The Enhanced Effect of Bicarbonate Anion for the Removal of 2,4-Dichlorophenoxyacetic Acid on a Palladium/Nickel-Foam Electrode

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Abstract. Palladium/nickel-foam (Pd/Ni) electrode is used as a typical efficient electrocatalytic electrode for the removal of 2,4-dichlorophenoxyacetic acid (2,4-D) in surface water and industrial wastewater. Many researches had reported how to enhance the dechlorination efficiency of the Pd/Ni electrode by using less Pd loading. However, there are few reports of choosing a suitable electrolyte solution to improve the efficiency of dechlorination. Efforts were made in this work of the different catholyte influenced the dechlorination efficiency. The results showed the fastest removal efficiency of 2,4-D in 34 mmol/L NaHCO₃ than in 34 mmol/L NaCl, 34 mmol/L NaClO₄, 17 mmol/L Na₂SO₄ catholyte, respectively on Pd/Ni electrode with Pd loading of 0.202 mg/cm² at constant potential of -0.55 V (vs saturated calomel electrode). The dechlorination current efficiency (CE) was 20.5% in the 34 mmol/L NaHCO₃ catholyte more than three times that in 17 mmol/L Na₂SO₄ catholyte for that HCO₃⁻ was the most likely source of protons for adsorbed active hydrogen (H*) in Pd active centers.

Keywords. Pd/Ni electrode, 2,4-dichlorophenoxyacetic acid, removal efficiency

1. Introduction

Chlorinated aromatic compounds in rivers, lakes and ground waters by pesticides are hazardous pollutants in the environment which have been listed as key pollutants by the U.S. Environmental Protection Agency for Toxicity to humans and organisms [1, 2]. They are present in effluents from agricultural activities because of its low price and good selectivity, 2,4-D is used to remove various weeds in crops [3]. However, 2,4-D is a kind of pollutant that is difficult to biodegrade, and it exists in rivers, lakes and ground waters, soil resources and agricultural products for a long time [4, 5]. Therefore, 2, 4-D is considered to be a pollutant harmful to public health, and it is necessary to study how to remove it.

Thus the reductive dechlorination treatment has become a research hotspot. In this dechlorination process, only the chlorine atom is selectively replaced by hydrogen, and the other structure of the reactant remains unchanged. The application of Pd/Ni electrode

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in reductive dechlorination faced same difficult problem such as the low current efficiency (CE) of dechlorination, the low removal efficiency, the large amount of precious metal palladium, the large power consumption, and so on [6]. In the present work the electrode studied by the group of Song [7], the removal efficiency of 2,4-D was as high as 98% and the maximum CE was 14% after 180 min dechlorination reaction controlled the current density of 1.5 mA/cm². The research group of Xu [6, 8] researched the dechlorination of 2,4-D using nanosized TiN doped Pd/Ni electrode achieved nearly 100% removal of 2,4-D (0.226 mmol/L) after 120 min dechlorination reaction controlled the current density of 1.667 mA/cm². A lot of work on electrode preparation have done by previous researchers in order to reduce energy consumption, improve dechlorination efficiency, and reduce palladium loading. But there are very little investigatory about the different electrolyte solutions impact on the dechlorination efficiency. In this study, trying to choose appropriate electrolyte solutions increase dechlorination efficiency at lower reduction potential and smaller palladium loading.

In this study, a novel electrolyte solution of NaHCO₃ for the electrochemical reductive dechlorination of 2,4-D on palladium/nickel-foam (Pd/Ni) electrode was introduced. Contrast tests found that the dechlorination efficiency in NaHCO₃ catholyte was much higher than in the NaCl, NaClO₄ or Na₂SO₄ catholyte which has achieved an unprecedented high dechlorination efficiency characterized by low energy consumption, the least Pd loading, the simplest electrode preparation process and the highest removal efficiency compared with previous researches [7, 8].

2. Experimental

2.1. Chemical Reagent

Palladium chloride (PdCl₂; ≥99.97%) were purchased from Aladdin Reagent Co., Ltd., China. Nafion-117 membranes were purchased from Du Pont de Nemours & Co., USA. All the other chemicals such as *o*-chlorophenoxyacetic acid (*o*-CPA), *p*-chlorophenoxyacetic acid (*p*-CPA), phenoxyacetic acid (PA) and so on were purchased from Huadong Medical Co., Ltd., China. Ultrapure water generated by a Millipore Milli-Q system with a specific conductivity ≥18.2 mΩ/cm was used all the experiments in the paper. Methanol (HPLC-grade) used as the fluidity of high performance liquid chromatography (HPLC) were bought from the Aladdin Reagent Co., Ltd., China.

2.2. Electrode Preparation

The cleaning method of the foamed nickel substrate (with the size of 20 mm × 20 mm × 1.2 mm) (the pore density of 110 ppi) was described in the previously published paper [7]. Pd/Ni electrode was prepared through the displacement reaction. Put the cleaned nickel foam into 40 mL of 0.5 mmol/L PdCl₂ and 34 mmol/L NaCl aqueous solution, and then shook it in an oscillator at a unchanged temperature of 30°C and a unchanged speed of 160 rpm for 90 min until the yellow reaction solution became colorless. Removed the Pd/Ni electrode from the faded solution, wash it with ultrapure water three times and dry it with high-purity nitrogen, then it could be used for dechlorination experiments. The electrochemical dechlorination reaction is a three-electrode electrolysis system: counter electrode(platinum), working electrode (Pd/Ni) and reference electrode (saturated calomel electrode (SCE)), respectively.

2.3. Batch Experiments

The 2,4-D reductive dechlorination experiments were carried out in a customized H-type cell located in an unchanged temperature water bath at the temperature of $25 \pm 0.1^\circ\text{C}$. H-type cell consisted of cathode and anode with a volume capacity of 100 mL and 50 mL, respectively. For every experiment, 30 mL NaHCO_3 (34 mmol/L) and 2,4-D (0.226 mmol/L) catholyte was added to the cathodic cell, which was stirred with a magnetic bar; 25 mL Na_2SO_4 (17 mmol/L) aqueous solution was added to the anode cell in order to provide a harmless electrolysis reaction ($\text{H}_2\text{O} - 2\text{e} \rightarrow (1/2 \text{O}_2) + 2\text{H}^+$). The comparative experiment of different catholyte were carried out, used the other three catholyte such as NaCl (34 mmol/L), NaClO_4 (34 mmol/L) or Na_2SO_4 (17 mmol/L) to replace NaHCO_3 (34 mmol/L). The working and reference electrodes were immersed in the cathodic cell, and the counter electrode was placed in the anode cell. All electrochemical experiment potential values were relative to SCE in this paper. All constant potential dechlorination experiments were carried out at -0.55 V. Both the dechlorination experiments and the Linear sweep voltammetry experiment were carried out at $298 \pm 1 \text{ K}$ using the CHI-660D electrochemical workstation made in CH Instruments, Inc. Each 2,4-D dechlorination experiment was reacted for 180 min, and 0.4 mL samples were taken from the cathodic cell at a certain time intervals for HPLC testing.

2.4. Analytical Methods

The content of palladium in the displacement solution were analyzed by an inductively coupled plasma optical emission spectrometry (ICP-OES), optima 7000DV Perkin-Elmer Instruments Inc. The concentrations of reactants and products such as 2,4-D, *o*-CPA, *p*-CPA and PA were detected by an HPLC, Agilent 1260 series instruments. Detailed detection methods and the calculation method of CE for the 2,4-D electrochemical reductive dechlorination could refer to [7].

3. Results and Discussion

3.1. The Pd Loading on the Ni Electrode

The palladium loading of Pd/Ni electrode was detected by ICP-OES, and Pd loading on electrode was 2.02 mg. Divide the total amount of palladium loading by the total area of the two sides of the nickel foam electrode by 10 cm^2 , and Pd loading of the Pd/Ni electrode was calculated to be 0.202 mg/cm^2 , which was much lower than that of Pd/Ni electrode prepared by electrochemical pulse method (0.668 mg/cm^2 and 3.4 mg/cm^2 , respectively) [7, 8]. The electrodes have the least amount of noble metals and thus greatly reduced the cost of the electrode.

3.2. The 2,4-D Removal Experiments in Different Catholyte by Pd/Ni Electrode

The 2,4-D removal efficiency experiments were carried out on the Pd/Ni electrode at constant potential of -0.55 V in four different catholytes. In figure 1, the concentration of 2,4-D decreased with the increasing dechlorination reaction time in four different catholyte, in particular displayed that 2,4-D was completely removed in the NaHCO_3 catholyte after 180 min of reaction. At this time, only 74.8-55.6% of 2,4-D were removed

in the other catholyte. The enhanced electrochemical dechlorination effect of bicarbonate anion can be speculated from the experimental results.

Figure 1. Time dependence of 2,4-D concentration in 34 mmol/L NaHCO₃, 34 mmol/L NaCl, 34 mmol/L NaClO₄, 17 mmol/L Na₂SO₄ catholyte, respectively on Pd/Ni electrode at constant potential of -0.55 V.

3.3. Dechlorination Activity and Selectivity

The changes in the amount of reactants, products and carbon mass with time during the reductive dechlorination of 2,4-D in 34 mmol/L NaHCO₃, 34 mmol/L NaCl, 34 mmol/L NaClO₄, 17 mmol/L Na₂SO₄ catholyte respectively on the Pd/Ni electrode were illustrated in figure 2. During the reaction, as the reaction time increased, the reactants continued to decrease, and the products of *p*-CPA, *o*-CPA and PA, were produced continuously. In addition, the total carbon content maintained at 94%-99%, only a small amount of *p*-CPA produced, and the main product was PA. An obvious result of the concentration of *o*-CPA was always higher than that of *p*-CPA during the reductive dechlorination, which was consistent with the results of previous studies, interpreted as the chlorine atom located in the para-position of 2,4-D was easy to be substituted than it in the ortho-position by active hydrogen (H*) as a function of the steric hindrance formed by the adjacent functional groups (-OCH₂COOH) of 2,4-D [9-11].

In figure 3, In the four different catholytes, the reductive reaction of 2,4-D is a pseudo-first order kinetic model, which can be shown as equation (1).

$$-\ln(C_t/C_0) = k t + b \quad (1)$$

where k is the observed rate constant (min^{-1}); t is the reaction time (min); b is a constant, and C_t and C_0 are the 2,4-D concentrations (mmol/L) at times of $t = t$ and $t = 0$, respectively. The k was 0.1375 min^{-1} in 34 mmol/L NaHCO₃ catholyte much larger than in other three catholyte. The enhanced dechlorination effect in 34 mmol/L NaHCO₃ catholyte can be further proved by hydrogen evolution reaction (HER). As the LSV curves shown in figure 4, among the four electrolytes, the rate of HER was the fastest in 34 mmol/L NaHCO₃ electrolyte solution. For the HER is a side reaction in the dechlorination of 2,4-D. Although it was not sufficient to infer the dechlorination rate based on the HER rate, it could provide some insights about the dechlorination effect. The faster the HER rate, the more H* was produced. The more production of H* were considered to be a key factor for effective dechlorination treatment [7, 12, 13]. In the NaHCO₃ electrolyte, the HER reaction was fastest, indicating the most H* were

produced for the dechlorination, which resulted to significantly improving the dechlorination efficiency of 2,4-D.

Figure 2. The changes in the amount of reactants, products and carbon mass with time in (a) 34 mmol/L NaHCO_3 , (b) 34 mmol/L NaCl , (c) 34 mmol/L NaClO_4 and (d) 17 mmol/L Na_2SO_4 catholyte on Pd/Ni electrode at constant potential of -0.55 V.

3.4. Enhanced Reductive Dechlorination Mechanism

CE is closely related to the number of H^* consumed during the removal of 2,4-D. As displayed in figure 5, with the reaction proceeded, the CE of reductive dechlorination of 2,4-D increased first and then decreased, the maximum CE value was 20.5% appeared in the reaction for 30 min in 34 mmol/L NaHCO_3 . However, the maximum CE value was about 6.2-8.2% at 60 min in 34 mmol/L NaCl , 34 mmol/L NaClO_4 , 17 mmol/L Na_2SO_4 catholyte, respectively.

In the first 30 minutes, H^* was mainly used to reach the balance between the hydrogen in the metal hydride phase and the hydrogen in the solid solution phase; then, with the decrease concentration of 2,4-D would reduce the consumption of H^* , which caused the CE to gradually decreased [14]. In the other three catholyte, the amount of H^* was relatively smaller, so the balance between the metal hydride phase and the solid solution phase arrived later, which could be explain by the CE value was smaller than that of in NaHCO_3 catholyte, the maximum CE was obtained delayed at 60 min. Therefore, it was appropriate to infer the 2,4-D removal efficiency improved by bicarbonate anion.

In figure 6, the values of pH in the catholyte with time were carried out. The initial pH value was 3.95, due to the acidity of 2,4-D in 34 mmol/L NaCl , 34 mmol/L NaClO_4 and 17 mmol/L Na_2SO_4 catholyte. As the reaction proceeds, the pH rose rapidly in catholyte at the first 2 min and then slightly increased about 12.00. However, there was different result in 34 mmol/L NaHCO_3 catholyte, the pH value was varied within 8.76-10.02. A low pH value was favorable to dechlorination in previous studies [15]. So the

accelerate dechlorination reaction maybe for bicarbonate anion can stabilize the pH in the NaHCO_3 catholyte.

Figure 3. Rate constant of 2,4-D dechlorination in 34 mmol/L NaHCO_3 , 34 mmol/L NaCl , 34 mmol/L NaClO_4 and 17 mmol/L Na_2SO_4 catholyte at constant potential of -0.55 V.

Figure 4. Linear sweep voltammetry curves in 34 mmol/L NaHCO_3 , 34 mmol/L NaCl , 34 mmol/L NaClO_4 and 17 mmol/L Na_2SO_4 with 0.226 mmol/L 2,4-D electrolyte solution.

Figure 5. Current efficiency as functions of dechlorination time in 34 mmol/L NaHCO_3 , 34 mmol/L NaCl , 34 mmol/L NaClO_4 , 17 mmol/L Na_2SO_4 catholyte, respectively at constant potential of -0.55 V.

Figure 6. pH change as function of dechlorination time in 34 mmol/L NaHCO_3 , 34 mmol/L NaCl , 34 mmol/L NaClO_4 , 17 mmol/L Na_2SO_4 catholyte, respectively at constant potential of -0.55 V.

The overall reaction mechanism of electrochemical removal of 2,4-D on Pd/Ni cathode had been researched in [6, 14, 16]. In this work, the reduction dechlorination mechanism may be inferred the following reaction pathways, which expressed in equations (2)–(5):

where M-Cl are chlorinated reactants, H^*_{ads} is adsorbed atomic, AS is the active sites on Pd/Ni electrode.

4. Conclusions

The different dechlorination efficiencies were compared in the four different cathode solutions for 2,4-D reduction with Pd/Ni electrode manufacture by replacement deposition method. The 2,4-D was completely removed for no detectable by HPLC after 180 min of reaction in the 34 mmol/L NaHCO₃ catholyte on Pd/Ni electrode at the constant potential of -0.55 V. The maximum CE of reductive dechlorination was 20.5% reached at 30 min. The removal efficiency and the maximum CE in the NaHCO₃ catholyte much larger than in the other catholytes. The experiments of enhanced reductive dechlorination mechanism indicated that more H⁺ were generated to participate the dechlorination reaction in NaHCO₃ catholyte. This accelerated reaction mechanism and the application of dechlorination to other pollutants are for further study.

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