig.1 shows the CV curves of the Pd/foam-Ni electrode under the above four conditions. In the electric potential range of −400 to −600 mV (vs. the reference electrode), evident adsorption peaks that were attributed to the adsorption/desorption transition of hydrogen on polycrystalline palladium were

<table>
<thead>
<tr>
<th>Electrodepositing current (mA)</th>
<th>Electrodepositing time (min)</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Green</td>
<td>Green</td>
<td>Green</td>
<td>Green</td>
<td>No change</td>
<td>Black deposition, green</td>
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<td>7.5</td>
<td>Green</td>
<td>Green</td>
<td>Green</td>
<td>Light green</td>
<td>No change</td>
<td>Black deposition, green</td>
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<td>10</td>
<td>Green</td>
<td>Green</td>
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<td>Light green</td>
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<td>Black deposition, green</td>
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<td>12.5</td>
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<td>Light green</td>
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observed. The maximal adsorption peak is obtained at an electrodepositing current of 10 mA and an electrodepositing time of 40 min. According to the mechanism of ECH, a high adsorption peak is favorable to electrochemically reductive dechlorination. Therefore, the electrodepositing current of 10 mA and the time of 40 min are selected as the constant parameters for the Pd/foam-Ni or Pd/PPy/foam-Ni electrode preparation.

The morphology of the films on electrodes was studied by SEM technique. Fig. 2 shows the images of the Pd/foam-Ni, Pd/PPy/foam-Ni, and PPy/foam-Ni electrodes. It is seen that the Pd microparticles disperse asymmetrically on the foam-Ni electrode with some cracks. The electrodeposition of pyrrole on the foam-Ni electrode make the Pd microparticles disperse more uniformly with a needle shape. In order to examine whether the polymeric pyrrole film altered the codeposited configuration of Pd microparticles on the foam-Ni supporting electrode, the SEM image of PPy/foam-Ni electrode was recorded and analyzed (Fig. 2c). The result shows that the polymeric pyrrole film exhibits a uniform shape of spherical apophysis on the foam-Ni surface. This configuration increases the surface area of the electrode. Compared with the Pd/foam-Ni and PPy/foam-Ni electrodes, the Pd/PPy/foam-Ni electrode shows favorable surface characteristics and thus may have a higher surface catalytic activity and a higher removal efficiency for chloroform (Fig. 2b).

2.2 Electrochemically reductive dechlorination of chloroform in neutral aqueous solution

The Pd/foam-Ni and Pd/PPy/foam-Ni electrodes that were individually prepared under the optimum conditions were used as the cathode in the process of electrochemically reductive dechlorination of chloroform in neutral aqueous solution. A constant-current (0.1, 0.5, 1, 2, 10, and 20 mA) electrolysis of 100 ml solution containing 0.05 mol/L sodium sulfate solution and 2.0 mg/L chloroform was conducted on these electrodes.

2.2.1 Removal efficiency of chloroform

Figure 3 shows the removal efficiencies of chloroform on the Pd/foam-Ni and Pd/PPy/foam-Ni electrodes at different dechlorination currents in neutral aqueous solution. The maximal removal efficiencies on the Pd/foam-Ni and Pd/PPy/foam-Ni electrodes reached 37.6% and 50.6%, respectively. It is seen that the removal efficiencies of chloroform are improved by the polymeric pyrrole film.
chlorofom on Pd/foam-Ni and Pd/PPy/foam-Ni electrodes increased with the increase of dechlorination current within the tested time range (30–180 min). In addition, the removal efficiency of chloroform on both electrodes improved with time at the same dechlorination current. According to this tendency, it is reasonably deduced that the removal efficiency of chloroform will increase further if the dechlorination time is extended. According to the theory of electrocatalytic hydrogenolysis, the electron-transfer speed increases at a higher dechlorination current, and increasing electron-transfer speed will result in increased electrode-reaction speed of active hydrogen production. This is favorable for the degradation of chloroform. However, the high electrode reaction speed will also promote the secondary reaction at the same time—the generation of hydrogen evolution. The amount of chloroform transferred from solution to the surface of electrode and the adequate adsorption of hydrogen atoms onto the electrode are the controlling steps of dechlorination reaction. The promotion of dechlorination reaction through prolonged dechlorination is only based on this reason. With prolonged dechlorination time, the chloroform molecules have enough time to be transferred and the adsorption of hydrogen atoms onto the electrode will relatively increase, which results in the effective utilization of active sites of the catalyst. However, considerable increase in dechlorination time can cause lower current efficiencies of dechlorination. Comprehensive consideration of removal efficiency and energy consumption, an appropriate dechlorination current and time are critical to dechlorination reaction.

Dechlorination results also indicate that within the wide range of dechlorination current (0.1–20 mA), Pd/PPy/foam-Ni electrode has a higher removal efficiency than Pd/foam-Ni electrode, agreeing with the SEM images. The removal efficiency of chloroform on the Pd/PPy/foam-Ni electrode is notably higher (about 10%) than that on the Pd/foam-Ni electrode at each of the electrolysis current investigated. This result demonstrates that the electrodeposition of PPY on foam-Ni electrode can modify the electrode-surface characteristics significantly and thus enhance the surface catalytic activity. The PPY film is used to separate the catalytic particles physically and to decrease their agglomeration rate. Meanwhile, the PPY film is believed to modify the electronic nature of the metal particles as well, thus affecting their chemisorptive and catalytic properties. The enhancement of surface catalytic activity by the metal-support interaction as well as the large surface area achieved with low loading levels makes such a system attractive for application in electrochemical dechlorination. So it is believed that the PPY film can provide more surface areas for depositing smaller Pd particles. Thus, the catalytic degradation capability of the Pd/PPy/foam-Ni electrode is higher.

2.2.2 Current efficiency of chloroform dechlorination

Figure 4 shows the current efficiencies on Pd/foam-Ni and Pd/PPy/foam-Ni electrodes at different dechlorination currents in neutral aqueous solution. The maximal current efficiencies on Pd/foam-Ni and Pd/PPy/foam-Ni electrodes reached 27.5% and 55.5%, respectively. It is seen that the current efficiencies on Pd/foam-Ni and Pd/PPy/foam-Ni electrodes decreased with the increase of dechlorination current at the beginning of dechlorination (0–60 min). With the prolonged dechlorination time (60–180 min), the current efficiencies tended towards stability and the decrease in amplitude is very small. In addition, the current efficiencies of Pd/PPy/foam-Ni electrode are evidently higher than those of Pd/foam-Ni electrode. When dechlorination current was 0.1 mA, the current efficiency of Pd/PPy/foam-Ni electrode was 33.0% at 180 min, which improves by almost 14% than that of Pd/foam-Ni electrode (19.03%).

With the integrated analysis of removal efficiency and current efficiency, it can be said that dechlorination current of 0.1 mA and the time of 180 min are the optimum dechlorination conditions within the range of experimental research. Removal efficiency of chloroform and current efficiency on Pd/foam-Ni electrode are 21.2% and 19.0%, respectively. And that of Pd/PPy/foam-Ni electrode are 36.8% and 33.0%. This result shows that higher removal efficiency and higher current efficiency can be obtained on Pd/PPy/foam-Ni electrode than on Pd/foam-Ni electrode. In addition, with the increase of dechlorination time, the removal efficiency of chloroform increases and the current efficiency tends toward stability on Pd/foam-Ni and Pd/PPy/foam-Ni electrodes at the same dechlorination current. According to this tendency, it is reasonably deduced that the removal efficiency of chloroform will increase further with an acceptable current efficiency if the dechlorination time is extended.

During the electrocatalytic reactions, the concentration
of $H_{\text{ads}}$ is mainly adjusted by the current or voltage of electrochemical reaction (Yoshio et al., 2003). As a heterogeneous catalyst, electrode is the reaction place of electrocatalytic hydrolysis (Sandra and Alberto, 2004). Electrode has evident activation effect toward molecules or ions participating in electrochemical reaction, which considerably reduce the reaction activation energy. Therefore, the Pd/PPy/foam-Ni electrode has favorable catalytic hydrogenation performance and certain value of application in actual engineering.

3 Conclusions

SEM images show that Pd microparticles disperse on Pd/PPy/foam-Ni electrode more uniformly with a needle shape than on Pd/foam-Ni electrode. PPy on foam-Ni electrode significantly modifies the electrode surface characteristics. Dechlorination experiments reveal that the removal efficiencies of chloroform and current efficiencies in neutral aqueous solution on Pd/PPy/foam-Ni electrode are higher than those on Pd/foam-Ni electrode, agreeing well with the SEM images. Pd/PPy/foam-Ni electrode dechlorinates chloroform in neutral aqueous solution more effectively than Pd/foam-Ni electrode because of its lacunaris and catalytic surface. Within the investigated ranges, the highest removal efficiency of 50.6% and highest current efficiency of 55.5% are obtained on the Pd/PPy/foam-Ni electrode. With the integrated analysis of removal efficiency and current efficiency, the dechlorination current of 0.1 mA and the dechlorination time of 180 min are the optimum dechlorination conditions. Under these conditions, the removal efficiency of 36.8% and the current efficiency of 33.0% are obtained on Pd/PPy/foam-Ni electrode. It is deduced that the removal efficiency of chloroform will increase further with an acceptable current efficiency if the dechlorination time is extended.

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