


## Article

# The Preparation of Pd/Foam-Ni Electrode and Its Electrocatalytic Hydrodechlorination for Monochlorophenol Isomers

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**Abstract:** Noble metal palladium modified foamed nickel electrode (Pd/foam-Ni) was prepared by electrodeposition method. The fabricated electrode showed better catalytic performance than the Pd/foam-Ni prepared by conventional electroless deposition. The catalysts were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). Electrocatalytic activity of the Pd/Ni was studied for the hydrodechlorination of monochlorophenol isomers. The Pd/Ni exhibited good catalytic activity for 3-chlorophenol (3-CP). Complete decomposition of chlorophenol isomers could be achieved within 2 h, and the hydrodechlorination process conformed to the pseudo-first-order kinetic model. It showed a supreme stability after recycling for 5 times. The Pd/Ni exhibited a promising application prospect with high effectiveness and low Pd loading.

**Keywords:** Pd nanoparticles; electrodeposition; nickel foam; hydrodechlorination (ECH); monochlorophenol isomers; kinetic

## 1. Introduction

Chlorinated organic compounds, persistent organic pollutants, are widely used in dyes, drugs, pesticides/herbicide precursors, and in the wood preservatives industry [1–3], and have been listed as a particular group of priority toxic pollutants by the United States Environmental Protection Agency in the Clean Water Act and by the European Decision 2455/2001/EC [4]. Chronic exposure to CPs can damage the liver, kidney, and nervous systems [5], and the chlorine atom in the CP structure is considered to be the main cause of its toxic properties [6]; in certain conditions, CPs can even react to produce more toxic carcinogens to threaten the health of human beings [7]. Recently, several methods, such as physical, chemical, biological, and electrochemical have been employed in the CP dechlorination process. Among the methods proposed for the destruction of CPs, electrocatalytic hydrodechlorination (ECH) is considered to be a promising approach, due to its high-energy efficiency,

low apparatus cost, rapid reaction rate, mild reaction conditions, and not producing more toxic compounds than the original chlorinated organic compounds [8–10].

The mechanism of ECH is that the chemisorbed hydrogen atoms ( $H_{ads}$ ) generated from electroreduction of  $H_2O$  or  $H^+$  will exchange chlorine in organic compounds [11], thereby decreasing the toxicity. It should be noted that catalysts play an important role in hydrodechlorination, which will affect the amount of active hydrogen. Recently, a great variety of metal, such as Pd, Ag, Ni, and Cu, as well as their alloys, have been reported to being used in dehalogenation applications of organic compounds [12–16]. Among them, Pd was considered as the most ideal catalyst, due to its high efficiency in  $H^*$  and maintenance via adsorption of  $H^*$  on the Pd surface and absorbed  $H^*$  into the Pd crystal lattice, forming Pd hydride [17]. Cui et al. [18] reported that palladized multiwalled carbon nanotubes electrode demonstrated better electrocatalytic activity for ECH of pentachlorophenol.

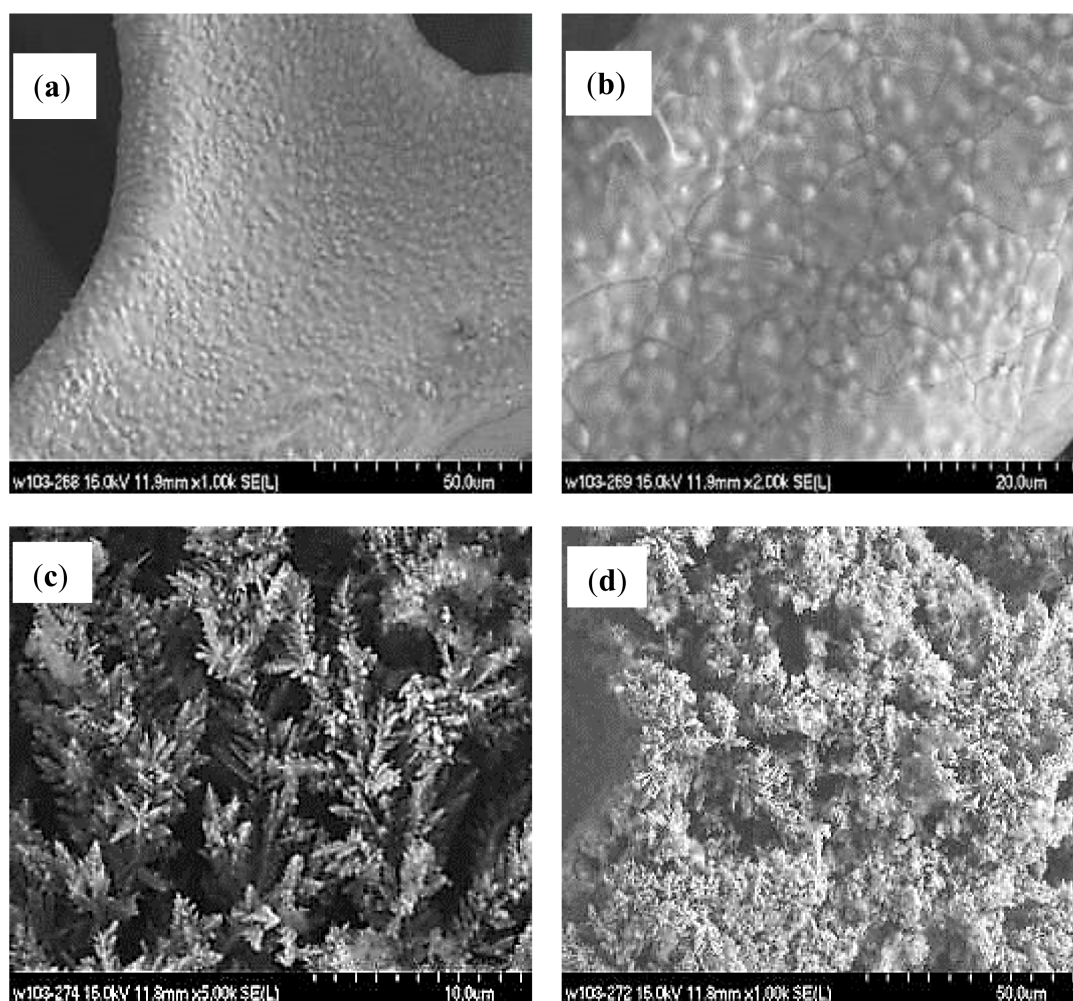
Nickel foam, a commercial material with desirable three-dimensional network structure [19], high catalytic activity and ductility [20], and excellent electrical conductivity [21], has been considered as an ideal electrode material. Thus, the combination of Ni foam and palladium nanocatalyst can show better catalytic performance toward hydrodechlorination of CPs. In recent years, a number of researchers have been carrying out investigations into the hydrodechlorination of palladium-based catalysts on CPs and their isomers. Xia et al. [22] reported that the CPs could undergo complete hydrodechlorination with 5% Pd/carbon catalyst at room temperature, and the C–Cl bond in the ortho-CP was the most difficult one to hydrodechlorination. Xia et al. [23] studied the influence of ions on the hydrodechlorination of 4-CP in liquid phase over 5% Pd/C catalyst. Results indicated that some transitional metal ions such as  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Ni^{2+}$ , and  $Pb^{2+}$  etc. would reduce the activity of Pd/C, thereby leading a low hydrodechlorination efficiency. However, to the best of our knowledge, no research focused on the ECH of CP isomers by Pd/foam-Ni prepared by galvanostatic electrodeposition. In addition, systematic studies on the electrochemical hydrodechlorination of CP isomers by Pd/Ni have not yet been reported.

Herein, we prepared the Pd/foam-Ni cathode by galvanostatic electrodeposition, which exhibited a high catalytic and stability property. The SEM and TEM images indicated that Pd nanoparticles are uniformly grown on the surface of the foam electrodes in the form of dendrites with the average diameter of 12 nm. The result of the XPS showed that Pd mainly exists in the form of  $Pd^0$  on Pd/foam-Ni electrodes. Moreover, the series of monochlorophenols were used as model pollutants, and relevant investigations of the ECH by Pd/foam-Ni were conducted.

## 2. Results and Discussion

### 2.1. Morphology Analysis

SEM and energy X-ray detector (EDX) were conducted to investigate the surface morphology and the nature of elements of the electrodes. The SEM images in Figure 1 revealed that the bare Ni foam Figure 1a,b exhibited a three-dimensional scaffold structure with a uniform convex surface, which improved the active surface area of the electrodes. However, after the loading of Pd, the Pd nanoparticles are uniformly grown on the surface of the foam electrodes in the form of dendrites Figure 1c,d. The surface area of the Pd/foam-Ni was  $5.6\text{ m}^2\text{ g}^{-1}$ , larger than that of the foam nickel substrate ( $1.2\text{ m}^2\text{ g}^{-1}$ ).



**Figure 1.** SEM micrographs of (a) foam nickel substrate (1000 $\times$ ), (b) foam nickel substrate (2000 $\times$ ), (c) Pd/Ni electrode (5000 $\times$ ) and (d) Pd/Ni electrode (1000 $\times$ ).

The energy dispersive X-ray detector (EDX), as shown in Figure 2, confirmed the existence of palladium and nickel elements, which indicates that palladium is successfully deposited on the nickel foam substrate. The deposition mechanism of Pd electrodeposition process included instantaneous nucleation and three-dimensional growth [24,25]. In view of this, the dendritic distribution of Pd particles indicates that palladium is preferentially grown in certain specific directions or locations on nickel foam. The palladium nucleation may be on an irregular ground, such as the edge of the electrode or the raised surface on the surface of the deposited substrate. The nucleation of Pd may have occurred on an irregular place of the deposited substrates, such as the edge, or tops of the electrode substrates [26–28]. Hence, the key factor in the entire deposition process is the nucleation site, which largely determined the morphologies of palladium nanoparticles.

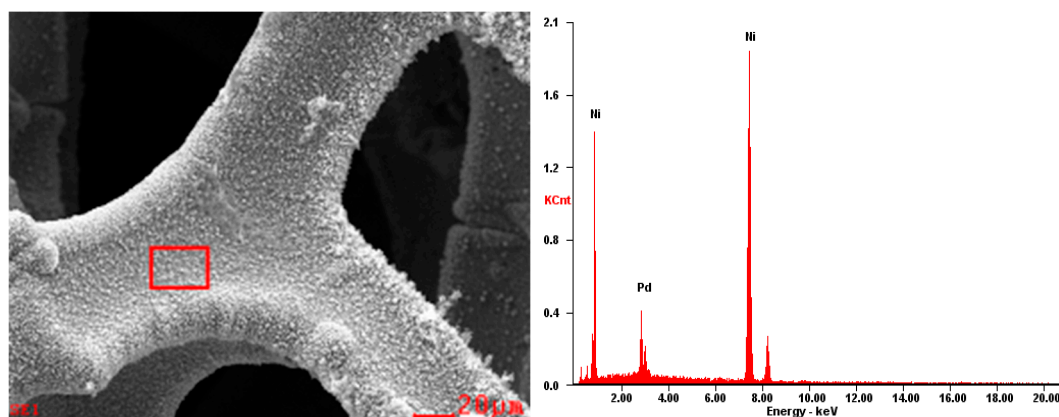


Figure 2. EDX elemental analysis of Pd/Ni electrode.

## 2.2. XRD and XPS Analysis

XRD pattern of the prepared electrodes was shown in Figure 3. For Pd/foam-Ni electrode, diffraction peaks at  $2\theta = 44.160^\circ$ ,  $51.520^\circ$ , and  $76.060^\circ$  can be assigned to the (111), (200), and (222) crystal planes of nickel foam, respectively. The other five diffraction peaks at  $39.840^\circ$ ,  $46.200^\circ$ ,  $67.520^\circ$ ,  $81.080^\circ$ , and  $86.000^\circ$  can be indexed to the (111), (200), (220), (311), and (222) faces of Pd, respectively, confirming that Pd mainly exists in the form of  $\text{Pd}^0$  on Pd/foam-Ni electrodes.

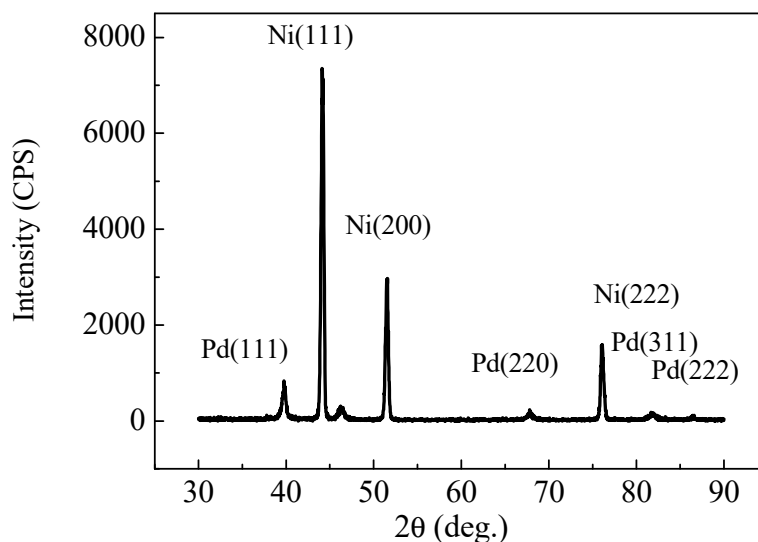
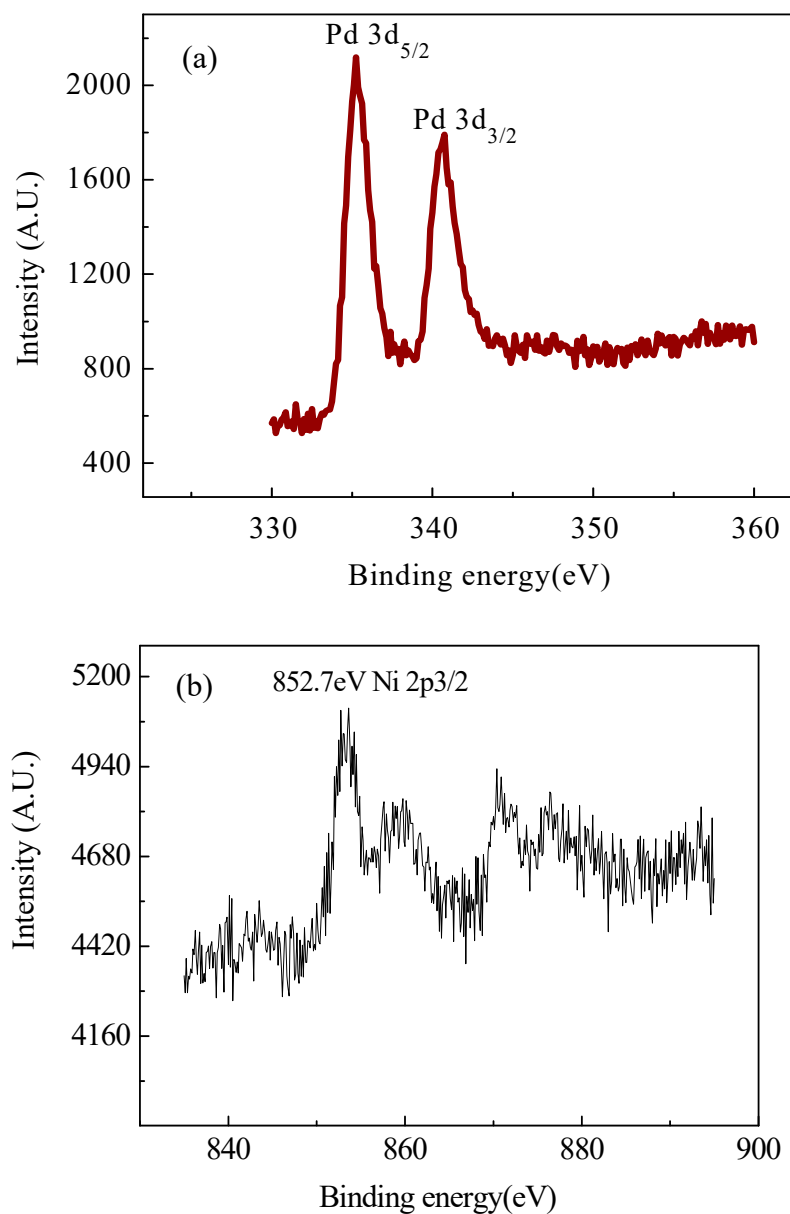


Figure 3. XRD patterns of Pd/foam-Ni electrode.

To further evaluate the surface state of the fabricated electrodes, the XPS measurement was conducted, as shown in Figure 4. Obviously, the results confirmed the presence of Pd, Ni, C, N in electrodes. Moreover, the two peaks on the XPS image (Figure 4a) respectively located at 335.2 eV and 340.7 eV, correspond to the  $\text{Pd}^0$   $3d_{5/2}$  and  $3d_{3/2}$ , indicating that  $\text{Pd}^0$  was the dominant component. Also, it can be observed in Figure 4b that the binding energies of  $\text{Ni}2p_{3/2}$  is 852.7 eV, which confirmed that Ni exists in the zero valence state in the electrodes.



**Figure 4.** XPS of Pd/Ni electrode: (a) Pd 3d core-level, (b) Ni 2P core-level.

### 2.3. TEM Analysis

TEM, high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) measurements were conducted to investigate the morphology of palladium on the electrode. Figure 5a (TEM of Pd/Ni electrode) revealed that Pd particles have a good dispersity with an average diameter of 12 nm. Moreover, the SAED patterns (inset in Figure 5a) of Pd (Pd/Ni) confirmed that palladium grains had growth maturation. The HRTEM image of Pd/Ni electrode was shown in Figure 5b. The lattice spacing of Pd is determined to be 0.227 nm, corresponding to the (111) plane of palladium, indicating that Palladium was successfully deposited on the prepared substrate, which was in accordance with the above results.



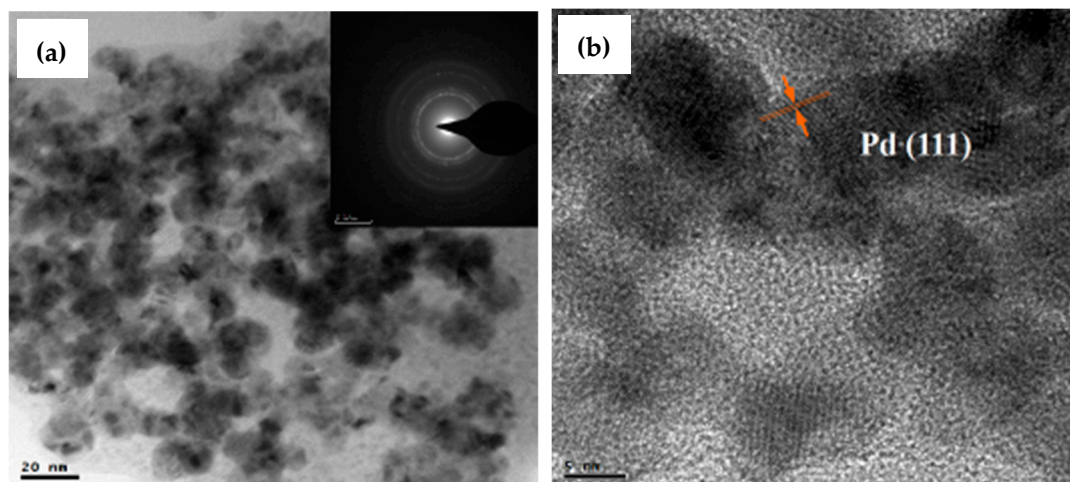


Figure 5. TEM (a) and HR-TEM (b) of Pd/Ni electrode.

#### 2.4. ECH of Monochlorophenol Isomers

The electrocatalytic hydrodechlorination of a  $0.5 \text{ mmol L}^{-1}$  solution of CP isomers in  $0.05 \text{ mol L}^{-1}$   $\text{Na}_2\text{SO}_4$  was studied. As shown in Figure 6a, similar removal results were obtained in the hydrodechlorination process. In the first 60 min, the cathode showed a high catalytic performance for 2-CP and 3-CP, higher than that of 4-CP. Then, the removal efficiency of the three CPs was basically the same. The completely degradation of CP isomers could be achieved after 80 min of electrochemical reaction. The current efficiency of monochlorophenols in the ECH is shown in Figure 6b. For all monochlorophenols, the relevant current efficiency increased rapidly in the first 40 min, and then decreased with time. The maximum was reached at the 40th minute within the range of 25–29%. After a period of hydrodechlorination, the concentration of the target contaminant was greatly reduced with the rapid removal of CPs. Therefore, as the speed of the reaction decreases, the amount of pollutants removed during the same time period decreases, resulting in a decrease in the current efficiency.

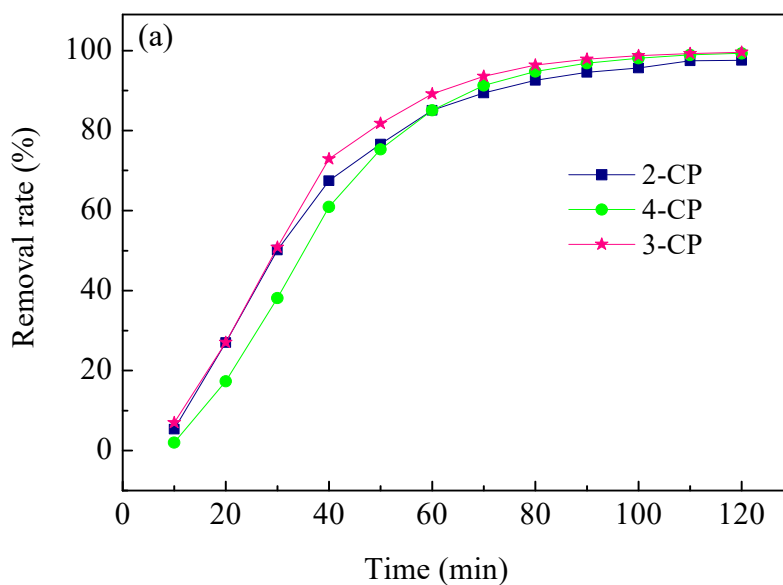
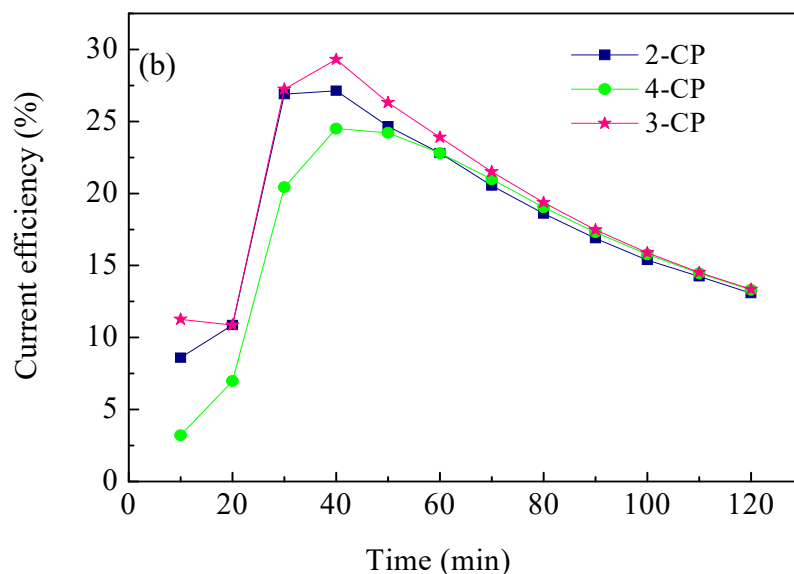
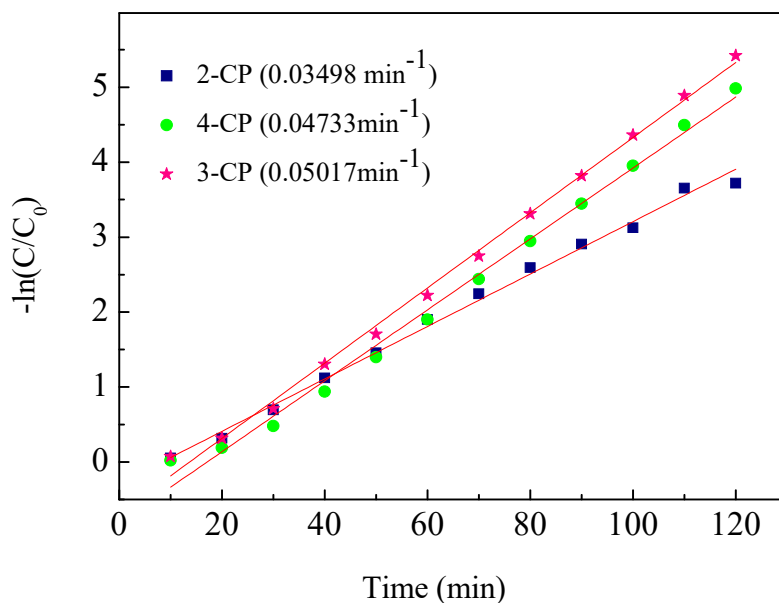


Figure 6. Cont.

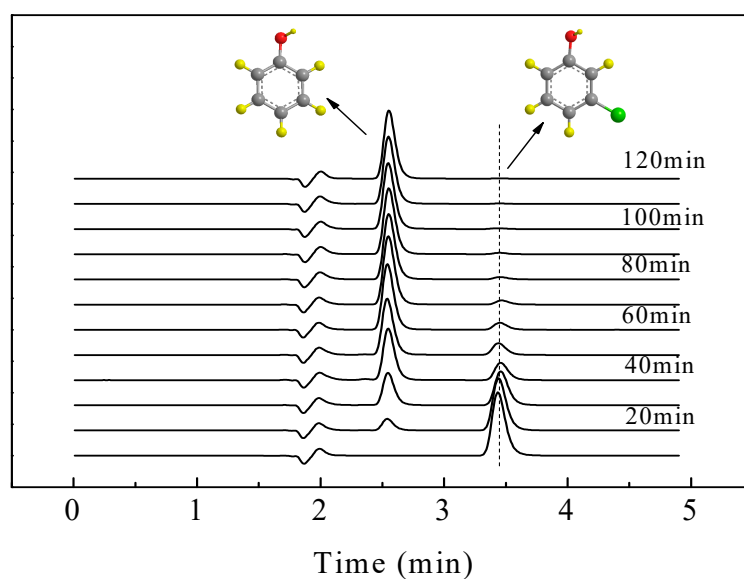


**Figure 6.** The removal rate (a) and current efficiency (b) as a function of time during the electrocatalytic hydrodechlorination (ECH) of monochlorophenols.

To further investigate the kinetics of the three kinds of monochlorophenols, the electrocatalytic data was fitted. As can be seen in Figure 7, the hydrodechlorination reaction of the CP isomers satisfied with the quasi-first-order reaction dynamics model well and the rate constant followed the following order: 3-CP ( $0.05017 \text{ min}^{-1}$ ) > 4-CP ( $0.04733 \text{ min}^{-1}$ ) > 2-CP ( $0.03498 \text{ min}^{-1}$ ), indicating that for monochlorophenols, the position of the chlorine on the phenyl ring relative to the hydroxyl group will affect the hydrodechlorination effect. The result also reflected that 3-CP was the most susceptible to degradation, while the 2-CP was the most difficult one. The probable reason was that *o*-chlorophenols were more stable than other CP isomers as a result of intramolecular hydrogen bonding [29]. Therefore, it is more difficult to be attacked by atomic hydrogen. Another reason may be attributed to the more pronounced steric hindrance effect of *o*-chlorophenols. In contrast to 2-CP, 3-CP has the highest rate constant in the reaction, which indicated that 3-CP was more conducive to being attacked by atomic hydrogen. Further, it was found that for monochlorophenols, phenol was the product in electrocatalytic hydrodechlorination. The chlorine atom was first attacked by active hydrogen, and then the chlorine atom, being replaced by active hydrogen, entered the solution as chloride ions. Taking 3-CP as an example, the prepared samples were sampled at intervals of 10 min. The chromatogram of the measured liquid was shown in Figure 8. As can be seen, the retention time of phenol and 3-chlorophenol were 2.552 and 3.449 min, respectively.



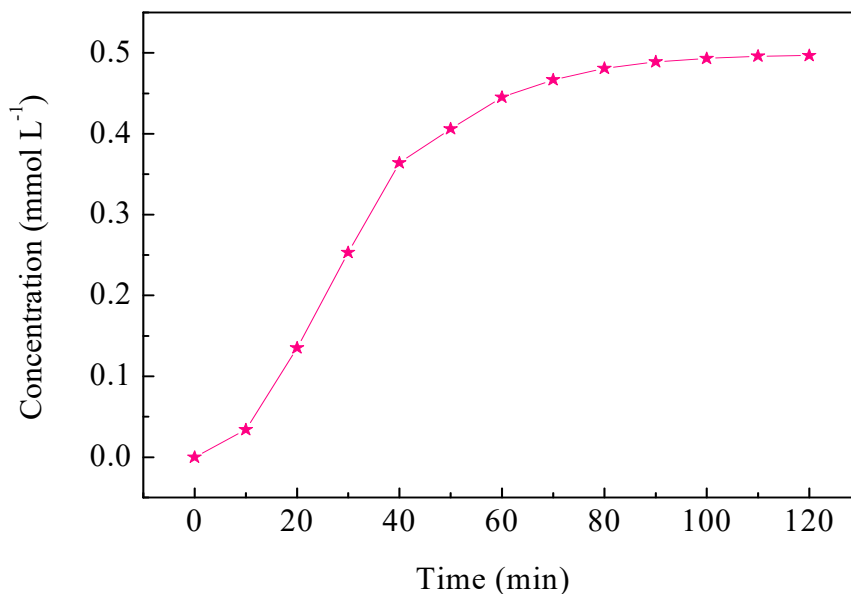
**Figure 7.** Kinetics during the ECH of 0.5 mmol L<sup>-1</sup> CP isomers.



**Figure 8.** HPLC spectra of sample solution with different reaction time during the ECH of 3-CP.

Meanwhile, the ion spectroscopy (IC) was carried out to detect the chlorine ions of 3-CP in the electrochemical reaction. Figure 9 plotted the content of chloride ions changed with time in the electrocatalytic reaction. Results indicated that the concentration of the chlorine ion increased gradually with time going. It was calculated that the content of chlorine ions was consistent with the removal of 3-CP and chlorine atom was conserved throughout the electrochemical reduction system.

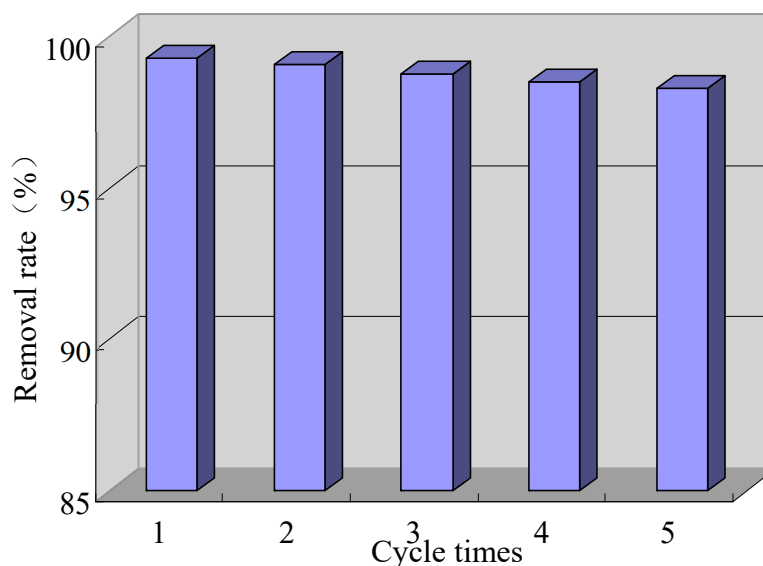




**Figure 9.** The variation of concentration of chlorine with time in the ECH of 3-CP.

### 2.5. Stability of Composite Electrode

To evaluate the stability of the prepared electrodes, five cycles of experiments for the electrocatalytic hydrodechlorination of 3-CP ( $0.5 \text{ mmol L}^{-1}$ ) were conducted under optimized conditions. As seen from Figure 10, there was a slight decline in removal efficiency, Pd/foam-Ni cathode exhibited a higher stability and catalytic activity with an average removal efficiency of 97%, which would have a good application prospect.



**Figure 10.** Effect of repeat use of Pd/Ni on the removal of 3-CP.

## 3. Materials and Methods

### 3.1. Reagents and Materials

Experimental chemicals include 2-CP, 3-CP, 4-CP, sodium chloride (NaCl), Pd chloride ( $\text{PdCl}_2$ ) powder, sodium sulphate anhydrous ( $\text{Na}_2\text{SO}_4$ ), were analytical reagent grade and purchased from Sinopharm Group Co., Ltd. (Shanghai, China). The nickel foam (99.9%, Pores Per Linear Inch: 110)

were from Changsha Liyuan New Material Co., Ltd. (Changsha, Hunan, China). and the saturated calomel electrode was from Shanghai REX Instrument Factory (Shanghai, China). The proton exchange membrane was Nafion-117.

### 3.2. Method

#### 3.2.1. Preparation of Pd/Ni Cathode

The pretreatment of foam nickel (30 mm × 10 mm × 1 mm) was realized according to our previous work [30]. The Pd/Ni was prepared through the constant current electrodeposition. Ni foam and platinum foil (20 mm × 10 mm × 0.2 mm) served as the cathode and the anode, respectively. Finally, the pretreated electrode substrate was immersed into the aqueous solution composed of 1 mmol L<sup>−1</sup> of PdCl<sub>2</sub> and 3 mmol L<sup>−1</sup> of NaCl at 6 mA for 2 h, followed by continuous stirring at 40 °C. The solution became clear and transparent after electrodeposition of Pd nanoparticles.

#### 3.2.2. Characterization of Pd/Ni Electrode

The surface morphologies of Pd/Ni electrode and foam nickel substrate were analyzed by scanning electron microscope (SEM, Quanta 200F, FEI Company, Hillsboro, OR, USA). The crystalline structure of the electrode was performed using X-ray diffractometer (XRD, D/max-IIIIB; Rigaku Company, Akishima, Tokyo, Japan), with Cu K $\alpha$  radiation ( $k = 1.54060$  Å; scanning rate: 5°/min). X-ray photoelectron spectroscopy (XPS) was carried out to analyze the element valence using a PHI 5700 ESCA apparatus (Perkin-Elmer, Waltham, MA, USA) with Al K $\alpha$  X-ray source. The spectra were corrected using the C1s line at 284.6 eV. The amount of chloride ions was measured by a Dionex 4500i Ion chromatography (Sunnyvale, CA, USA). The Brunauer-Emmett-Teller (BET) surface area was conducted on Autosorb-iQ (Quantachrome, Boynton Beach, FL, USA). TEM images were taken on a Tecnai G<sup>2</sup>-F30 TEM microscope (FEI Company, Hillsboro, OR, USA) with accelerating voltage of 120 kV. SAED and HRTEM were carried out to evaluate the crystal size and structure of the Pd deposits. The TEM samples were prepared by scraping off the Pd nanoparticles of the prepared electrode with a blade, and then the particles were placed in absolute ethanol for ultrasonic dispersion for 15 min. A small amount of the supernatant was taken with a syringe and dispersed on a microgrid copper mesh, followed by being dried under an infrared lamp to being mounted into the instrument.

#### 3.2.3. ECH of Monochlorophenols

The hydrodechlorination of chlorophenols was carried out on a two-compartment cell separated by a Nafion-117 cation-exchange membrane, which was to prevent Cl<sup>−</sup> flowing into the anode to generate Cl<sub>2</sub>. Pd/Ni was used as the working electrode, Pt sheet was used as the counter electrode. The cathode compartment contained 50 mL of aqueous solutions of Na<sub>2</sub>SO<sub>4</sub> (0.05 mol L<sup>−1</sup>) and CPs (0.5 mmol L<sup>−1</sup>); the anodic compartment held 50 mL of a 0.05 mol L<sup>−1</sup> Na<sub>2</sub>SO<sub>4</sub> aqueous solution. The prepared cathode was immersed in the catholyte, and the reaction was carried out with continuous stirring. All electrochemical experiments were conducted under a constant current of 5 mA for 2 h at 40 °C. The concentration of CPs was monitored by the High Performance Liquid Chromatograph (HPLC, Shimadzu LC-10A, Tokyo, Japan) with a Zorbax SB-C18 column (4.6 mm × 150 mm × 5  $\mu$ m) and column temperature of 30 °C. The detector used was a UV detector and ultraviolet absorbance was 254 nm. Aliquots (10  $\mu$ L) were withdrawn from the catholyte at 20 min intervals with a microsampler. The flow rate and the mobile phase of methanol/water was 1.0 mL/min and (v/v = 70:30), respectively. It was noted that the mobile phase should be sonicated to remove dissolved gas.

## 4. Conclusions

Pd/Ni electrode were successfully prepared by electrodeposition for the ECH of monochlorophenol isomers. Compared with the Pd/foam-Ni prepared by conventional electroless deposition, the electrode exhibited excellent electrocatalytic performance with low Pd loading [31].

The palladium particles displayed a dense dendritic for the electrode with an average diameter of 12 nm. The results from XRD and XPS indicated that Pd is modified in the form of Pd<sup>0</sup> on the surface of the electrode. The hydrodechlorination process conformed to the pseudo-first order kinetic model and the following order of *k* (rate constant) is: 3-CP (0.05017 min<sup>−1</sup>) > 4-CP (0.04733 min<sup>−1</sup>) > 2-CP (0.03498 min<sup>−1</sup>). The Pd/Ni exhibited a good stability in the electrocatalytic hydrodechlorination (ECH) of 3-CP after five recycles.

**Author Contributions:** Conceptualization, J.L.; Methodology, H.W.; Validation, L.W.; Formal Analysis, C.L. and B.Z.; Investigation, Z.Z.; Writing-Original Draft Preparation, J.L.; Writing-Review & Editing, H.Z.; X.C. and J.L.; Supervision, L.W. and C.M.; Project Administration, B.Z.; Funding Acquisition, Z.Z.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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