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Preparation of the Palladium/Polymeric Pyrrole-Multi-Walled Carbon Nanotubes Film/Titanium Electrode and Its Performance for the Dechlorination of 4-chlorophenol

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The electrochemically reductive dechlorination of 4-chlorophenol (4-CP) in aqueous solution on a palladium/polymeric pyrrole-multi-walled carbon nanotube film/meshed titanium electrode (Pd/PPy-MWCNTs/Ti) was examined in this paper. The Pd/PPy-MWCNTs/Ti cathode was prepared through electrodepositing cauliflower-like palladium nanoparticles onto a PPy-MWCNTs/Ti electrode (that was a titanium electrode coated with pyrrole and functionalized multi-walled carbon nanotubes by co-deposition). The physical properties of this electrode were characterized by scanning electron microscope (SEM) and X-ray diffraction (XRD). Various factors influencing the dechlorination of 4-CP were also investigated. The results indicated that the removal rate of 4-CP reached 99.82% within 120 min and the current efficiency of 13.8% was obtained under the optimum conditions (the dechlorination density of 1.0 mA/cm^2, the initial pH of 2.08 and the electrolyte of 0.1 mol/L Na_2SO_4). The predominant product was phenol. In addition, the electrode was found to be still stable after being used for six cycles and the dechlorination efficiency was over 93.3%.

Keywords: Polymeric pyrrole, Multi-walled carbon nanotubes, Palladium, Dechlorination, 4-chlorophenol

1. INTRODUCTION

Chlorophenols (CPs), including 4-chlorophenol (4-CP), have been widely used as intermediates to produce insecticides, herbicides, wood preservatives and fungicides [1-3]. Nevertheless, chlorophenols are a kind of persistent organic pollutants, which can cause serious health problems because of their carcinogenesis, carcinogenic and mutagenesis effects [4, 5]. Furthermore, some chlorophenols have been classified as priority pollutants by different countries [6, 7]. Therefore, it is important to explore a pragmatic approach to eliminate these pollutants.

Recently, electrochemically reductive dechlorination has been successfully confirmed as a promising technology, owing to its rapid rate, economical cost effect, mild reaction condition and absence of secondary contaminants [8-10]. This could selectively remove chlorine atoms of chlorophenols and contribute to further treatment. Electrocatalytic hydrogenolysis (ECH) has been considered as the mechanism of electrochemically reductive dechlorination [11-14]. It was a process in which chemisorbed hydrogen atoms generated on the electrode surface by electrolysis of water could attack the CPs molecules chemisorbed on the electrode surface, resulting in the addition of hydrogen to π bonds or the reductive cleavage of σ bonds [15, 16].

Electrochemical catalysis reduction reaction had a great relationship with the catalyst used. Among noble metals catalysts, such as silver (Ag) [17], copper (Cu) [18] and palladium (Pd) [19-22], palladium was regarded as the most efficient catalyst in electrocatalytic hydrogenolysis due to its excellent ability to absorb hydrogen [23, 24]. However, the pure palladium coating on the surface of cathodes had some drawbacks of high cost and poor stability. Hence, these disadvantages limited its practical application. High dispersion and large specific surface area of Pd particles was important for the process of electrochemical reduction. It was found that the preparation of a conductive film, such as polyaniline (PANI), polypyrrole (PPy) and polythiophene (PTh), on the electrode substrate could effectively promote the dispersion of catalytic particles and improve the catalytic performance. Recently, PPy has received a lot of attention due to its properties of easy preparation, excellent stability, high electronic conductivity and nontoxicity [25]. Therefore, to combine PPy with Pd in the preparation of electrodes might improve their performance. Carbon nanotubes (CNTs) are a kind of versatile materials and have received extensive concern because of their superior properties, for example, high surface area and energy, abundant pore structures and chemical stability, etc [26, 27]. In recent years, CNTs doped in the conductive polymers have been extensively researched [28, 29], but most of the studies were on the preparation of supercapacitors [30, 31]. The composite material of CNTs and conductive films has still needed further exploration as an electrode substrate in the field of pollutants removal, e.g. electrochemically reductive dechlorination.

In this paper, a palladium/polypyrrole-multi-walled carbon nanotubes/titanium mesh composite electrode (Pd/PPy-MWCNTs/Ti) was prepared through electrodepositing palladium nanoparticles onto a composite electrode of CNTs and conductive films. The surface morphology and crystalline structure of the proposed electrode were characterized by a FESEM and XRD, respectively. In addition, 4-CP was chosen as a model pollutant to examine the performance of the electrodes prepared here. The operating conditions of electrochemically reductive dechlorination were optimized too.

2. EXPERIMENTAL

2.1. Materials

A titanium mesh (pore density 80 pores per inch, line diameter 0.10 mm, purity > 99.5%) used as the electrode substrate was purchased from Baoji Titanium Materials Ltd. (Baoji, China). Multi-walled carbon nanotubes (MWCNTs) purchased from Beijing DK Nano Technology Co. Ltd. (Beijing, China) would be purified before use. Pyrrole purchased from Sinopharm Chemical Reagent Co. Ltd. (Beijing, China) was of chemical pure and needed vacuum distillation before use. The other chemicals, (Na_2CO_3, $H_2C_2O_4$, alcohol, Na_2SO_4, HNO_3, 4-CP, $PdCl_2$, etc) obtained from Sinopharm Chemical Reagent Co. Ltd. (Beijing, China) were of analytical reagent grade and used without further purification. Millipore-Q water was used throughout all the experiments.

2.2. Preparation of electrodes

A piece of titanium mesh plate (5 × 2 cm) was put into 5 wt% Na_2CO_3 solution at 333 K for 45 min to remove the surface grease. Afterwards, it was put into 10 wt% oxalic acid solution at 333 K for 120 min to remove the surface oxides. Finally, it was put into Millipore-Q water under ultrasonic treatment for three times and kept in alcohol for use later.

The purchased pyrrole should be pretreated by vacuum distillation (its color would change from yellow to no color) and then kept at 277 K for use later. Additionally, the purchased MWCNTs should be purified in a concentrated solution of H_2SO_4/HNO_3 (3:1) at 353 K for 6 h in order to reduce the obvious agglomeration in aqueous solutions [32]. After purification, the residual catalyst and ash carbon would be removed and the MWCNTs could be functionalized. It is known that the functional groups such as –COOH could result in partial ionic bonds and transform the nonpolar MWCNTs to polar ones. Therefore, the functionalized carbon nanotubes have better solubility and wettability in aqueous solutions than their as-received counterparts [33].

Electrochemical polymerization was completed in a three-electrode system with the pretreated mesh Ti plate and a platinum foil as the working electrode and the counter electrode, respectively. A saturated calomel electrode (SCE) was employed as the reference electrode. The electrolyte (100 mL) consisted of 0.1 mol/L pyrrole, 0.2 mol/L p-toluene sulfonic acid and a certain amount of MWCNTs. The solution was deoxygenated by N_2 for 10 min before electrochemical polymerization. The PPy-MWCNTs film could be formed on the meshed Ti plate by applying a potential of 0.6 V (vs. SCE) for 20 min at room temperature.

Electrodeposition of palladium nanoparticles on the PPy-MWCNTs film (as cathode) was carried out in a two-electrode system containing 80 mL of $PdCl_2$ solutions at a certain current density (4 mA/cm^2). Finally, the Pd/PPy-MWCNTs/Ti electrodes were obtained until the color of $PdCl_2$ solutions disappeared. For comparison, a Pd/Ti electrode was prepared by directly electrodepositing Pd on a Ti mesh substrate using the same electrodeposition conditions.

2.3. Characterization

The surface morphologies of the proposed electrodes were characterized by scanning electron microscope (SEM, JSM-7500F, Japan). The crystalline structure was analyzed by X-ray diffraction (XRD, D/max200PC, Japan).

2.4. Dechlorination

The dechlorination experiments were implemented in a two-compartment unit separated by a proton exchange membrane (Nafion-117, DuPont). The anolyte was 100 mL of 0.1 mol/L Na_2SO_4 solution. The catholyte was 100 mL of 0.1 mol/L Na_2SO_4 solution with different pH values containing 100 mg/L 4-CP. The Pd/PPy-MWCNTs/Ti electrode (as the cathode) paralleled to the anode (a platinum foil, 5 cm × 2 cm) with a distance of 8 cm. The typical dechlorination processes were performed by a potentialstat at a certain current density for 120 min at room temperature. At specified time intervals, 2.0 mL of samples were withdrawn from the solution of cathode for analysis. The magnetic stirring condition around the cathode was used to promote mass transfer. In order to examine the stability of the prepared electrodes, several reaction cycles would be conducted under the same experimental conditions as described above.

The concentrations of 4-CP and phenol were determined by a high-performance liquid chromatograph (HPLC, Shimadzu, Japan) with a TC-C18 column (150 mm × 4.6 mm). The column temperature was 303 K, and the sample volume was 20 μL. The mobile phase was methanol and water (70:30) and its flow rate was 1.0 mL/min. The wave-length of ultraviolet detector was 280 nm.

3. RESULTS AND DISCUSSION

3.1. Characterization

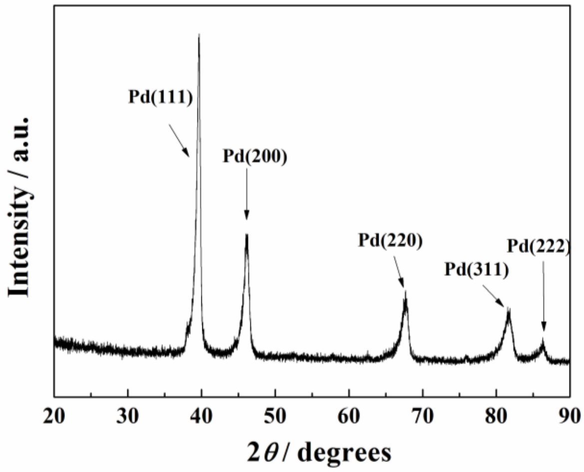

Figure 1. XRD pattern of the Pd/PPy-MWCNTs/Ti electrode.

Figure 1 displays the XRD pattern of the Pd/PPy-MWNTs/Ti electrode. As seen from Figure 1, all the diffraction peaks could be attributed to Pd lattice diffraction according to the JCPDS card 87-0643. The diffraction peaks at 2θ values of 39.92^o, 46.43^o, 67.76^o, 81.64^o and 86.12^o could be respectively ascribed to the (111), (200), (220), (311) and (222) reflection of the crystal lattice of Pd. According to the Scherrer's equation and the full width half-maximum peak of (111) crystal plane of Pd, the average particle size was about 13.9 nm. The Pd nano particles obtained here were a little smaller than those on the similar electrodes in the literatures [34, 35]. Catalysts with smaller diameter might provide more active sites and would be of benefit to electrochemically reductive dechlorination. Additionally, the same as what demonstrated in the literatures [34-36], no dispersing diffraction peak of PPy was observed either in this XRD pattern due to its amorphous structure or low diffraction intensity. No diffraction peak of MWNTs was found, probably resulting from its low doping content.

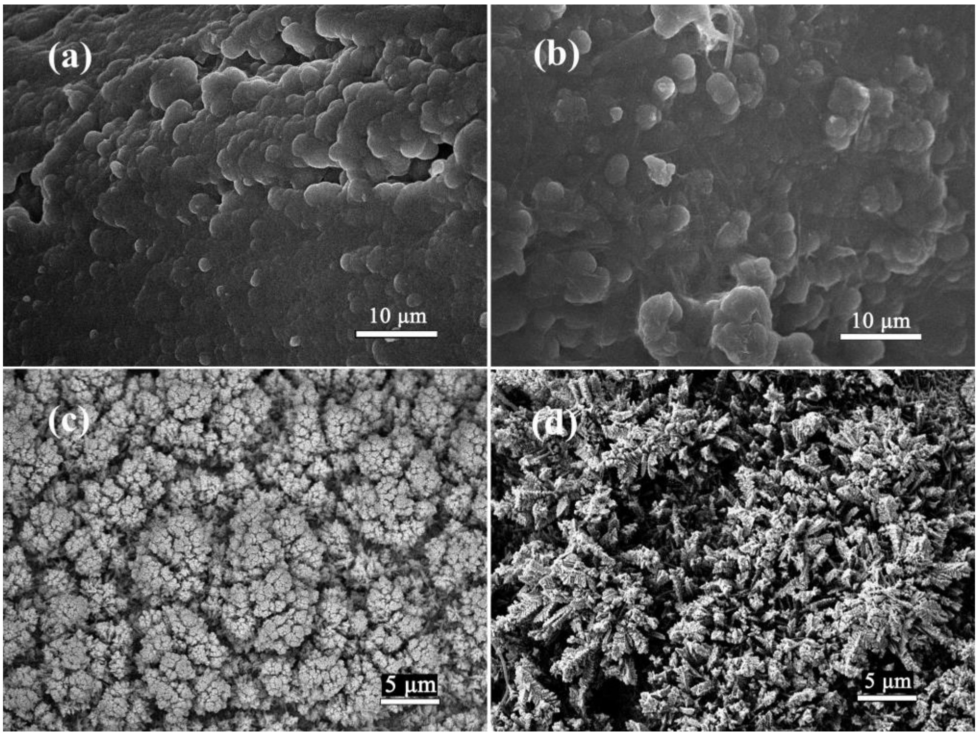

Figure 2. SEM images of the PPy/Ti electrode (a), the PPy-MWCNTs/Ti electrode (b), the Pd/PPy-MWCNTs/Ti electrode (c) and the Pd/PPy-MWCNTs/Ti electrode after being used for eight cycles (d).

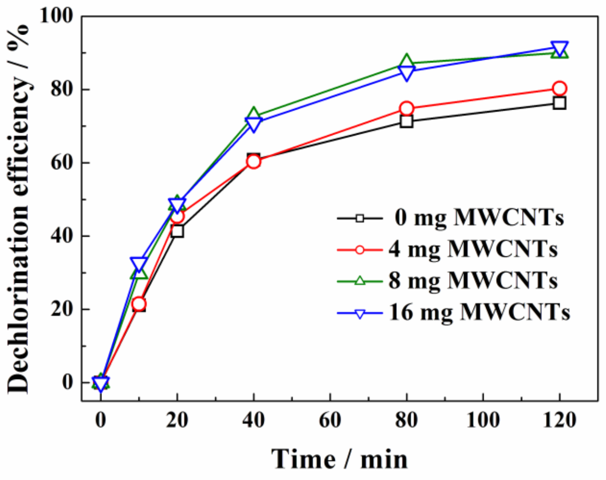

Figure 3. Effects of MWCNTs dosage on the dechlorination efficiency using the Pd/PPy-MWCNTs/Ti electrode (4-CP 100 mg/L, $PdCl_2$ 5 mM, pH 2.2, Na_2SO_4 0.1 mol/L, current 1.0 mA/cm^2).

Figure 2 shows the surface morphologies of the PPy/Ti electrode, the PPy-MWCNTs/Ti electrode and the Pd/PPy-MWCNTs/Ti electrode by SEM. As demonstrated in Figure 2a and b, the addition of MWCNTs resulted in a composite film. PPy and MWCNTs integrated with each other closely. Functionalized MWCNTs both acted as dopants and also provided a large surface area for the polymerization process [37]. It could be seen from Figure 2c that the Pd nanoparticles on the Pd/PPy-MWCNTs/Ti electrode dispersed uniformly as cauliflower-like clusters. This cauliflower-like undoubtedly could increase the surface area and supply more catalytic sites to benefit the electrochemically reductive dechlorination. Figure 2d showed that the Pd/PPy-MWCNTs/Ti electrode changed greatly after being used for eight times. This phenomenon might lead to a loss in active sites and electrocatalytic performance.

3.2. Effect of MWCNTs dosage

The effect of MWCNTs dosage (0 mg, 4 mg, 8 mg and 16 mg) on the dechlorination performance was studied by constant current electrolysis. As indicated in Figure 3, the dechlorination efficiency was only 76.3% after 120 min electrolysis for the electrode in absence of MWCNTs. Functionalized MWCNTs would act as dopants to improve the conductivity of polymer films [37]. Therefore, the 4-CP would be dechlorinated more efficiently with the increase in the doping amount of MWCNTs until 8 mg (This amount was used throughout the subsequent experiments). However, further increasing MWCNTs did not result in a significant improvement. Anyway, addition of appropriate MWCNTs could promote the polymerization process and improve the polymer conductivity so that a better dechlorination performance was obtained.

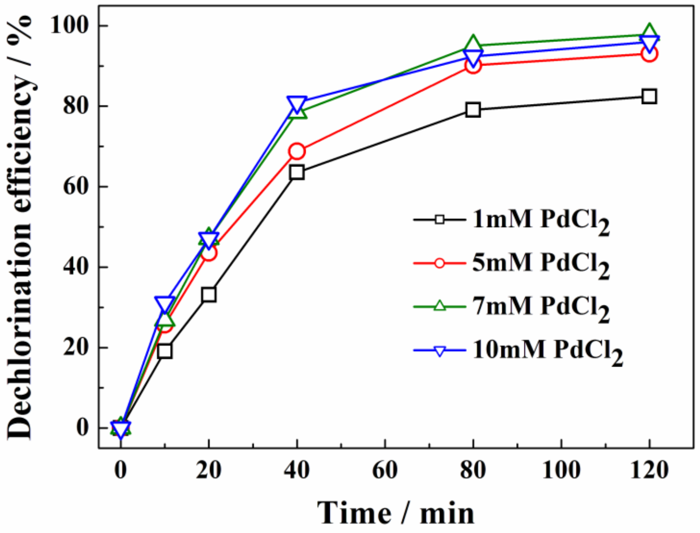

Figure 4. Effects of the concentration of $PdCl_2$ on the dechlorination efficiency (4-CP 100 mg/L, pH 2.2, Na_2SO_4 0.1 mol/L, current 1.0 mA/cm^2).

3.3. Effect of $PdCl_2$ concentration

Figure 4 shows the effects of the concentration of $PdCl_2$ on the performance of the Pd/PPy-MWCNTs/Ti electrode. As can be seen, the dechlorination efficiency of the 4-CP enhanced by about 13.5% with the increase in the concentration of $PdCl_2$ from 1 mM to 7 mM. This was because Pd was mainly responsible for the electrocatalytic dechlorination of 4-CP. Palladium could provide catalytic active sites to produce high concentration of reactive phase (chemical adsorption of H atoms, $H_{(ads)}$) [38], promoting chlorine removal. When the concentration of palladium chloride increased, more Pd nano particles would be electrodeposited, thus the electrode could provide more catalytic active centers. However, a higher concentration of palladium chloride used here, i.e. 10 mM $PdCl_2$, contributed to the dechlorination little instead. This was because too much deposition of Pd particles might enhance the effect of agglomeration.

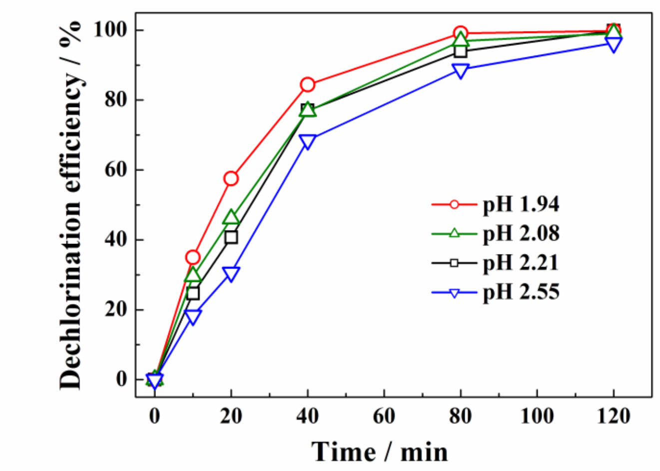

Figure 5. Dechlorination efficiency at different initial pH values using the Pd/PPy-MWCNTs/Ti electrode (4-CP 100 mg/L, $PdCl_2$ 7 mmol/L, Na_2SO_4 0.1 mol/L, current 1.0 mA/cm^2).

3.4. Effect of initial pH value

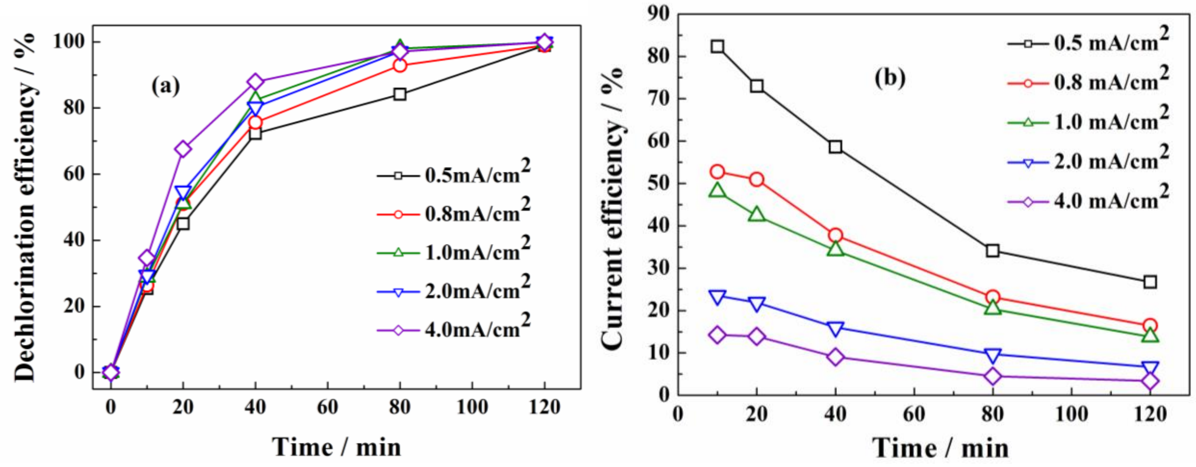

Figure 6. Effects of current density on the dechlorination efficiency (a) and the current efficiency (b) (4-CP 100 mg/L, $PdCl_2$ 7 mmol/L, pH 2.08, Na_2SO_4 0.1 mol/L).

A low pH value was beneficial to electrocatalytically reductive dechlorination because a large number of free hydrogen ions in acidic solution could occupy more active sites on the electrode surface and contribute to the generation of H_{ads} [38]. Under alkaline condition, 4-CP existed in the form of negative ions, and thus the electrostatic repulsion would prevent 4-CP from transferring to the electrode surface and hinder the reactions. Therefore, only acidic conditions were investigated here. Figure 5 shows the dechlorination efficiencies of 4-CP in different initial pH solutions. It could be seen that the initial pH values had a significant effect on the dechlorination process, but the dechlorination efficiencies were nearly identical after electrolysis for 120 min. Nevertheless, the terminal pH values varied greatly. At the initial pH value of 1.94, the rate of dechlorination was highest and the corresponding final pH was 2.62. At the initial pH of 2.08 and 2.21, the removal efficiencies of 4-CP were similar in the processes of dechlorination, but the terminal pH values were 6.06 and 11.24, respectivley. Taking into account the subsequent treatment of chlorphenol wastewater, such as biological methods, the terminal pH close to neutral was undoubtedly more appropriate. The results were coincident with what reported in the literatures [34-36].

3.5. Effect of current density

The current density had a significant effect on the electrochemically reductive process of 4-CP. As shown in Figure 6a, the dechlorination performed more quickly when higher current densities were used, whereas the removal efficiencies of 4-CP were almost identical at the end of dechlorination (120 min). This indicated that, to some extent, the electrode used here had a good catalytic activity even if a small current density was used. When the current density was higher than 1.0 mA/cm^2, the dechlorination efficiency enhanced slowly, especially, at the dechlorination time of 80 min. In view of the energy consumption during dechlorination, 1.0 mA/cm^2 was an optimal current density. This would be further discussed in the following section.

In the reductive electrolysis process, the side reaction of hydrogen evolution usually occurred and was even unavoidable. In our experiments, the side reaction also occurred and accelerated with the increase in the current density. Figure 6b exhibits the variation of current efficiency with current densities. Overall, the current efficiencies of dechlorination gradually decreased over time and also reduced with the increase in the current densities. When the current density was higher than 2.0 mA/cm^2, the current efficiencies were throughout lower than 25%. Therefore, considering both dechlorination efficiency and current efficiency, the optimum current density should be selected as 1.0 mA/cm^2. The corresponding current efficiency was 13.8%. This value was comparable to the results obtained in the literatures, where some similar polymeric pyrrole electrodes modified with surface active agents [34, 35] and the electrode modified with reduced graphene oxide [36] were used to dechlorinate chlorophenols.

3.6. Effect of supporting electrolyte

Sodium sulfate was selected as the supporting electrolyte in the experiments. As shown in Figure 7, the dechlorination efficiency enhanced with the concentration of Na_2SO_4 from 0.03 to 0.1

mol/L. This result revealed that the supporting electrolyte Na_2SO_4 provided a large amount of free ions in the solution. This was favorable to increasing the ionic strength and guaranteed the smooth flow of circuit [39], thus improving the dechlorination of 4-CP. It was worth noting that the dechlorination performance actually improved slightly when the Na_2SO_4 concentration increased from 0.08 to 0.1 mol/L. Accordingly, the effect of the concentration higher than 0.1 mol/L was not further examined.

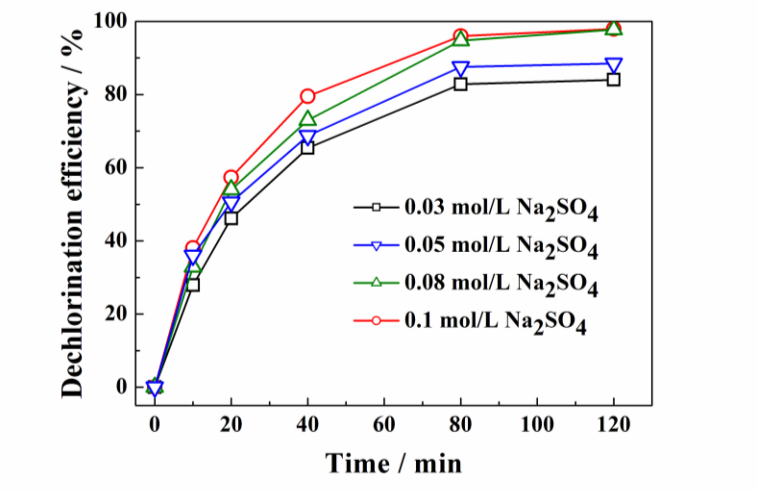

Figure 7. Effects of Na_2SO_4 concentration on the dechlorination of 4-CP (4-CP 100mg/L, $PdCl_2$ 7 mmol/L, pH 2.08, current 1.0 mA/cm^2).

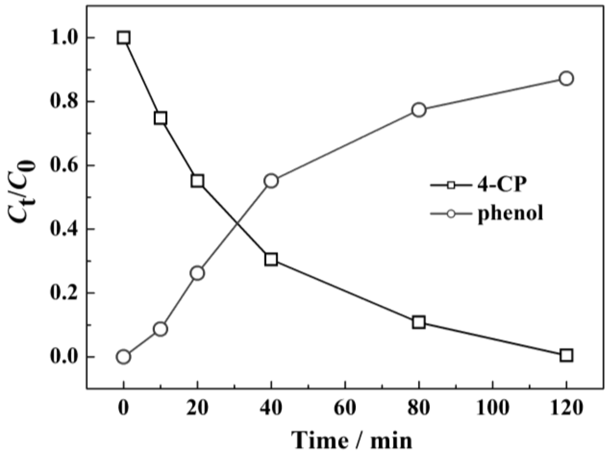

Figure 8. Dechlorination process analysis (4-CP 100 mg/L, $PdCl_2$ 7 mmol/L, pH 2.08, Na_2SO_4 0.1 mol/L, current 1.0 mA/cm^2).

3.7. Dechlorination

Under the optimized conditions, the main dechlorination product of 4-CP, i.e. phenol, was also examined. Figure 8 shows 4-CP and phenol varied over dechlorination time. As illustrated, the concentration of phenol gradually increased with the decrease in the amount of 4-CP. After electrolysis for 120 min, the dechlorination efficiency reached 99.56%, whereas the maximum concentration of phenol was 60.49 mg/L corresponding to 87.2% of the theoretical yield. This implied that although phenol was the predominant product, there were other products generated during dechlorination. It was reported in the literatures that phenol could be further reduced to cyclohexanone [40, 41]. Unfortunately, the precise composition was not effectively identified by HPLC-MS in this work. The removal process of 4-CP could be fitted by the pseudo first-order kinetics. Namely, $\ln(C_t/C_0)$ was linear with the dechlorination time. The fitted equation was $\ln(C_t/C_0) = -0.0389t$, $R^2 = 0.9673$. The rate constant normalized by current density obtained here for the Pd/PPy-MWCNTs/Ti electrode was 0.0389 min-1 mA-1 cm2. This value was 81.8% higher than that reported in the literature (0.0214 min-1 mA-1 cm2) for the Pd/RGO/Ni electrode [36].

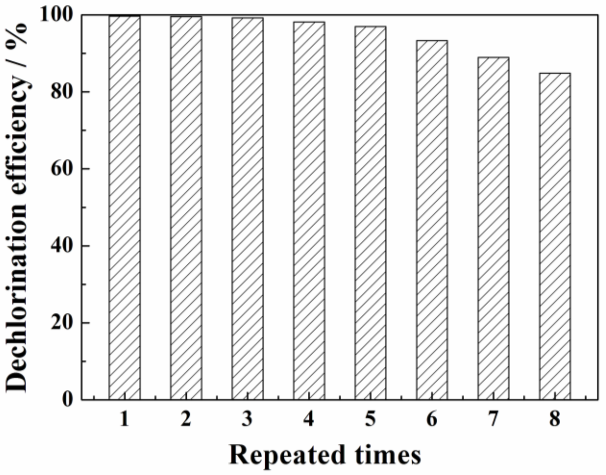

Figure 9. The dechlorination of 4-CP in eight reaction cycles using the Pd/PPy-MWCNTs/Ti electrode.

3.8. Stability of the Pd/PPy-MWCNTs/Ti electrode

In order to examine the stability of the Pd/PPy-MWCNTs/Ti electrode, eight successive experiments were conducted under the same experimental conditions. As seen in Figure 9, the dechlorination efficiency of 4-CP remained relatively high in the first six cycles (over 93.33%). In the following two cycles, the value decreased slightly to 84.6%. The reason for the mildly decrease of the electrode activity might be that, on one hand, the surface active sites would decrease due to the accumulation of adsorbates [25]. On the other hand, the loss of active component, i.e. Pd nanoparticles, would also lead to the deterioration of electrode activity, which could be proved by the SEM results (Figure 2d). Anyhow, the composite electrode prepared here was relatively stable even after being used for eight cycles. For comparison, a Pd/Ti electrode was prepared by directly electrodepositing Pd on a Ti mesh substrate. It was found that the dechlorination performance of the Pd/Ti electrode decreased by 37% after being used four times. To some extent, the existence of the PPy-MWCNTs layer improved the stability and performance of the Pd/PPy-MWCNTs/Ti electrode.

4. CONCLUSIONS

The Pd/PPy-MWCNTs/Ti composite electrode with high catalytic activity was successfully prepared via an electrodeposition process and used for the dechloriantion of 4-CP. The dechloriantion efficiency could be promoted significantly compared with no MWCNTs doping in the electrode. The electrode preparation and the electrocatalytic reaction conditions were optimized. The stability of the prepared electrode kept well in six repeated cycles and the dechlorination efficiency was over 93.3%. The dechlorination process followed the pseudo-first-order reaction in the experiments and phenol was the predominant product during dechlorination.

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