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Research Article

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Preparation of Pd modified electrode and its electrochemical degradation for 2, 4-dichlorophenol

Zhang Jian[1], Liu Huiling[1*], Fu Huan[1], Bai Haina[2], Mohamed Thabit[1] and Wang Bing[1]

[1]State Key Laboratory of Urban Water Resource and Environment, School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin, China
[2]School of Food Science and Engineering, Harbin Institute of Technology, Harbin, China

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ABSTRACT

This research we etched the surface of titanium plate by electrochemical methods and prepare Pd modified electrode by using electro-deposition to improve the load capacity of the matrix Ti. This process improved the ability of matrix Ti loading Pd and reduce the shedding Pd from Ti electrodes and extended the electrode's life. The apparent morphology and surface morphology were characterized by Scanning electron microscopy (SEM) method, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). That electrode was applied to electrochemical degradation of 2, 4-DCP through studying current intensity's effect on its degradation efficiency. In the degradation, 2, 4-DCP removal rate increased gradually with current intensity which went on to 5mA, the removal rate was 90.1%, then when it went on at 10mA and 20mA, the rate almost unchanged which is between 91.9% and 90.9%. The degradation of 2, 4-DCP followed false kinetics levels.

Keywords: Pd/Ti electrode 2, 4-dichlorophenol; Electrocatalysis; Modified electrode; Kinetics.

INTRODUCTION

Chlorophenols aromatic compounds are the typical symbol of toxic organics which is difficult to be removed by common water treatments[1]. Most of Chlorophenols are highly toxic and have three effects which are carcinogenic, teratogenicity and mutagenesis. At the same time, because of the long degradation period， it is hard to be removed from ecological environment[2]. Chlorophenols cover 25 kinds out of 129 most hazardous pollutants those were indicated in the CWA of USEPA[3], therefore in both Europe and China the Chlorophenols is defined as priority control toxic pollutants [4]. Because the structure of Chlorophenol which contains aromatic ring and the chlorine atom it can form a stable conjugate system with a highly toxicity and stability, and are difficult to biodegradable. The number of chlorine atoms, the higher level of toxic[5].

The common Chlorophenol processing methods mainly include physical -chemical methods [6-8], biochemical methods [9, 10] and chemical methods [1, 11]. Electrochemical treatment method commonly used as a modern processing method has been widely applied in the treatment of chlorine compounds pollutants. The stability of combination between Palladium electrode and the carrier is not enough in the application of Palladium modified electrodes. In this paper, substrate was modified by electrochemical method to improve the binding force between substrate and Palladium particles.

This paper apply the titanium plate etched in the surface by anodic oxidation method to increase the specifically designated surface area for the electrode substrate material. Palladium nanoparticles were loaded on the surface by the electrode position method that is made into palladium modified titanium electrode. Finally, the palladium modified titanium electrode was used for the degradation experiment of 2, 4-dichlorophenol (2, 4-DCP).

EXPERIMENTAL SECTION

2.1 Experimental materials and reagents
The purity of titanium is more than 99.5% in the titanium sheet purchased from Baoji and Baoye titanium-nickel Manufacturing Co., Ltd. NaF、Na_2SO_4、$PdCl_2$、2, 4-DCP are analytical reagent purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. HF is analytical reagent purchased from Beijing Chemical Workers. The water used in the experiment is deionized water.

2.2 Electrode preparation
The size of the strip titanium sheet is 90 mm x 10 mm x 0.5 mm. the effective work area part is 40 mm x 10 mm x 0.5 mm. In order to remove oil and oxide film from the surface of the titanium plate, at the beginning, the pretreatment of titanium sheet is necessary. Titanium sheet is separately placed in the Acetone and ethanol for 15min to remove oil with ultraphonic. Then, it is washed for 1min in the mixture of Hydrofluoric acid and nitric acid to remove the surface oxide. Next, it is rinsed again and again with a large amount of distilled water to remove fluoride ions on the surface of the titanium sheet. In the end, it is cleaned for 15min in deionized water with sonic oscillation. The cleaning titanium sheet is ready after drying.

Anodic oxidation method is used to electrochemical etching. The reactor is a composition of dc regulated power supply, electrolytic reaction pool and the constant temperature water bath pot. Electrolyte solution is a mixed solution of Na_2SO_4 and NaF in the process of anodic oxidation. While the anode is the previously prepared titanium sheet. The cathode is a pure platinum electrode.

The work cathode is the disposed titanium sheet after electrochemical etching and the anode is platinum sheet. The reactor is composed by constant potential rectifier, electrolytic reaction tank and collector type magnetic stirrer. Electrolyte solution is a mixed solution of Na_2SO_4 and $PdCl_2$. The electrical Current strength is 10 mA. Solution temperature is 40℃. Electrodeposition time is 60 min.

2.3 ElectrodeCharacterization
SEM is used to observe the surface characteristics of electrode including the distribution and dispersion of the electrode surface metal particle. X-ray Diffraction(XRD) is used to measure electrode surface of the catalyst particles, crystalline structure, grain size and structure of the elements. X-ray photoelectron spectroscopy(XPS) is used to analyze the binding energy of each element in order to determine the character of the different valence state elements in the sample.

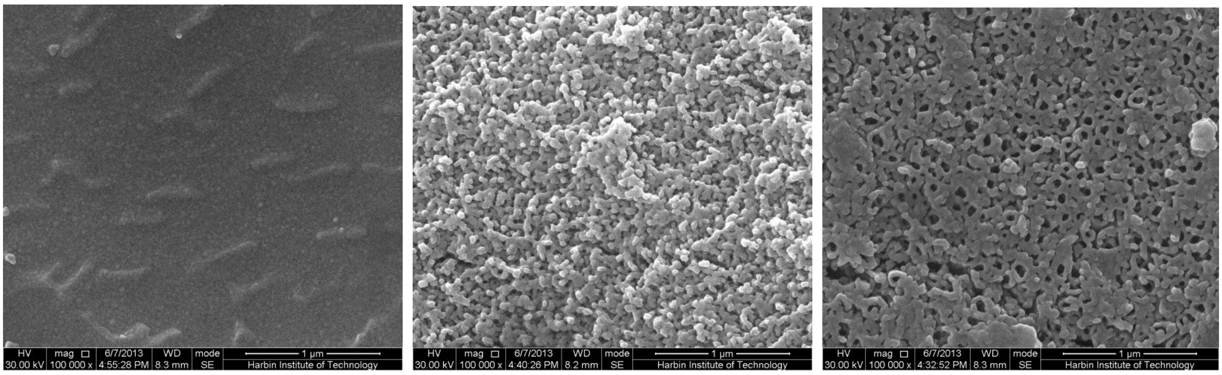
2.4 The performance evaluation of thePd/Ti electrode
For the performance evaluation of Pd/Ti electrodes, the target of degradation is 2, 4-DCP.2, 4-DCP 100 ml solution is prepared for every time with the concentration of 10 mg/L. The electrolyte solution is Na_2SO_4 with the concentration of 0.05mol/L. The work cathode is Pd/Ti electrode andanode is platinum sheet. The constant current method is used to the degradation of 2, 4-DCP. Thermal type magnetic stirrer is applied for reaction system to provide constant temperature and to eliminate the difference of concentration. The concentration of 2, 4-DCP is measured by HPLC. The removal efficiency is according to the following formula:

Removal efficiency $R = (C_0 - C)/C_0 * 100\%$

Where,$C_0$is the initial concentration of 2, 4-DCP; C is the real-time concentration of 2, 4-DCP.

RESULTS AND DISCUSSION

3.1 Results of the electrode characterization
3.1.1 Results of SEM test in electrode surface morphology
Scanning electron microscope is used to observe the surface morphology of titanium substrate, the etched titanium substrate, Pd/Ti electrode and analysis the change of before and after treatment. Pictured above is the surface morphology under the condition of 100000 x magnification resolution by scanning electron microscopy (SEM) analysis. It is observed that because of the smooth surface of titanium substrate, the metal loaded directly on the electrode substrate is easy to fall off from the surface. After electrochemical etching, the surface of the titanium substrate becomes uneven and shows an apparent spatial extension. Thus, the specific surface area has a significant beneficial increase of palladium particles' deposit on the surface. The deposition Pd particles form the space grid structure on the surface which changes the form of the titanium substrate surface. The distribution of Pd particles on the surface of the electrode and the opportunities of contact between Pd particles and targets in the solution has been greatly increased. Therefore, this method provides the possibility that 2, 4-DCP can be effectively removed.



(a)Titanium substrate **(b)The etched titanium substrate** **(c)Pd/Ti electrodes**

Fig. 1 SEM photos for electrodes under the same magnification

3.1.2 XRD test for the surface of the electrode

The test of X-ray diffraction for the prepared Pd/Ti electrodes reveals the crystal structure of the electrodes. XRD pattern for Pd /Ti electrode as shown in figure 2. The picture shows that the diffraction peak which has the value of 2 theta at 40.1, 46.7, 68.1, 82.1 and 86.6 respectively belongs to the crystal plane diffraction peak of Pd (111), Pd (002), Pd (022), Pd (311) and Pd (222)[12]. In addition, the diffraction peak in the value of 2 theta at 40.1 is not completely for Pd (111) crystal plane [13]. Meanwhile, the titanium substrate also has diffraction peak in here. The diffraction peaks of the titanium substrate materials is the main contribution to its peak value.

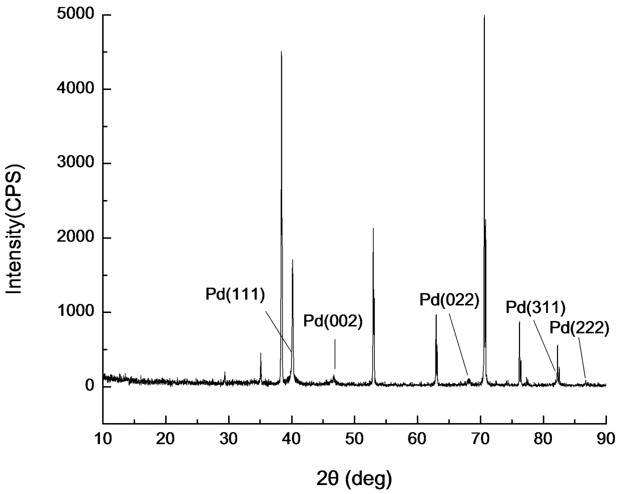


Fig.2 XRD pattern for Pd /Ti electrode

3.1.3 XPS test for the electrode

X-ray photoelectron spectroscopy analysis is adopted for the electrode to study the state of palladium on Pd/Ti electrodes. Figure 3 is the results of detection. From the narrow Pd (3d) scanning spectra in the figure 3b, we can see that two characteristic peaks of palladium appear at the binding energy of 336.8 eV and 342.2 eV. It also illustrates that palladium is successfully loaded on the electrode surface. At the same time, it shows that palladium on the Pd/Ti electrodes is zerovalent[14, 15].

3.2 The degradation performance of electrodes for 2, 4-DCP

3.2.1 Effects of electrolysis current on conversion efficiency of 2, 4-DCP

The degradation experiment of 2, 4-DCP is applied by using Pd/Ti electrodes as catalytic electrodes. The initial concentration of 2, 4-DCP is 10 mg/L, and electrolyte concentration of Na_2SO_4 is 0.05 mol/L. Effects of electrolysis current on conversion efficiency of 2,4-dichlorophenol is showed in figure 4.When the used electrical currents strength are 2 mA and 3mA, the removal rate of 2,4-dichlorophenol increases gradually per every second passes. The removal rate of 2, 4-DCP are 46.9% and 51.3% respectively. When the current strength increased to 5 mA, the removal rate also significantly increases during the processing time. The removal rate of 2, 4-DCP is 90.1%. When the current strength is increased to 10 mA and 20 mA, there weren't any improvements on the removal rate of 2,4-dichlorophenol above the maximum obtained removal rate. The removal rate of 2, 4-DCP are 91.9% and 90.9%

respectively. Besides, the removal efficiency at the current of 10 mA is higher than when using 20 mA. The reason is that side effects of water electrolysis appear as the current intensity increases and electrode potential also increases. The increasing electric current is mainly used for side effects.

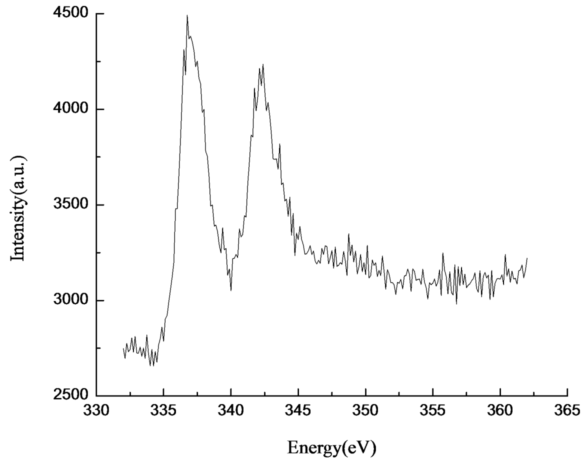


Fig. 3 XPS spectra of Pd/Ti electrode

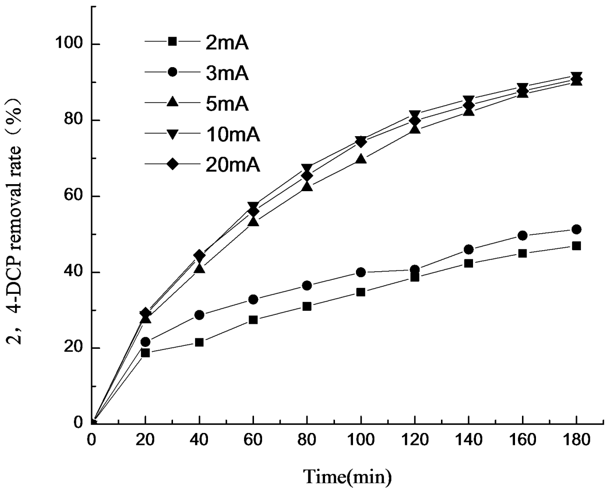


Fig.4 Effects of electrolysis current on conversion efficiency of 2,4-dichlorophenol

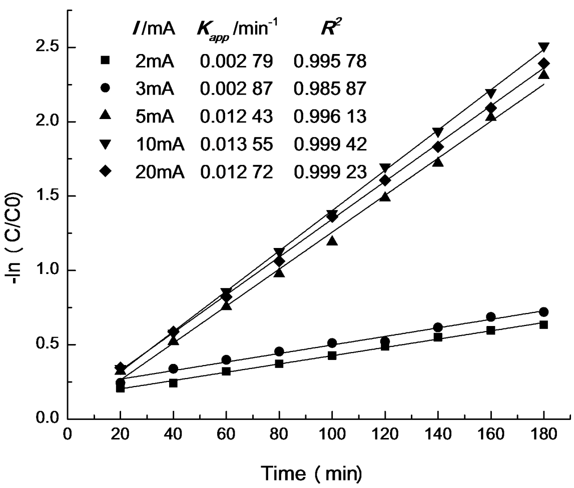


Fig.5 Kinetics of 2,4- dichlorophenol on Pd/ Ti electrode

3.2.2 Reaction dynamics

Due to the electrical current influence to removal rate of 2, 4-DCP, the curve fitting is adopted under different currents conditions as the concentration of2, 4-DCP changes with the time. The result is as shown in figure 5 illustrates that under the different currents, the 2, 4-DCP degradation with Pd / Ti electrodes meets L-H (Langmuir-Hinshelwoo) pseudo first order kinetics model.

CONCLUSION

The palladium modified titanium electrode was prepared by using modified titanium substrate by the electrochemical etching method. This method improves the ability of titanium substrate loading palladium and reduces the shedding of palladium in titanium electrode surface. The durability of the electrode increases in this method. From the results of SEM, XRD and XPS, palladium particles can be effectively loaded on the surface of titanium electrode, and palladium exists in the form of zero valent state. The degradation experiments for 2.4-DCP shows that the removal rate of 2.4-DCP increases gradually with the increase of current strength. When the current strength is 5 mA, the removal rate reaches to 90.1%. However, the removal of 2, 4-DCP reaches its maximum rate when the electrical current strength continues increasing to either 10 mA or 20 mA. The removal rate are 91.9% and 90.9% respectively. At last, the degradation of 2.4-DCP is in accordance with L-H pseudo first order reaction kinetics model under different current strength.

Acknowledgements

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