Contents lists available at SciVerse ScienceDirect







journal homepage: www.elsevier.com/locate/electacta

Electrochemical reductive dechlorination of 2,4-dichlorophenoxyacetic acid using a palladium/nickel foam electrode

Kairan Zhu, Shams Ali Baig, Jiang Xu, Tiantian Sheng, Xinhua Xu*

Department of Environmental Engineering, Zhejiang University, Hangzhou 310058, People's Republic of China

ARTICLE INFO

Article history: Received 16 December 2011 Received in revised form 5 March 2012 Accepted 7 March 2012 Available online 16 March 2012

Keywords: Dechlorination Electrochemical Palladium Nickel foam Kinetics

ABSTRACT

The electrochemical reductive dechlorination of 2,4-dichlorophenoxyacetic acid (2,4-D) in an aqueous solution was investigated at ambient temperature using a palladium/nickel foam (Pd/Ni foam) electrode in batch mode experiments. The catalytic electrode prepared using the standard chemical deposition method was further characterized using X-ray diffraction and scanning electron microscopy. It was observed that the reaction followed a pseudo-first-order kinetics model, the magnetic agitatorsupported system could achieve 87% removal of 2,4-D within 4h, which is 16% higher than the efficiency obtained under a nitrogen atmosphere. No organic intermediates other than phenoxyacetic (PA), o-chlorophenoxyacetic acid (o-CPA) and p-chlorophenoxyacetic acid (p-CPA) were observed to be generated during the reaction. The dechlorination efficiency depended on several factors including the current density, the palladium loading and the initial concentrations of the supporting NaCl electrolyte and the 2,4-D. The palladium loading and the NaCl concentration had a greater effect on the dechlorination kinetics of 2,4-D. Furthermore, the efficiencies of dechlorination and PA formation could be improved by optimizing the reaction system by modifying the ventilation conditions.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

The contamination of surface and ground waters by pesticides is a matter of environmental concern that is recognized because of the potential toxic, carcinogenic, mutagenic effects and mobility of the pesticides [1,2]. 2,4-D is an herbicide belonging to the chlorophenoxyacetic acid group. Because of its low cost and good selectivity, 2,4-D is one of the most commonly used herbicides in the agriculture sector around the world for controlling a wide range of broadleaf weeds and grasses from crops such as sugar cane, oil palm, cocoa and rubber [3,4]. The application of 2,4-D for high-yield farming is frequent in China and many other countries, and 2,4-D can be easily transported into water bodies as a result of surface runoff and leaching [5,6]. As a result of its widespread use and high water solubility, 2,4-D has been frequently detected as a major contaminant in both surface and ground water sources [7]. Conversely, 2,4-D is a weakly biodegradable pollutant that has existed in natural water, soil resources and agricultural food products [8,9]. Additionally, 2,4-D poses a risk for dioxin formation because it contains chlorine [10] and introduces threats to public health. The toxicological effects of 2,4-D on human health have recently been studied extensively by different researchers [11,12]. A connection between 2,4-D and the development of cancer in mammals, the endocrine disrupting activities in both animals and humans and irreparable damage to the central nerve system has been reported [11,12].

Due to the deleterious effects of 2,4-D on human health and the serious risks this chemical poses to wildlife, the World Health Organization (WHO) defined 2,4-D as moderately toxic (class II) and recommended a maximum allowable concentration of 0.1 ppm in drinking water in 1982 [13]. Subsequently, the United States Environmental Protection Agency (US-EPA) also recommended that the permissible level of 2,4-D in potable water be 0.1 ppm [14]. The prevalence and toxicity of 2,4-D has triggered the development of effective degradation techniques for this chlorinated aromatic herbicide that are aimed at environmental protection. To date, a variety of individual or integrated methods have been developed for the removal of pesticides from water, including adsorption, photocatalysis, photoelectrochemistry, sonoelectrochemistry, biological degradation, electrochemistry assisted by microwave and membrane technology [15-20]. Despite these advances, there is no universally applied technique available for the treatment of 2,4-D.

Numerous published articles regarding the electrochemical reductive dechlorination of chlorinated organic compounds (COCs) are widely available [21–24]. Matsunaga and Yasuhara [25] investigated the complete dechlorination of 1-chloronaphthalene using an electrochemical reduction process. Sun et al. [26] reported the electrochemical reductive dechlorination of 2,4-dichlorophenol. Because there are several intrinsic advantages of using mild reaction conditions, including a rapid reaction rate, good recovery of the catalyst and the absence of recalcitrant secondary contaminants

^{*} Corresponding author. Tel.: +86 571 88982031; fax: +86 571 88982031. *E-mail address:* xuxinhua@zju.edu.cn (X. Xu).

^{0013-4686/\$ -} see front matter © 2012 Elsevier Ltd. All rights reserved. doi:10.1016/j.electacta.2012.03.038

[27], the electrochemical reductive approach has been suggested as a promising method for the detoxification of chlorine-containing aromatic hydrocarbons [28]. This technology can work without additional chemicals and energy; thus, it is environmentally compatible, versatile, safe and easy to handle [19]. The electrochemical reductive approach is the most common technology used to address the purification of pesticides and related compounds in contaminated water. Tsyganok [29,30] explored the electrocatalytic reductive dechlorination of 2,4-D on carbon materials containing supported palladium and several other noble metals. Among the noble metals, palladium is generally utilized as the catalyst loaded on inert supports for the electrochemical reactions. Many publications have reported the application of palladium in the degradation of aromatic compounds in an aqueous medium via electrochemical dechlorination [31]. Currently, nickel foam is being extensively applied in controlling environmental pollution due to its high porosity and large specific surface area, which are desirable characteristics for hydrogenation catalysts or electrode materials in rechargeable batteries [32].

In the current study, the electrochemical reductive dechlorination method was chosen because of its affordability and ecological importance. The aim of this work was to evaluate the performance of a Pd/Ni foam as the working cathode for the electrochemical reductive dechlorination of 2,4-D in a two-compartment electrochemical system. Nickel foam was also employed as the electrode substrate. Various factors that might affect the dechlorination of 2,4-D were systematically investigated, including the initial concentrations of the supporting electrolyte NaCl and 2,4-D, the applied current density and the palladium loading rate. Moreover, to improve the efficiency of dechlorination under relatively optimal conditions, the reaction system was optimized using different ventilation conditions in the cathode chamber. The kinetics of the electrochemical dechlorination of 2,4-D using the Pd/Ni foam electrode were also studied. We chose NaCl as the supporting electrolyte based on the fact that the actual wastewaters contain NaCl [33]. Additionally, many studies have reported the use of NaCl as the widely used supporting electrolyte [15,34].

2. Experimental

2.1. Materials and methods

Palladium chloride (PdCl₂; ≥99.97%) was used as the main source of palladium and was purchased from the Sinopharm Chemical Reagent Co., Ltd., China. The chemical was of analytical grade and was used as received without any further purification. The nickel foam from Shenzhen Rolinsia Power Materials, Ltd., was used as the electrode. 2,4-D (\geq 97%), p-chlorophenoxyacetic acid (p-CPA; >98%) and phenoxyacetic acid (PA; >98%) were obtained from Jingchun Reagent Co., Ltd., Shanghai, o-Chlorophenoxyacetic acid (o-CPA; >98%) was purchased from Alfa Aesar Chemical Co., Ltd., Tianjin. The original 2,4-D did not contain o-CPA or p-CPA. N₂ gas (\geq 99.9%) stored in a steel cylinder was provided by the Jingong Special Gas Co., Ltd., China. A stock solution of 2,4-D with a concentration of 5 g L^{-1} was prepared by dissolving 0.25 g of 2,4-D in methanol and diluting this solution to 50 mL in a volumetric flask. The stock solution was stored in a refrigerator at 4°C before use. The reaction solutions were prepared by diluting the stock solution of 2,4-D to the desired concentration using a 2 g L^{-1} aqueous solution of NaCl.

2.2. Electrode preparation and characterization

Prior to palladization, the nickel foam $(20 \text{ mm} \times 30 \text{ mm}; \text{ thick-ness}, 1.2 \text{ mm}; \text{ pore density}, 110 ppi; S_{BET}, 1.2 \text{ m}^2 \text{ g}^{-1})$ was cleaned and etched using the following steps. After ultrasonic cleaning in

acetone for 20 min, the nickel foam was rinsed with deionized water and immersed in $80 \, g \, L^{-1}$ sulfuric acid for 5 min to remove the oxide layer. Finally, the nickel foam was thoroughly washed with deionized water.

For the chemical deposition of palladium, a supporting nickel foam electrode was placed in a conical flask (with a volume of 100 mL) consisting of 20 mL of 10 mM PdCl₂ and 30 mM NaCl. This electrode-containing solution was then incubated at 32 °C with shaking until the original yellow solution became colorless.

The surface morphology of the Pd/Ni foam electrode was observed under an XL-30 environmental scanning electron microscope (ESEM; Philips, Netherlands) at 2 kV, and the X-ray diffraction (XRD) analysis of the structural properties of the electrode was performed using a Rigaku D/max 2550 PC X-ray diffractometer. The analysis was performed at 40 kV and 300 mA, and copper metal radiation was used to produce X-rays ($\lambda = 0.1542$ nm).

2.3. Bulk electrolysis

The electrochemical reductive dechlorination of 2,4-D was carried out in a cell that consisted of two compartments separated by a Nafion-117 cation-exchange membrane to prevent the diffusion of the chloride ions produced in the cathode compartment into the anode compartment to form Cl₂. A Pd/Ni foam electrode was used as the cathode, and a platinum foil was used as the anode. The distance between the anode and the cathode was approximately 80 mm. The cathode compartment contained 80 mL of a 2 g L^{-1} aqueous solution of NaCl with a known amount of 2,4-D, and the anode compartment contained 40 mL of a $2 g L^{-1}$ aqueous solution of NaCl. A reductive atmosphere around the cathode was maintained by sparging with nitrogen during the dechlorination experiments. The electrolysis was performed at a constant current density, which was controlled by an SK1760SL20A direct-current regulated power supply for 4 h, and the samples (0.8 mL) were withdrawn from the cathode compartment at pre-determined time points for further analysis.

2.4. Analytical methods

The concentrations of 2,4-D, o-CPA, p-CPA and PA that were generated during the electrolysis were determined using a SHI-MADZU high-performance liquid chromatograph at 283 nm with an Agilent TC-C18 column (150×4.6). The mobile phase was a 60:40 (v/v) mixture of methanol:water (0.2% H₃PO₄), and a flow rate of 0.5 mL min⁻¹ was used. The volume of the injected sample was 20 μ L.

3. Results and discussion

3.1. Characterization of electrodes

Fig. 1 shows the XRD patterns of the nickel foam electrode, the Pd/Ni foam electrode before the dechlorination reaction and the Pd/Ni foam electrode after the reaction. All of the patterns exhibited peaks at 44.1° , 51.5° and 76° , corresponding to the (1, 1, 1), (2, 0, 0) and (2, 2, 0) planes of nickel metal, respectively. Additionally, three diffraction peaks at 39.7° , 46.2° and 67.7° corresponding to the weak (1, 1, 1), (2, 2, 0) and (3, 1, 1) planes of palladium could also be observed in the patterns of the palladium-deposited samples, indicating the presence of palladium on the surface of the electrodes. This result was important because it directly impacted the efficiency of the dechlorination. The difference between Fig. 1(b) and (c) demonstrates that the presence of palladium was slightly modified after the reaction. The strength of the palladium peak decreased after the dechlorination reaction compared with that before the reaction at the same degree. This result could be due



Fig. 1. XRD patterns of (a) the nickel foam electrode, (b) the Pd/Ni foam electrode before the reaction and (c) the Pd/Ni foam electrode after the reaction.

to the contamination or passivation of palladium or the loss of palladium from the nickel foam during the dechlorination process.

SEM was used to image the surface morphology of a fresh nickel foam and the Pd/Ni foam, and the results are shown in Fig. 2. The nickel foam had a smooth surface with clear zigzag lines (Fig. 2(a)), and the fresh Pd/Ni foam electrode exhibited a thick uniform film of palladium with deep grooves on the surface of the Pd/Ni foam electrode (Fig. 2(b)), indicating that palladium was successfully deposited on the nickel foam. This surface coating appeared to enhance the dechlorination efficiency. In contrast, the palladium film appeared thinner after 4 h of reaction, as shown in Fig. 2(c). The grooves became less prominent, more granular palladium domains were observed and the zigzag nickel lines were looming. These observations might be due to the loss of part of the palladium film during the reaction, which could also be verified by the XRD results.

According to the results of the Brunauer–Emmett–Teller (BET) test, the surface area of the Pd/Ni foam was $3.5 \text{ m}^2 \text{ g}^{-1}$, which is much larger than that of the nickel foam (S_{BET}: $1.2 \text{ m}^2 \text{ g}^{-1}$). Thus, the large surface area of the palladium particles provided adsorption sites for [H] and pollutants.

3.2. Factors affecting 2,4-D dechlorination

The catalytic dechlorination of 2,4-D using a Pd/Ni foam electrode was investigated at ambient temperature. During the catalytic dechlorination process, 2,4-D was initially transformed into o-CPA and p-CP and then converted to PA. Hence, o-CPA and p-CPA were the chlorinated intermediates, and PA was the sole final organic product of the reaction. No other chlorinated intermediates or final organic products were detected.

3.2.1. Effects of NaCl concentration on 2,4-D dechlorination

NaCl was selected as the supporting electrolyte in the present study. The effect of the NaCl concentration on the dechlorination of 2,4-D using the Pd/Ni foam electrode was examined. Fig. 3 illustrates the dechlorination of 2,4-D using the Pd/Ni foam electrode at various NaCl concentrations ranging from 1 gL^{-1} to 4 gL^{-1} . As shown in Fig. 3, the 2,4-D concentration rapidly decreased, and the removal percentage reached 71% in 4 h using the Pd/Ni foam electrode in the presence of a 2 gL^{-1} NaCl solution. In contrast, only approximately 65%, 48% and 18% of the 2,4-D was removed in the



Fig. 2. SEM micrographs of (a) the fresh nickel foam electrode, (b) the Pd/Ni foam electrode and (c) the Pd/Ni foam electrode after the dechlorination of 2,4-D.

presence of 4 g L^{-1} NaCl, 1.5 g L^{-1} NaCl and 1 g L^{-1} NaCl, respectively. Meanwhile, PA and inorganic chlorine were detected as final products of the reaction. A low NaCl concentration decreased the PA production rate, which was expressed as the ratio of the actual



Fig. 3. Effects of the supporting electrolyte NaCl concentration on the 2,4-D dechlorination using the Pd/Ni foam electrode (initial concentration of 2,4-D: 50 mg L^{-1} , current density: 1.667 mA cm⁻² and palladium loading: 1.78 mg cm⁻²).

PA amount produced to the theoretical PA amount during the total dechlorination of 2,4-D, from 70% in 2 g L^{-1} NaCl to 13% in 1 g L^{-1} NaCl in 4 h. The coinciding decrease of both the 2,4-D removal percentage and the PA production rate with the decrease in the NaCl concentration suggested that the presence of NaCl played a significant role in the dechlorination of 2,4-D. Concurrent with the removal of 2,4-D, we observed a lower PA production in 4 g L^{-1} NaCl, which was 57%. Furthermore, we observed that the initial output potential differences were negatively correlated with the NaCl concentration was increased from 1 g L^{-1} , 1.5 g L^{-1} and 2 g L^{-1} to 4 g L^{-1} , the initial output potential differences were 19.3 V, 14.3 V, 11.0 V and 9.8 V, respectively. Consequently, we chose 2 g L^{-1} NaCl as the supporting electrolyte in the subsequent studies.

The underlying phenomenon appeared to be that the use of a NaCl solution as the supporting electrolyte provided a large number of conductive free ions in the solution, which ensured the smooth flow of the circuit. In addition, when the NaCl concentration was high, more conductive free ions would be ionized to exist outside the system, thus increasing the ionic strength and the conductivity of the solution [35] and enhancing the dechlorination of 2,4-D. This explanation also supported the phenomenon that explains why the initial output potential difference increased as the NaCl concentration decreased at the beginning of the reaction process. Notably, the efficiency of 2,4-D dechlorination would actually decrease slightly if the NaCl concentration increased continually.

3.2.2. Effects of 2,4-D initial concentration on 2,4-D dechlorination

Four different 2,4-D initial concentrations (20, 35, 50 and 80 mg L⁻¹) were employed in batches during the reaction process. The effective electrode area remained constant during the reaction. The 2,4-D reduction profiles with different initial 2,4-D concentrations using the Pd/Ni foam electrode and the amounts of chlorinated intermediates detected are shown in Fig. 4. The removal percentages of 2,4-D reached 34, 63, 60 and 71% after 2 h and then increased to 45, 70, 71 and 80%, respectively, after 4 h of electrolysis. It was obvious that the chlorine atoms were removed individually from the benzene ring of 2,4-D, which is similar to other dechlorination processes of chlorinated organic compounds [36]. CPA was detected as the only intermediate generated during the electrolysis, and the chlorinated intermediate was observed to continually increase throughout the electrolysis (Fig. 4). However, it should be noted that the accumulation of CPA did not simply indicate that there was no dechlorination reaction of CPA. With an increased number of chlorine atoms, the electron density on the benzene ring will be lower and vice versa. The lower electron density of benzene is more susceptible to nucleophilic attack of the reducing agents, so the chlorine atoms can easily be replaced by other atoms [37]. Therefore, it was observed that the chlorine intermediate was continuously accumulated during the experiments. This observation could be explained by studying the kinetics of the reaction and calculating the reaction rate constants as explained in Section 3.5.

The PA that was detected as the final product continuously increased with the degradation of the target pollutant 2,4-D throughout the electrolysis. The PA production percentages observed were nearly 28, 63, 70 and 77%, respectively, when the initial 2,4-D concentration increased from 20, 35 and 50 to 80 mg L^{-1} after 4 h of the electrolysis.

Although the 2,4-D removal percentages were similar when the initial 2,4-D concentration was high, the absolute 2,4-D removal amount increased with the increase of the initial 2,4-D concentration. The absolute 2,4-D removal amount increased from 9, 24 and 35 to 64 mg L^{-1} in 4 h as the initial 2,4-D concentration was varied from 20, 35 and 50 to 80 mg L^{-1} .

3.2.3. Effects of current density on 2,4-D dechlorination

The 2,4-D reduction profiles at various current densities and the amounts of the chlorinated intermediates detected in the reaction are shown in Fig. 5. Increasing the apparent current density from 0.833 mA cm⁻² (according to the surface area; actual current density: $0.00042 \text{ mA cm}^{-2}$) to 1.667 mA cm^{-2} (actual current density: 0.00083 mA cm⁻²) elicited a distinct increase in the 2,4-D conversion efficiency from 35% to 71% in 4h using the Pd/Ni foam cathode for the electrolysis. However, a further increase of the apparent current density from $1.667 \,\mathrm{mA \, cm^{-2}}$ to $2.5 \,\mathrm{mA \, cm^{-2}}$ (actual current density: 0.00125 mA cm⁻²) did not enhance the dechlorination efficiency, but instead slightly reduced the dechlorination efficiency from 71% to 68% using the Pd/Ni foam cathode. In general, a lower current density could guarantee that a sufficient amount of fresh adsorbed reactive hydrogen ((H)_{ads}M) is generated by the electrolysis of water, thereby ensuring an increase in the dechlorination rate. At a relatively higher current density, the electric potential would be more negative, consequently leading to a faster generation of (H)_{ads}M. However, a large portion of adsorbed reactive hydrogen tends to generate H₂ gas rather than reacting with 2,4-D at a relatively high current density. Thus, the polarized part of the catalysts that are thought to adsorb pollutants will be covered by a H₂ layer, which will hinder the further mass transfer of the chlorinated organics to the polarized active sites [38]. This hindrance leads to the inhibition or the reduction of the 2,4-D conversion. Based on these results, 1.667 mA cm⁻² was chosen as the current density to be used for the remainder of this study as an optimal value for the dechlorination process

During the catalytic degradation process, 2,4-D was initially reduced to o- and p-CPA and then converted to PA, which was evident from the concentration changes. The reduction of 2,4-D resulted in an increased PA concentration. Hence, PA and inorganic chlorine were detected as the final products of the reaction. The generation and further catalytic degradation process of o- and p-CPA during the same reaction period with different current density values are presented in Fig. 5(c) and (d). The results demonstrated that the generation of o-CPA was much faster than that of p-CPA, and without considering the current density value, p-CPA did not appear until the reaction was allowed to proceed for 1 h. In addition, with the ongoing degradation process, the o-CPA production was much higher than that of p-CPA. This difference is likely because the chlorine atom located at the para position was more reactive than that at the ortho position as a result of steric hindrance [39]. The chlorine located at the para position was surrounded by a much larger space than was the chlorine located at the ortho-position, and it could be easily replaced by adsorbed reactive hydrogen. Therefore, the generation of o-CPA occurred faster than did the generation of p-CPA, and the amount of o-CPA generated was much higher than that of p-CPA.

Although o-CPA and p-CPA could be reduced to PA in the further catalytic degradation process, it was observed that the o-CPA and p-CPA concentrations were continually increasing instead of decreasing even after 4 h of the reaction process. Hence, the concentration of o-CPA was much higher than that of p-CPA during the catalytic dechlorination of 2,4-D.

3.2.4. Effects of palladium loading on 2,4-D dechlorination

The reductive dechlorination of 2,4-D using the Pd/Ni foam electrode occurs on the surface of particles; hence, palladium loading is also a significant variable. The amount of surface area available is among the most significant experimental variables affecting the contaminant reduction.

Several electrodes with different palladium loadings $(0.44 \text{ mg cm}^{-2}, 0.855 \text{ mg cm}^{-2}, 1.33 \text{ mg cm}^{-2}, \text{ and } 1.78 \text{ mg cm}^{-2})$ were prepared by varying the amount of PdCl₂ available while



Fig. 4. Effects of the initial concentration of 2,4-D on the 2,4-D dechlorination using the Pd/Ni foam electrode (supporting electrolyte NaCl concentration: $2 g L^{-1}$, current density: 1.667 mA cm⁻² and palladium loading: 1.78 mg cm⁻²).

making the electrode to explore the influence of catalyst loading on the dechlorination of 2,4-D. Fig. 6 shows that the dechlorination rate was strongly influenced by the palladium loading during the reaction. As the palladium loading was increased from 0.44 mg cm^{-2} , 0.885 mg cm^{-2} and 1.33 mg cm^{-2} to 1.78 mg cm^{-2} , the 2,4-D removal percentage using the Pd/Ni foam electrode increased dramatically from 19%, 39% and 47% to 71%, respectively. Consequently, the production yield of PA increased from 20%, 34% and 50% to 70%, respectively. Moreover, both the 2,4-D removal percentage and the PA production rate increased with the increase in the palladium loading, suggesting that palladium played an important role as a catalyst in the dechlorination of 2,4-D.

3.3. Reaction and equilibrium analysis

A quantitative analysis of the intermediates is required to determine the conservation of mass during the dechlorination of 2,4-D. Fig. 7(a) illustrates the intermediates and the carbon mass balance during the dechlorination of 2,4-D using the Pd/Ni foam electrode. Other conditions such as the supporting electrolyte concentration, the initial concentration of 2,4-D, the current density and the palladium loading were $2 g L^{-1}$, $50 mg L^{-1}$, $1.667 mA cm^{-2}$ and $1.78 mg cm^{-2}$, respectively.

The 2,4-D concentration decreased with the increasing electrolysis time, and the reaction intermediates were released



Fig. 5. Effects of the current density on the 2,4-D dechlorination using the Pd/Ni foam electrode (supporting electrolyte NaCl concentration: $2 g L^{-1}$, initial concentration of 2,4-D: 50 mg L⁻¹ and palladium loading: 1.78 mg cm⁻²).



Fig. 6. Effects of palladium loading on the 2,4-D dechlorination using the Pd/Ni foam electrode (supporting electrolyte NaCl concentration: 2 g L^{-1} , initial concentration of 2,4-D: 50 mg L⁻¹ and current density: 1.667 mA cm⁻²).

accompanied by the sequential hydrogenolysis of 2,4-D, indicating the absence of any additional organic products apart from CPA and PA. The initial concentration of 2,4-D was 50 mg L⁻¹, and the total carbon mass balance recorded was greater than 99.5%; thus, almost no carbon mass was lost during the reaction. The carbon loss that



Fig. 7. Dechlorination of 2,4-D (a) and the current efficiency (b) during the electrochemical dechlorination of 2,4-D using the Pd/Ni foam electrode (supporting electrolyte NaCl concentration: $2 g L^{-1}$, initial concentration of 2,4-D: $50 mg L^{-1}$, current density: 1.667 mA cm⁻² and palladium loading: 1.78 mg cm⁻²).



Fig. 8. Variation of the concentration of 2,4-D and the final product PA using the Pd/Ni foam electrode under different ventilation conditions (supporting electrolyte NaCl concentration: $2 g L^{-1}$, initial concentration of 2,4-D: $50 m g L^{-1}$, current density: 1.667 mA cm⁻² and palladium loading: 1.78 mg cm⁻²).

was observed could be considered within the allowable error limits, such as operation error, test error, etc. The 2,4-D concentration rapidly decreased within the first 1 h of the reaction, while the final PA product was generated quickly and approached the maximum attainable limit.

The current efficiency (CE) of the 2,4-D dechlorination in the period of t=0-t using the Pd/Ni foam electrode can be calculated as follows:

$$CE = \frac{(n_1C_{PA} + n_2(C_{o-CPA} + C_{p-CPA}))FV}{Q}$$
$$= \frac{(n_1C_{PA} + n_2(C_{o-CPA} + C_{p-CPA}))FV}{\int_{t=0}^{t=t} I \, dt}$$

In these equations, n_1 and n_2 are the electron transfer numbers per one molecule of PA $(n_1 = 2)$ and CPA $(n_2 = 4)$, respectively, C_{PA} , $C_{\text{o-CPA}}$ and $C_{\text{p-CPA}}$ are the concentrations (M) of PA, o-CPA and p-CPA, respectively, F is the Faraday constant (96,500 As mol^{-1}), V is the volume of the total cathode electrolyte (L), Q is the total electric charge (As) and *I* is the electrolysis current (A). As calculated using the above equation, the CE of the 2,4-D dechlorination using the Pd/Ni foam electrode is shown in Fig. 7(b). Although the current efficiency of the dechlorination reaction obtained in the study did not exceed 10% and the current efficiency diminished as the electrolysis time increased beyond 1 h, the 2,4-D dechlorination to PA was readily achieved. The results [30] presented in A.I. Tsyganok's study also demonstrated a low current efficiency, which did not exceed 10%. Li et al. [40] described a decay in the current efficiency with thane increase in the reaction time. The current efficiency can be influenced by many factors, such as the catalytic electrode, the current density and the pollutant type. We could not determine which factor has a greater influence on the current efficiency in this study. Future work will focus on improving the current efficiency.

3.4. Improved dechlorination efficiency

To improve the dechlorination efficiency, many researchers have already conducted studies on various applicable options [41]. However, this part of the investigation introduces another applied perspective in improving the dechlorination efficiency.

Fig. 8 demonstrates the results of the laboratory-scale dechlorination of 2,4-D and the PA production rate under different ventilation conditions. The best dechlorination efficiency was obtained when the reaction was stirred using a magnetic agitator during the reaction process. The removal percentage of 2,4-D was 87%, and the PA production rate reached 83% when the reaction underwent magnetic stirring. Furthermore, these reaction conditions resulted in an efficiency that was 16% higher than the efficiency obtained in a recent study conducted in the presence of nitrogen, which was aimed to guarantee the reductive atmosphere of the cathode chamber throughout the degradation process [26]. Additionally, it was estimated from the trend charts of 2,4-D and PA that the reaction rate remained relatively stable during the entire degradation process under the magnetic stirring conditions, whereas the reaction rates during the entire experimental procedure under the nitrogen atmosphere were changed. These phenomena can be explained by the mechanism of the electrochemical reductive dechlorination reaction. It is well known that the adsorbed reactive hydrogen that is produced on the surface of the cathode is used to break the C--Cl bond and replace the chlorine atom on the benzene ring of chlorinated organic compounds [36,42]. This process is the most important step of the 2,4-D dechlorination reaction, which results in the reduction or even the disappearance of the toxicity of 2,4-D. Thus, it can be observed that the generated reactive hydrogen plays an important role in the dechlorination of 2,4-D. However, this reactive hydrogen may be stripped off by nitrogen gas throughout the reaction and thus may impede the reaction. The ventilation conditions are thus critical for this type of reaction.

Two sets of experiments were conducted to investigate the effect of the presence of air on the reaction. The removal percentages of 2,4-D reached up to 43% and 26%, and the PA productions were 45% and 14%. Magnetic stirring was used to achieve an even distribution of the reaction solution in the cathode chamber during the entire reaction process, and the reactive hydrogen generated could stably be adsorbed onto the electrode surface, thus facilitating the dechlorination reaction. However, although the presence of nitrogen in the cathode chamber could ensure the reductive atmosphere, it affected the dechlorination efficiency. The presence of gases reduced the efficiency of 2,4-D dechlorination by causing the reactive hydrogen to be stripped from the surface of the catalytic electrode or, more often, to be completely removed from the reaction system. Significantly, the reductive dechlorination process was negatively affected in the presence of the air because the air contains more than 20% oxygen. These batch-mode experiments suggested that the reaction system could be optimized by modifying the ventilation, and the electrochemical reductive 2,4-D dechlorination using the Pd/Ni foam catalytic electrode performed better under magnetic stirring conditions.

3.5. Electrode recovery

Good reproducibility and stability are generally considered to be important factors in choosing an ideal electrode. The electrode stability was evaluated in terms of the change of the 2,4-D removal percentage using the same Pd/Ni foam electrode after three consecutive dechlorination cycles. All of the reactions were conducted under magnetic stirring conditions. Fig. 9 shows the removal percentage of 2,4-D in each 4 h experiment. The 2,4-D removal percentage decreased from 87% or 84% to 78% at the Pd/Ni foam electrode. This result suggested that the stability of the electrode was not very good. This phenomenon might be due to the desquamation of palladium particles from the catalysts [43]. This result was consistent with the characterization of the electrodes described in Section 3.1, which caused a reduction of the catalyst lifetime.



Fig. 9. Removal percentage of 2,4-D using the same Pd/Ni foam electrode under magnetic stirring conditions for three cycles of dechlorination (supporting electrolyte NaCl concentration: 2 g L^{-1} , initial concentration of 2,4-D: 50 mg L^{-1} , current density: 1.667 mA cm⁻² and palladium loading: 1.78 mg cm⁻²).

3.6. Kinetics for the dechlorination of 2,4-D by a freshly prepared Pd/Ni electrode

Fig. 7 illustrates the transformations of 2,4-D to PA using the Pd/Ni foam electrode, and the values in the figure are expressed in molar concentrations. The organic products consisted of PA and o- and p-CPA. Another two sets of experiments were performed in which the initial waste waters contained 50 mg L^{-1} o-CPA and 50 mg L^{-1} p-CPA. The other conditions were the same as described in Section 3.3. PA was detected as the only organic product. Thus, it was deduced that the hydrodechlorination step of 2,4-D can be described in the following sequence:

$$2, 4-D \xrightarrow{k_1} CPA \begin{cases} o-CPA + Cl^{-\frac{k_{21}}{2}}PA + 2Cl^{-1} \\ p-CPA + Cl^{-\frac{k_{22}}{2}}PA + 2Cl^{-1} \end{cases}$$
(1)

In this sequence, CPA represents the total combination of o-CPA and p-CPA in the reaction process. Previously established literature results have shown that the degradation reaction of chlorinated solvents in an aqueous solution followed a pseudo-first-order kinetics mechanism [44]. The corresponding reaction rate equation for the disappearance of 2,4-D, o-CPA and p-CPA can be represented as follows:

$$\frac{-dC_{2,4-D}}{dt} = k_1 C_{2,4-D} \tag{2}$$

$$\frac{-dC_{\text{o-CPA}}}{dt} = k_{21}C_{\text{o-CPA}} \tag{3}$$

$$\frac{-dC_{\text{p-CPA}}}{dt} = k_{22}C_{\text{p-CPA}} \tag{4}$$

After solving the above simultaneous rate equations, the reaction leads to the following molar fractions:

$$\alpha_{2,4-\mathrm{D}} = e^{-k_1 t} \tag{5}$$

$$\alpha_{\text{o-CPA}} = e^{-k_{21}t} \tag{6}$$

$$\alpha_{\rm p-CPA} = e^{-k_{22}t} \tag{7}$$

In the above equations, α represents the molar fraction of the subscript compound to the initial concentration of the parent compound (i.e., 2,4-D). The *k* values were derived from fitting the experimental data into Eqs. (5)–(7) according to the non-linear least-square regression. The results showed that the k_1 value for

396

 Table 1

 k1 values under different reaction conditions.

Reaction conditions	$k_1 ({ m min}^{-1})$
NaCl concentration (g L^{-1})	
1	0.0008
1.5	0.0027
2	0.005
2,4-D initial concentration (mg L ⁻¹)	
20	0.0043
35	0.0047
50	0.005
80	0.0061
Current density (mA cm ⁻²)	
0.833	0.0018
1.667	0.005
2.5	0.005
Palladium loading (mg cm ⁻²)	
0.44	0.0007
0.885	0.0018
1.33	0.0018
1.78	0.005
Ventilation condition	
Magnetic stirring	0.0088
N ₂	0.005
No ventilation	0.0025
Air	0.0012

2,4-D dechlorination was 0.005 min^{-1} , and the k_{21} and k_{22} values for o-CPA and p-CPA dechlorination were 0.0033 min^{-1} and 0.0037 min^{-1} , respectively. From the calculated data, we could infer that the k_{21} and k_{22} values were smaller than the k_1 value for 2,4-D dechlorination. This result is consistent with the common phenomenon that CPA accumulated continually as the intermediates during the 2,4-D dechlorination reaction.

Table 1 lists the k_1 values under different reaction conditions. These data showed that k_1 value for the 2,4-D dechlorination increased from 0.0008 or 0.0027 to 0.005 min⁻¹ with increasing NaCl concentrations from 1 or 1.5 to $2 g L^{-1}$. However, the k_1 did not change significantly when the initial concentration of 2,4-D was increased from 20, 35 or 50 to 80 mg L^{-1} . In short, the k_1 value for the 2,4-D dechlorination changed from 0.0018 to 0.005 min⁻¹ when the current density was increased from 0.833 to 1.667 mA cm⁻², but this value did not increase with a further increase in the current density to 2.5 mA cm^{-2} . The k_1 value also varied from 0.0007, 0.0018 and 0.0018 to 0.005 min⁻¹ with increases in the palladium loading from 0.44, 0.885 and 1.33 to 1.78 mg cm^{-2} , respectively. Finally, this k_1 value obviously increased from 0.0012, 0.0025 and 0.005 to 0.0088 min⁻¹ if the reaction condition changed from air or nitrogen atmosphere to a magnetic stirring environment. The influence of palladium loading and the supporting NaCl concentration on the k_1 value was quite evident.

4. Conclusion

Our experimental results indicated that the electrochemical process using the Pd/Ni foam cathode electrode could efficiently degrade 2,4-D in an aqueous solution. In these experiments under the optimal circumstances—namely 2 g L^{-1} NaCl, an initial 2,4-D concentration of 50 mg L⁻¹, 1.78 mg cm⁻² palladium loading and a current density of 1.667 mA cm⁻²—71% removal of 2,4-D and 70% PA production could be achieved during a 4-h reaction period. Moreover, the efficiencies would be enhanced by improving ventilation of the system, and a dechlorination efficiency of 87% could be achieved under magnetic stirring conditions. For 2,4-D, the concentration decay was fitted to a pseudo-first-order kinetics model, and

both the NaCl concentration and palladium loading had a substantial impact on the reaction kinetics. In conclusion, electrochemical reduction using the Pd/Ni foam cathode is a promising technology for the degradation of 2,4-D in the environment.

Acknowledgments

This research was supported by the Fundamental Research Funds for the Central Universities, the National Water Pollution Control and Management Project of China (2011ZX07101-012-008) and the National Natural Science Foundation of China (No. 20977086).

References

- Y. Sunohara, S. Shirai, N. Wongkantrakorn, H. Matsumoto, Environ. Exp. Bot. 68 (2010) 157.
- [2] I. Vergili, H. Barlas, Desalination 249 (2009) 1107.
- 3] Y.F. Xi, M. Mallavarapu, R. Naidu, Appl. Clay Sci. 49 (2010) 255.
- [4] N. Maleki, A. Safavi, H.R. Shahbaazi, Anal. Chim. Acta 530 (2005) 69.
- [5] R.A. Rebich, R.H. Coupe, E.M. Thurman, Sci. Total Environ. 321 (2004) 189.
- [6] K. Shareef, G. Shaw, Chemosphere 72 (2008) 8.
- [7] S. Deng, R. Ma, Q. Yu, J. Huang, G. Yu, J. Hazard. Mater. 165 (2009) 408.
- J.R. Lipthay, S.R. Sorensen, J. Aamand, Environ. Pollut. 148 (2007) 83.
 Y. Yasman, V. Bulatov, V.V. Gridin, S. Agur, N. Galil, R. Armon, I. Schechter,
- [9] Y. Yasman, V. Bulatov, V.V. Gridin, S. Agur, N. Galil, R. Armon, I. Schechter, Ultrason. Sonochem. 11 (2004) 365.
- [10] H. Aydin, N. Ozdemir, N. Uzunoren, Forensic Sci. Int. 153 (2005) 53.
- [11] S. Cenkci, M. Yildiz, I.H. Cigerci, A. Bozdag, H. Terzi, E.S.A. Terzi, Ecotoxicol. Environ. Saf. 73 (2010) 1558.
- [12] B. Bukowska, K. Hutnik, Pestic. Biochem. Physiol. 85 (2006) 174.
- [13] B.H. Hameed, J.M. Salman, A.L. Ahman, J. Hazard. Mater. 163 (2009) 121.
- [14] LJ. Merini, V. Cuadrado, C.G. Flocco, A.M. Giulietti, Chemosphere 68 (2007) 259.
- [15] S.A. Neto, A.R. Andrade, Electrochim. Acta 54 (2009) 2039.
- [16] V.K. Gupta, I. Ali, Suhas, V.K. Saini, J. Colloid Interface Sci. 299 (2006) 556.
- [17] A.M.D. Freitas, C. Sirtori, P. Peralta-Zamora, Environ. Chem. Lett. 9 (2011) 97.
- [18] N. Philippidis, S. Sotiropoulos, A. Efstathiou, I. Poulios, J. Photochem. Photobiol. A 204 (2009) 129.
- [19] J.X. Gao, G.H. Zhao, W. Shi, D.M. Li, Chemosphere 75 (2009) 519.
- [20] M.D. Esclapez, V. Saez, D. Milan-Yanez, I. Tudela, O. Louisnard, J. Gonzalez-Garcia, Ultrason. Sonochem. 17 (2010) 1010.
- [21] V. Saez, M.D. Esclapez, A.J. Frias-Ferrer, P. Bonete, J. Gonzalez-Garcia, Water Res. 43 (2009) 2169.
- [22] O. Scialdone, A. Galia, L. Gurreri, S. Randazzo, Electrochim. Acta 55 (2010) 701.
- [23] S.M. Kulikov, V.P. Plekhanov, A.I. Tsyganok, C. Schlimm, E. Heitz, Electrochim. Acta 41 (1996) 527.
- [24] V.A. Sauro, D.C. Magri, J.L. Pitters, M.S. Workentin, Electrochim. Acta 55 (2010) 5584.
- [25] A. Matsunaga, A. Yasuhara, Environ. Sci. Technol. 37 (2003) 3435.
- [26] Z.R. Sun, H. Ge, X. Hu, Y.Z. Peng, Sep. Purif. Technol. 72 (2010) 133
- [27] Z.Q. He, L.Y. Zhan, Q. Wang, S. Song, J.M. Chen, K.R. Zhu, X.H. Xu, W.P. Liu, Sep. Purif. Technol. 80 (2011) 526.
- [28] A.I. Tsyganok, K. Otsuka, Appl. Catal. B: Environ. 22 (1999) 15.
- [29] A.I. Tsyganok, I. Yamanaka, K. Otsuka, J. Electrochem. Soc. 145 (1998) 3844.
- [30] A.I. Tsyganok, K. Otsuka, Electrochim. Acta 43 (1998) 2589.
- [31] A.I. Tsyganok, I. Yamanaka, K. Otsuka, Chemosphere 39 (1999) 1819.
- [32] B. Yang, G. Yu, D.M. Shuai, Chemosphere 67 (2007) 1361.
- [33] C. Sirtori, A. Zapata, I. Oller, W. Gernjak, A. Aguera, S. Malato, Water Res. 43 (2009) 661.
- [34] Z. Zainal, C.Y. Lee, M.Z. Hussein, A. Kassim, N.A. Yusof, J. Photochem. Photobiol. A 172 (2005) 316.
- [35] M. Boroski, A.C. Rodrigues, J.C. Garcia, L.C. Sampaio, J. Nozaki, N. Hioka, J. Hazard. Mater. 162 (2009) 448.
- [36] Z. Zhang, Q.H. Shen, N. Cissoko, J.J. Wo, X.H. Xu, J. Hazard. Mater. 182 (2010) 252.
- [37] J. Wiegel, Q.Z. Wu, FEMS Microbiol. Ecol. 32 (2000) 1.
- [38] H. Cheng, K. Scott, P.A. Christensen, J. Electrochem. Soc. 150 (2003) 17.
- [39] K. Miyoshi, T. Nishio, A. Yasuhara, M. Morita, Chemosphere 41 (2000) 819.
- [40] Y.P. Li, H.B. Cao, Y. Zhang, Chemosphere 63 (2006) 359.
- [41] M.A. Prasad, M.V. Sangaranarayanan, Electrochim. Acta 51 (2005) 242.
- [42] Y. Han, W. Li, M.H. Zhang, K.Y. Tao, Chemosphere 72 (2008) 53.
- [43] E.N. Alvar, M.R. Golmohammadi, M. Rezeai, H.N. Alvar, A. Mardanloo, S.H. Nouhian, M. Didari, J. Nat. Gas. Chem. 17 (2008) 321.
- [44] M.A. Oturan, I. Sires, N. Oturan, S. Perocheau, J.L. Laborde, S. Trevin, J. Electroanal. Chem. 624 (2008) 329.