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Electrochemical Dechlorination of 3-chlorophenol with Palladium-Loaded Carbon Felt Electrode

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Abstract: Electrochemical dechlorination with Pd-loaded electrodes offers an effective method for detoxification of wastewater. Electro-reductive dechlorination of 3-chlorophenol (3-CP) with Pd loaded on carbon felt (Pd/CF) was investigated. Pd was loaded on carbon felt by electrolytic method. The prepared electrodes were characterized by XRD, SEM, EDS, S-TEM and CV. The sizes of the Pd particles loaded on CF were found in the range of 100–400 nm. The preparing conditions including loading amount of Pd and loading currents were investigated. Moreover, the reduction conditions including electrolytes, reductive currents and recycle times were also studied. The Pd/CF cathodes with Pd loading of 0.5 mg/cm², preparing current of 5 mA, electrolyte concentration of 30 mmol/L NaCl and 30 mmol/L CH₃COONa were used to reduce 3-CP for dechlorination. When CH₃COONa was used as the electrolyte, the current was 5 mA, the initial pH was 7.5, the initial 3-CP concentration was 1 mmol/L and the degradation rate of 3-CP could reach 95.81% after reduction of 150 min under an argon atmosphere. The electrochemical reduction of 3-CP was confirmed to follow the first-order rate law. 3-CP was qualitatively dechlorinated to phenol on electrodes with Pd. The fact that active hydrogen formed on palladium during preliminary electrolysis could be proved by the dechlorinated 3-CP in non-electroreduction after preliminary electrolysis. A possible reduction pathway was proposed based on the results.



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Keywords: electrolysis; dechlorination; palladium hydride; loading; reaction rate

1. Introduction

Over the last several decades, wastewaters containing persistent organic pollutants (POPs) have been causing a lot of environmental problems [1]. Chlorophenols (CPs), typical POPs, have been widely used in industry, agriculture and for domestic purposes over more than 50 years. It is well-known that they are toxic even at low levels. Thus, various techniques have been developed for the degradation of CPs, including biological, thermal, reduction and advanced oxidation processes (AOPs) [2–4]; for example, complete mineralization of 4-chlorophenol (4-CP) by UV/porous TiO₂ layers and porous multiwalled carbon nanotube TiO₂ composite layers were reported by Zouzelka and Rathousky [5,6]. Among these methods, electro-reductive dechlorination is one of the most promising [7], due to the following significant advantages: (i) effective dechlorination is possible at ambient temperatures, (ii) no highly active chemicals are required, (iii) selective removal of chlorine occurs while the organic skeleton remains to be digested by another cheap (e.g., bacterial) route, and (iv) no toxic by-products (i.e., chlorinated dioxins) are formed [6].

Electrocatalytic reductive dechlorination of monochlorophenols (2-CP and 4-CP) has been widely studied and proved to be efficient [8–13]. On the other hand, 3-CP, another

monochlorophenol, which has been classified as priority pollutants by the U.S. Environmental Protection Agency (EPA) [14], was also harmful to humans and needed to be treated [15]. Several processes have been used to degrade 3-CP, such as electrocatalytic oxidation, ultrasound-assisted electrocatalytic oxidation, photocatalytic TiO_2 , and electrochemical-assisted photocatalytic processes [16–20]. Electro-catalytic reductive dechlorination was one of the most promising and attractive [7]. Pd was considered as the best catalyst for electro-reduction dechlorination due to its unique function in adsorption of hydrogen [21]. Moreover, aside from the retardation of the H combination, the H_2 generated from the cathode could be further adsorbed on Pd and dissociated into two atomic H, reducing the contaminant [22]. However, the high cost of the pure Pd cathode was a particular disadvantage for use [21]. Thus, Pd loaded on different materials such Ti mesh, carbon felt, and so on were investigated [23–25]. The most activity catalyst for the electro-dechlorination of chlorinated organic compounds have been reported as palladium-loaded catalysts [26–29]. Though the electro-reduction of 3-CP by Pd loading on carbon felt was reported by Cai et al. [24], important and detailed information about reduction affecters, such as the preparing conditions of Pd loading cathodes, reduction conditions, and so on, were still unknown. Thus, in this paper, we report the electro-dechlorination of 3-CP on Pd-loaded carbon felt (Pd/CF) electrodes, focusing on the cathode preparing conditions, affect factors, reaction kinetics, and dechlorination mechanism.

2. Materials and Methods

2.1. Materials and Instruments

Carbon felt was supplied by Gun-Ei Chemicals Industries Co. (Takasaki, Japan). Its areal weight was 274 g/m^2 and the thickness was 5 mm. Palladium chloride and 3-CP were purchased from Wako Chemicals. Water purified by Milli-Q (Millipore) was used for the electrolyte solution.

A H-type glass cell separated with the N117 membrane was employed as shown in Figure 1. The capacity was 100 mL for each compartment. Electrolysis processes were carried out with the aid of Potentiostat/Galvanostat HABF-501 (Hokuto Denko Co., Tokyo, Japan).

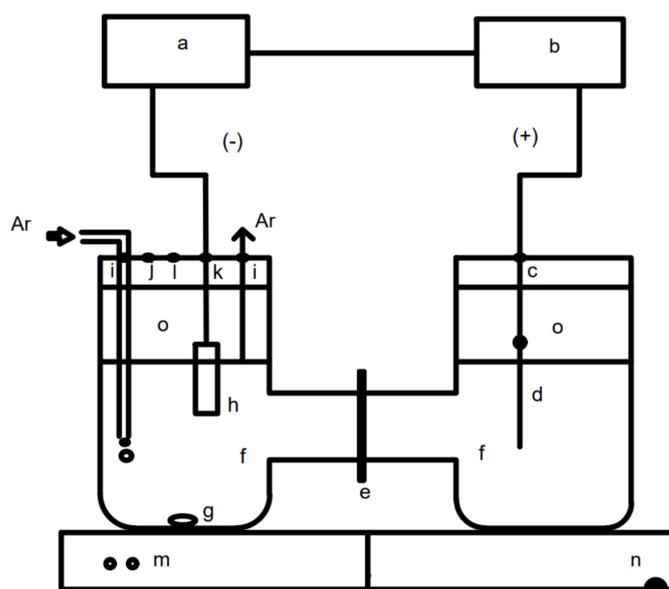


Figure 1. Experimental apparatus for dechlorination: (a) digital coulometer, (b) DC power supplier, (c) anode hole, (d) anode, (e) Nafion membrane-N117, (f) electrolytic solution, (g) teflon-coated magnet bar, (h) cathode, (i) gas hole, (j) sampling hole, (k) cathode hole, (l) reference electrode hole, (m) magnetic stirrer, (n) packing block, and (o) glass tube.

2.2. Electroloading of Palladium on Carbon Felt

The loading of palladium was executed by electrolytic means. Carbon felt cut into $25 \times 15 \times 5$ mm was dipped into 2000 mmol/L sulfuric acid over one night and rinsed with water. One piece of the felt was connected with SUS wire and used as a cathode. The immersed depth of the cathode was 20 mm and, therefore, the electro-loaded surface was 20×15 mm. The electrolyte solution was 30 mmol/L NaCl for certain amount of palladium chloride, and the solution was stirred with magnet stirrer. The carbon felt electrode was used as a cathode and platinum foil was used as an anode. Both electrolytic solutions were purged with argon. The current in electro-loading was 5 mA and the reaction time was 30 min. Then, galvanostatic electro-plating was continued until the Pd^{2+} ion in the solution was consumed. After electro-loading, the amount of residual Pd^{2+} in the reaction solution was analyzed by ICP-Mass. The results showed that for each case, at least above 99.5% of Pd^{2+} was loaded on CF.

2.3. Electrolysis and Non-Electrolysis of 3-CP

After purging the electrolyte solution with argon, a given amount of 3-CP was injected into catholyte solution. Electrolysis was performed in galvanostatic mode under maximum stirring with magnet stirrer under certain currents. Non-electrolysis was performed under maximum stirring with magnet stirrer. Before non-electrolysis, the Pd/CF cathodes were prepared under certain currents for 90 mins without 3-CP. The proceeding of dechlorination was monitored by quantitative analysis of 3-CP and phenol (the single product) with HPLC [24].

3. Results and Discussion

3.1. The Characterization of Pd/CF Cathode

In order to obtain the information of Pd loading on CF, CF and Pd/CF cathodes were characterized by XRD, SEM, EDS, S-TEM, and CV, as shown in Figures 2–6. As shown in Figure 2, the diffraction peaks corresponding to Pd were found after electro-deposition of Pd on CF, indicating that Pd might be successfully loaded on CF. It can be seen in Figure 3 that lots of particles scatter over the surface of CF. With the results of EDS in Figure 4, the small particles could be confirmed as Pd particles. In Figure 5, the sizes of the Pd particles were found in the range of 100–400 nm. The fine scattering nano Pd particles might lead to good electro-dechlorination of 3-CP.

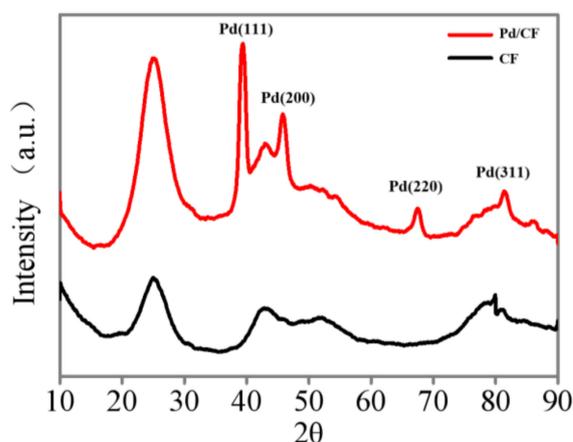


Figure 2. XRD of carbon felt electrode and Pd-loaded carbon felt electrode (0.5 mg/cm^2).

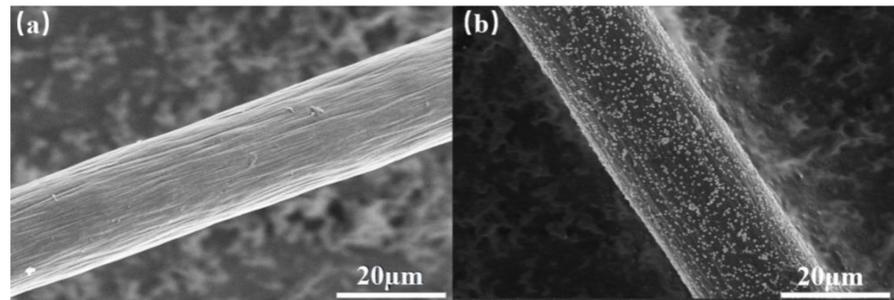


Figure 3. SEM of cathode: (a) raw carbon felt electrode and (b) Pd-loaded carbon felt electrode (0.5 mg/cm²).

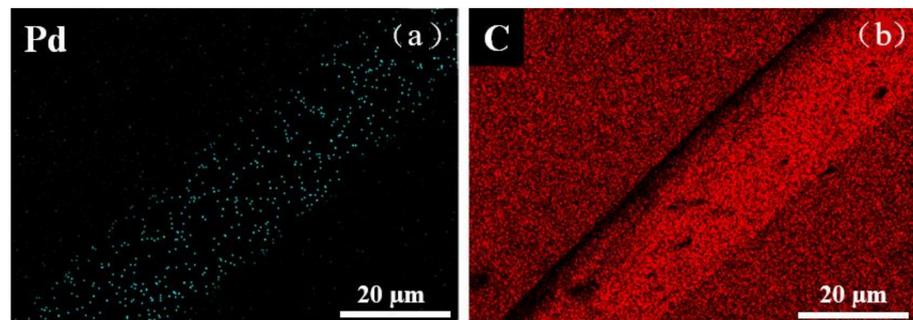


Figure 4. EDS of Pd-loaded carbon felt electrode (0.5 mg/cm²), (a) Pd element scatter, (b) C element scatter.

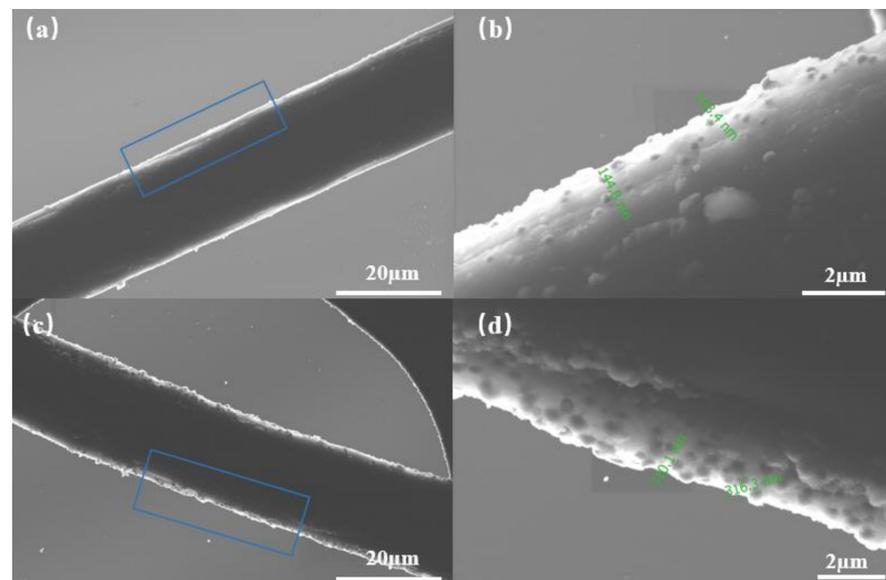


Figure 5. S-TEM of cathodes with different amount of Pd loading. (a,b) Pd-loaded carbon felt electrode (0.25 mg/cm²); (c,d) Pd-loaded carbon felt electrode (0.5 mg/cm²).

The H atom adsorbed (H_{ads}) on the Pd surface has been considered as the key species in electro-dechlorination [30]. Thus, CV characterizations of Pd/CF with different Pd loading were obtained in order to study the catalytic ability of these carbon-supported catalysts. As shown in Figure 6, an oxidation peak was observed in the CVs of bare carbon supports from -1.5 V to -0.75 V, attributing to the water decomposed into H_2 and OH^- ($2H_2O + 2e = H_2 + OH^-$, $\varphi_{H_2O/OH^-} = -0.828$ V vs. NHE). After the deposition of the Pd catalyst on CF support, the current density of oxidation peak increased slightly with the increase of the amount of Pd loaded on CF, which was consistent with the mechanism of

water split by the Pd catalyzer. Furthermore, the hydrogen adsorption–reduction peak was also observed at 0.25 V, and the peak current density was strengthened with the amount of Pd on CF. This result might indicate that Pd loading would improve the electrocatalytic ability of these Pd-loading catalyzers. However, for all cases, no obvious reduction peaks of 3-CP in the range of potential window was observed. Based on these results, the dechlorination could not be identified by CVs in this work.

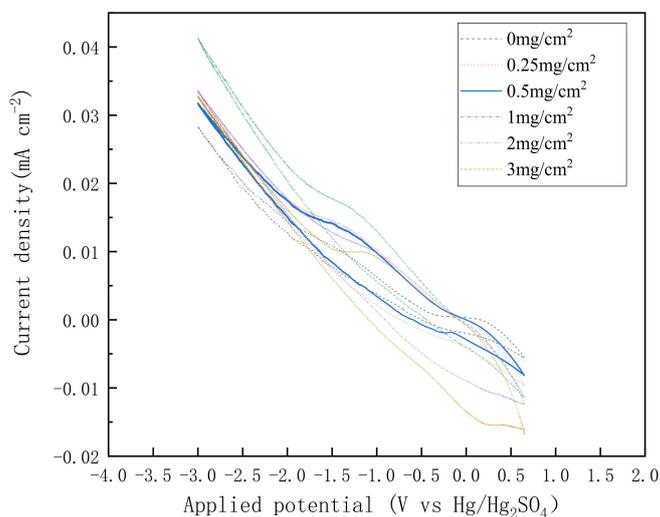


Figure 6. Cyclic voltammogram (CV) curves of Pd/CF, electrolyte of 30 mM CH_3COONa , scan rate of 0.03 V/s, number of the scans 6, and 1 mM 3-CP.

The CV processes revealed that activated H atoms were adsorbed on Pd/CF electrode along with the electrolytic process. Because hydrogen oxidation was inhibited by coverage of H_2 on the surface of Pd particles, hydrogen oxidation was not observed. Though for all cases no obvious reduction peaks of 3-CP in the range of potential windows was observed, the strength of peaks for reduction peak of H^+ suggested that the Pd loading would improve the electrocatalytic ability of 3-CP reduction. Accordingly, the dechlorination efficiency was also closely related to the combination of activated H atoms and the Pd catalyzer.

3.2. Influence of the Loaded Amount of Pd

Pd was widely used as a catalyst for the hydrogenation of chlorinated organic compounds [31,32], and the activity for a given reaction can be affected significantly by the different amount of Pd loaded [33]. Thus, carbon felt with different amounts of Pd loaded were employed as cathodes for the dechlorination of 3-CP.

The results were shown in Figure 7. Once Pd was loaded (0.25 mg/cm^2) onto the carbon cathode, the removal rates of 3-CP increased markedly. This result could be rationalized by the idea that Pd particles loaded on the surface can enhance the reductive ability of the cathodes [34].

As shown in Figure S2, the removal rates of 3-CP increased with the increase of Pd loading and reached the value 95.81% at a loading of approximately 0.5 mg/cm^2 Pd on carbon felt; then, the removal rates were kept around 95% with further increase of Pd loading. As shown in Figure 5, for lower Pd loadings (0.25 mg/cm^2), both the size and the number of the Pd particles were smaller (about 140 nm in diameter) than those (about 320 nm in diameter) of the best Pd loadings (0.5 mg/cm^2), indicating that Pd particle size might not be most important for the electro-catalyst ability, while the number of the Pd particles and particle size together, which would correspond to the surface of Pd loaded on CF, might be the key roles for the dechlorination of 3-CP.

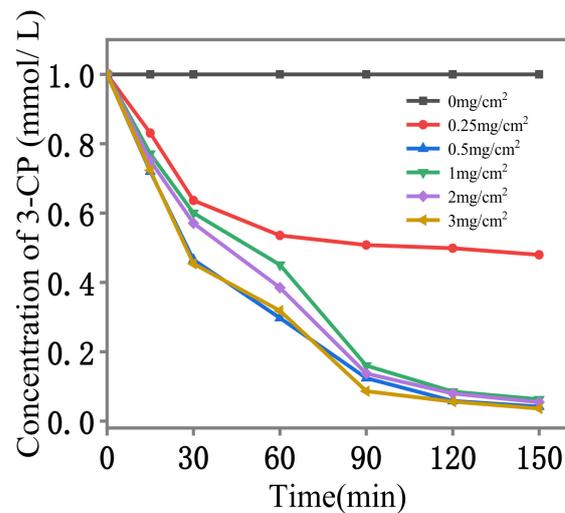


Figure 7. Effect of loading amount of Pd on variation of the concentration of 3-CP.

3.3. Influence of the Loading Currents

When the Pd/CF cathodes were prepared by electroloading method, the current was an important factor. Thus, the influence of the currents on the degradation of 3-CP were investigated. As shown in Figures 8 and S3, firstly the removal rates of 3-CP increased with the increase of loading currents from 1 mA to 5 mA, then an obvious decrease appeared corresponding to the loading current 10 mA, and the removal rates kept increasing with the increase of loading currents. Since the loading current might affect the morphology of Pd/CF, the SEM of Pd/CF cathodes prepared under 1 mA, 5 mA, 10 mA, and 50 mA were investigated. As shown in Figures 3 and 9, compared to the cases of Pd/CF with a preparing current of 1 mA and 10 mA, the better degree of dispersion of the Pd particles of Pd/CF with a preparing current of 5 mA was observed. The degree of dispersion for Pd/CF with a preparing current of 50 mA was similar to that of Pd/CF with a preparing current of 5 mA. While for the case of Pd/CF with a preparing current of 1 mA, several large Pd particles with a size of about 10 μm were found, and for the case of a preparing current of 10 mA, there was also one large Pd particle with a size of about 5 μm . These results suggested that the degradation rates might depend on the degree of Pd particle dispersion.

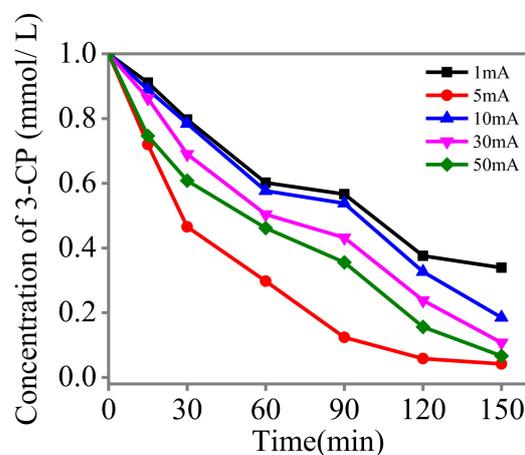


Figure 8. Effect of the currents for the variation of the 3-CP concentration.

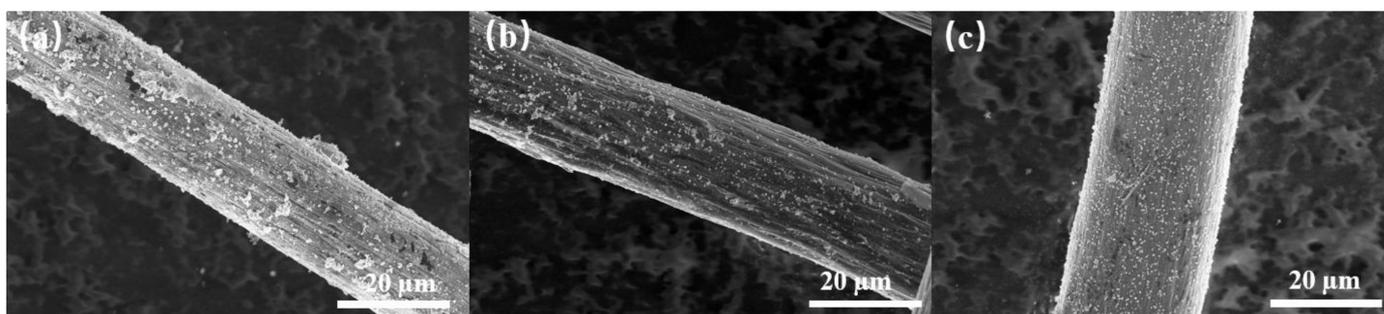


Figure 9. SEM of cathodes prepared under different currents: (a) Pd-loaded carbon felt electrode (1 mA), (b) Pd-loaded carbon felt electrode (10 mA), and (c) Pd-loaded graphite felt electrode (50 mA), (0.5 mg/cm²).

3.4. Influence of the Electrolytes

In the reduction, the electrolytes might affect the reduction of 3-CP; thus, NaCl, Na₂SO₄, and CH₃COONa were investigated as electrolytes. As shown in Figures 10 and S4, the removal rates of 3-CP increased in this order: NaCl, Na₂SO₄, and CH₃COONa. The lowest removal rate corresponded to NaCl and was 49.99%, the highest removal rate of 3-CP was 95.81% corresponding to CH₃COONa. According to Xu's investigation of Pd/C, there were Pd²⁺ ions on the surface of the Pd particle [30]. The Cl[−] ions might connect with Pd²⁺ to form a Pd–Cl bond, resulting in reducing the formation of H_{ads} and absorption of 3-CP. Thus, the highly negative influence of NaCl on the reduction of 3-CP might be explained.

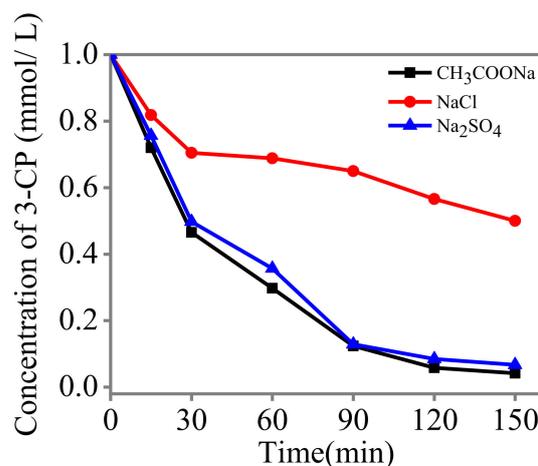


Figure 10. Effect of different electrolytes on the variation of the 3-CP concentration.

3.5. Influence of the Concentrations of Reduction Electrolyte

The variations of the 3-CP concentrations were shown in Figure 11. For most cases, 3-CP decreased smoothly. As shown in Figures 11 and S5, the reduction of 3-CP corresponding to 30 mM CH₃COONa was obviously better than other cases. This result could be rationalized by the idea that the concentration of CH₃COONa would result in higher conductivity, which would be beneficial for the reduction reaction; and the CH₃COO[−] might also react with Pd²⁺, resulting in reducing the reduction of 3-CP.

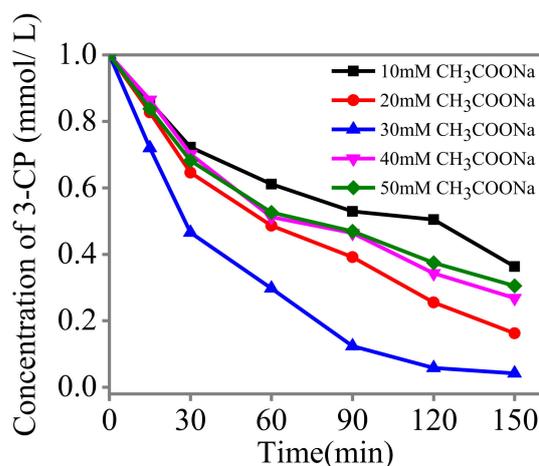


Figure 11. Effect of concentrations of CH₃COONa on variation of the 3-CP concentration.

3.6. Influence of the Reducing Currents

When 3-CP is electro-chemically reduced, the reducing currents could be an important factor. Thus, the influence of the reduction currents on the degradation of 3-CP were investigated. As shown in Figures 12 and S6, for the reducing current of 1 mA, the lowest removal rate of 5.97% was obtained; then, with the increase of the reducing current to 5 mA, the highest removal rate of 95.81% was obtained; the removal rates decreased in the range of reducing currents from 5 mA to 20 mA. At the lower reducing current, there was not enough highly reactive H_{abs} bound to the Pd surface for dechlorination. At the higher reducing current, the local current density for H⁺ reduction was too high, resulting in excessive hydrogen gas evolution, thus disturbing the mass transfer of 3-CP to the surface of the Pd-loaded carbon felt cathode [24].

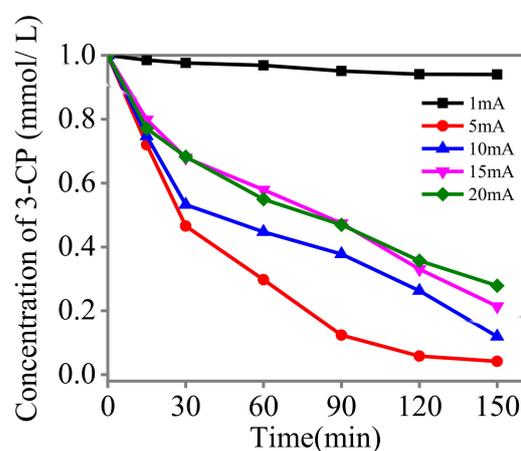


Figure 12. Effect of reduction current on the variation of the 3-CP concentration.

3.7. Kinetics of 3-CP Degradation

The 3-CP decay curve under the best condition, as shown in Figure 12, was exponential degradation. Consequently, we fit the data to the integral rate equation for the first-order reaction, shown as Equation (1):

$$\ln(C_0/C) = kt \quad (1)$$

where C , C_0 , k , and t denote the concentration of 3-CP at the given reaction time, at $t = 0$, the rate constant, and the reaction time, respectively.

In consequence, for the set of data concerning decay, a straight line with good correlation was obtained, as shown in Figure 13. This result indicates that 3-CP reacted per the

first-order rate law. The apparent rate constants, k , for the decay of 3-CP was calculated from the slope to be $k = 2.23 \times 10^{-2} \text{ min}^{-1}$.

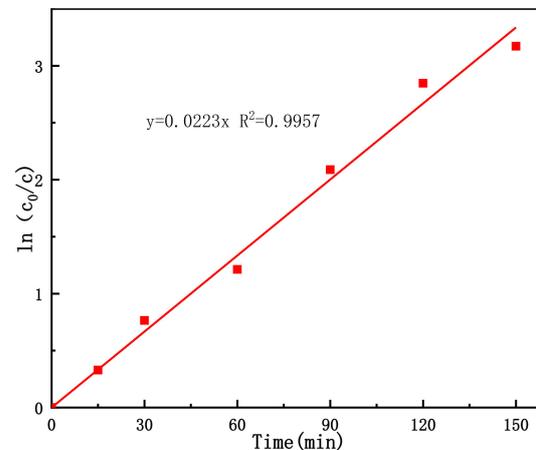


Figure 13. Kinetical plots of 3-CP degradation in optimum condition.

3.8. Mechanism and Possible Degradation Pathways

In order to get the mechanistic information about the indirect reduction of 3-CP on the Pd surface, the effect of preliminary electrolysis was examined. Figure 14 showed example of the non-electroreduction of 3-CP. After preliminary electrolysis, about 1 mmol of the substrate was introduced and stirred to contact with the activated electrode. For all the cases mentioned above, it decreased in 10 minutes to reach a constant level, meaning approximately 20% of 3-CP was already dechlorinated. This implied that the reactive species responsible for the dechlorination of 3-CP would be formed during preliminary electrolysis. The most probable seemed $(\text{Pd})_n\text{H}$, which might result from the adsorption of electrogenerated hydrogen on metallic Pd [24]. The possible reduction pathway was proposed in Scheme 1.

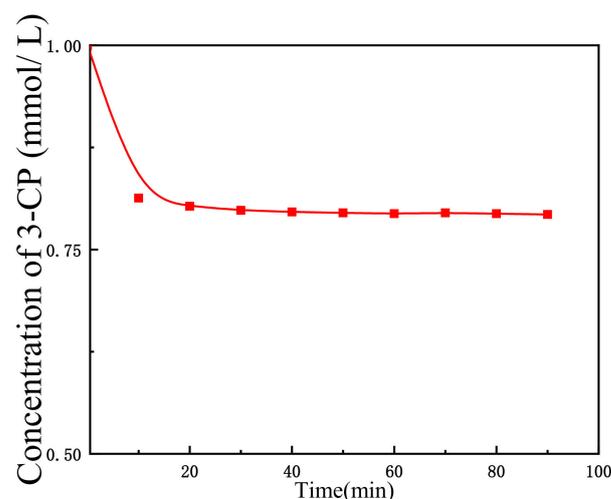
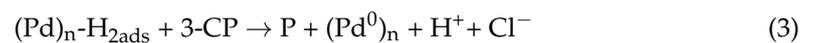
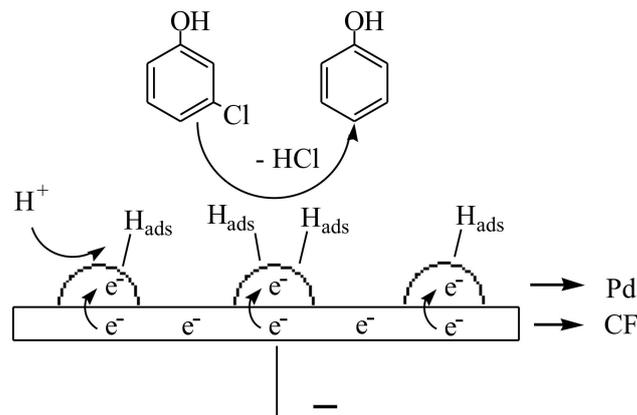


Figure 14. The variation of 3-CP in non-electrolytic dechlorination after preliminary electrolysis.



Scheme 1. Indirect reduction of monochlorophenol on Pd-loaded carbon felt electrode.

3.9. Reuse of Pd/CF

To assess the stability of the Pd catalyst, Pd/CF electrodes were repeatedly used in the electro-reductive dechlorination. The results were summarized in Figure 15. Up to 5 times of use, the dechlorination rates were found to decrease from 95.8% to 92.3%. Thus, it was confirmed that the Pd catalyst possessed a satisfactory durability under the present condition.

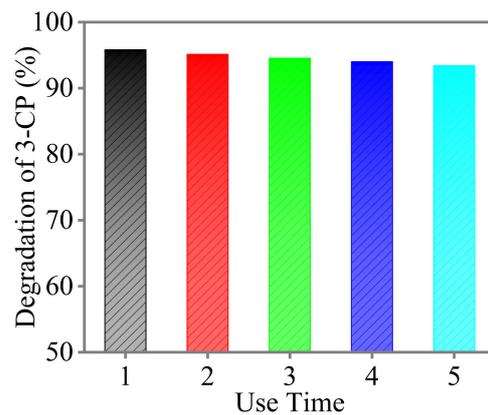


Figure 15. Reuse of Pd/CF in electro-reductive dechlorination.

3.10. Comparison with Other Processes

In Table 1, the representative performance on the degradation of 3-CP by using ultrasound-assisted electrocatalytic oxidation [16], electrocatalytic oxidation [17], electrochemical and photocatalytic process [18], photo-catalyst [19], electro-Fenton [20], and electro-reduction reported by Cai [26] were summarized along with that by electro-reduction. It should be remarked that most of solution treated by other methods were comparatively dilute. As a whole, electro-reduction seems considerably superior to ultrasound-assisted electrocatalytic oxidation, electrochemical and photocatalytic processes, and photocatalysts, substantially comparable to the electrocatalytic oxidation, electro-Fenton process and electro-reduction reported by Cai. After repeated use, the decrease in removal rate for this work was also comparable to electrocatalytic oxidation.

Table 1. Comparison of electro-reduction with other processes for degradation of 3-CP. (1)^a 3-CP removal/reaction time (%/min).

C ₀ /mM	Method	pH	(1) ^a	k/10 ⁻² min ⁻¹	Decrease in Removal Rate (%)/Reuse Times	References
1.00	electroreduction	7.5	96/150	2.23	3/5	This work
1.00	ultrasound assisted electrocatalytic oxidation	9.1	35/60			[16]
0.39	electrocatalytic oxidation	5	98/120	3.84		[17]
0.39	electrochemical and photocatalytic process (tungsten supported ZnO/Solar)		84/150	1.10		[18]
0.08	photocatalytic TiO ₂ (0.2 g/L)	7.0	77/300		4/5	[19]
0.50	UV energy electroreduction	4.0	98/		3/4	[24]

4. Conclusions

3-CP could be dechlorinated by the electro-reductive method with Pd loaded on carbon felt. And Phenol and chloride ions were found to be the products. The electrochemical dechlorination of 3-CP was confirmed to follow the first-order rate law. Both the size and number of Pd particles would affect the dechlorination rate of 3-CP. The fact of active hydrogen formed on palladium during preliminary electrolysis could be proved by the dechlorinated 3-CP in non-electroreduction after preliminary electrolysis, indicating that indirect reduction of 3-CP by Pd/CF should be one of the possible reaction pathways.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/coatings11101188/s1>, Figure S1: SEM of cathode (a) Raw carbon felt electrode, (b) Pd loaded carbon felt electrode (0.5 mg/cm²). Figure S2: Effect of loading amount of Pd on the removal rates of 3-CP, Figure S3: Effect of the currents for the preparation electrode on the removal rates of 3-CP, Figure S4: Effect of different electrolytes on the removal rates of 3-CP, Figure S5: Effect of concentrations of CH₃COONa on the removal rates of 3-CP, Figure S6: Effect of reduction current on The removal rates of 3-CP.

Author Contributions: Conceptualization, H.Y. and S.Z. (Siqi Zhang); methodology, D.L.; Formal analysis, D.L. and Y.C.; Data curation, J.L. and S.Z. (Suying Zhao); Writing—original draft preparation, H.Y. and D.L.; Supervision, X.G. and L.L. All authors have read and agreed to the published version of the manuscript.

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

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