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Electrochimica Acta

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

Optimisation of electrocatalytic dechlorination of 2,4-dichlorophenoxyacetic acid on a roughened silver-palladium cathode

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ARTICLE INFO

Article history: Received 2 December 2012 Received in revised form 8 February 2013 Accepted 14 February 2013 Available online 21 February 2013

Keywords: Electrochemical hydrodechlorination Palladium/silver cathode Dechlorination mechanism 2,4-Dichlorophenoxyacetic acid

Chlorinated aromatic compounds

ABSTRACT

Electrocatalytic hydrogenolysis (ECH) dechlorination of 2,4-dichlorophenoxyacetic acid (2,4-D) in an aqueous solution was investigated at room temperature using a roughened silver–palladium cathode (Pd/Ag(r) cathode) in batch-mode electrolysis experiments. The Pd/Ag(r) cathode was prepared by gal-vanic replacement reaction (GRR) of a roughened silver (Ag(r)) electrode with PdCl₂ solution. The effect of preparation conditions on the catalytic activity and stability of the Pd/Ag(r) cathode and of operating parameters on the rate and current efficiency (CE) of the ECH dechlorination reaction were evaluated. In particular, the ECH dechlorination mechanism of 2,4-D was analysed with regard to the dependence of dechlorination efficiency on the different operating parameters. Moreover, preliminary assessments of product selectivity and carbon mass balance of the dechlorination reaction were carried out. The results demonstrate that a moderate GRR time and GRR temperature favoured the catalytic activity and cathode stability and that a basic aqueous solution without ethanol, high 2,4-D concentration, and moderate current density had the most beneficial effects on the dechlorination process. Under the optimised conditions, 25 mM of 2,4-D could be selectively dechlorinated to phenoxyacetic acid with 85% yield and 66% CE at 298 K after 6 h electrolysis. The only products generated during the electrolysis process were phenoxyacetic acid, 2-chlorophenoxyacetic acid, and 4-chlorophenoxyacetic acid.

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1. Introduction

Chlorinated aromatic compounds (CACs) are widespread environmental contaminants found in both groundwater and soil. Many of these are toxic, persistent, and strongly resistant to chemical, physical, and biological degradation. They gradually accumulate in the environment, achieving concentrations that are hazardous to living organisms, including humans [1,2]. Therefore, the development of an efficient and cost–effective technology for the detoxification and destruction of CACs is highly sought after.

Among the different types of potential methods for treating CAC-containing effluents, electrochemical techniques are considered to be intrinsically milder and more efficient. Electro-oxidation [3,4] and electro-reduction processes [5,6] can both be used for breaking the C—Cl bond within the CACs. During the oxidation processes, undesired reactions may arise because of the formation of reactive radicals, either on the electrode surface or in the solutions. However, cathodic processes, especially electrocatalytic hydrogenolysis (ECH) using Pd-modified cathodes, have been shown to achieve the goal without producing toxic by-products

[7,8]. This technology ensures complete removal of the Cl atoms under mild experimental conditions (aqueous medium, ambient temperature, and no chemical additives). The resulting Cl-free organic compounds are usually less toxic and thus can be disposed by using more convenient and economic methods such as biodegradation. However, it is difficult to achieve a high current efficiency (CE) using conventional Pd-modified cathodes to dechlorinate CACs. For example, previous studies have demonstrated that less than 20% current could be effectively utilised in the ECH dechlorination of chlorinated biphenyls [9] and chlorinated phenoxyacetic acid (PAA) [8,10–12]. Concomitant reduction of H₂O is the main cause of such low CE, which not only drastically increases electrical energy consumption but also results in an abundance of volatile H₂. These two drawbacks to ECH dechlorination technology largely limit its application in the practical disposal of CACs.

Cathode substrates have a major effect on the efficiency of ECH dechlorination of chlorinated compounds, and therefore, large numbers of materials with a highly porous structure have been investigated as potential catalyst supports (i.e. cathode substrates). These include various carbon-based materials such as activated carbon fibre/cloth/felt [8,10,7], reticulated vitreous glassy carbon [13], MoO_x -modified glassy carbon [14], granular graphite [15], and carbon nanotubes [16]; different metal materials such as Ti mesh [17], Fe gauze [18], and Ni foam [9,19]; and other substances such as

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^{0013-4686/\$ –} see front matter © 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.electacta.2013.02.068

polypyrrole [20], polypyrrole/Ni foam composite [21], and surfactant/polypyrrole/meshed Ti [22].

Ag, as a cathode catalyst, has recently been receiving much attention for its extraordinary electrocatalytic activity towards the reduction of halogenated organic compounds [23–27]. The electrocatalytic process is probably related to the formation of a bridge-like R…X…Ag adsorbed intermediate, although the catalytic role of Ag in the reduction process still needs to be further explored. Simonet's group chose Ag as the cathode substrate for preparing a new cathode material, palladised Ag [28–30], that exhibited greater electrocatalytic activity towards the reduction of alkyl bromides and alkyl iodides than an electrode consisting of Ag alone. In addition, the Song group developed a new Pd/Ag/Ni foam cathode that showed very high CE for the dechlorination of dichloroacetic acid [31].

Recently, we prepared a roughened Pd/Ag (Pd/Ag(r)) cathode using a galvanic replacement reaction (GRR) and demonstrated its excellent electrocatalytic activity towards the ECH dechlorination of 2,4-dichlorophenoxyacetic acid (2,4-D) [32]. Here, this work is taken forward with the aim of optimising various factors that might affect the electrocatalytic activity and stability of the Pd/Ag(r) cathode and the rate and CE of the dechlorination reaction, including GRR time, GRR temperature, electrolyte composition, initial concentration of 2,4-D, and current density. In addition, product selectivity and carbon mass balance of the dechlorination reaction were investigated, and the reaction mechanism was analysed in detail from the perspective of the dependence of operating parameters on dechlorination efficiency.

2. Experimental

2.1. Chemicals

Ag (99.9%, mesh; open area 37% or plate) was obtained from Cells Electrochemistry Experiment Equipments Co., Ltd., China (www.hzcell.com). PdCl₂ (99.5%), 2,4-D, 2-chlorophenoxyacetic acid (2-ClPAA), 4-chlorophenoxyacetic acid (4-ClPAA), PAA, NaOH, NaCl, HCl, H₂SO₄, Na₂SO₄, KH₂PO₄, and ethanol, all with 97–99% purity, were obtained from the Aladdin Reagent Co., China, and used as received. Acetonitrile and methanol (HPLC-grade) were purchased from the National Medicines Co. Ltd., China. All solutions were prepared using H₂O with a resistivity of 18.2 M Ω cm obtained from a Millipore Milli-Q system.

2.2. Electrode modification

Ag was degreased with 10% NaOH, boiled in concentrated HCl for 10 min, and then washed with H₂O. Roughened Ag (Ag(r)) electrodes were obtained using an oxidation–reduction cycle (ORC) process in an aqueous solution of 0.5 M NaOH and 0.5 M NaCl, at a scanning rate of 10 mV s⁻¹, in the range -0.3 to 0.7 V, within 400 s, at 298 ± 1 K, as described in Ref. [23]. The resulting Ag(r) cathodes were immersed in 50 mL aqueous solution of 0.1 M HCl containing 2.0 mM PdCl₂ for different lengths of time (GRR time) at different temperatures (GRR temperature) to prepare the Pd/Ag(r) cathodes. Pd loading on the surface of the Pd/Ag(r) cathodes was indirectly determined using inductively coupled plasma mass spectrometry (ICP-MS) (PerkinElmer, Elan DRC-e).

2.3. Apparatus

Linear sweep voltammograms (LSVs) and electrolysis experiments were carried out with a PAR 273A potentiostat. A threeelectrode cell composed of an aqueous saturated calomel electrode (SCE) as reference electrode, a platinum sheet ($0.5 \text{ cm} \times 1 \text{ cm}$) as the counter electrode, and a Pd/Ag(r) electrode as working electrode (Ø 2 mm) was used for the voltammetric investigations with IR compensation (10 Ω). The Pd/Ag(r) electrode was prepared using a GRR time of 60 min and a GRR temperature of 298 ± 1 K. Electrolysis experiments were carried out in a two-compartment cell divided by a cation-exchange membrane (Nafion[®] 117), with catholyte and anolyte volumes of 40 cm³. The cathode consisted of a rectangular palladised Ag metal mesh (4 cm × 3 cm × 0.1 cm), and a Pt sheet (4 cm × 3 cm × 0.05 cm) in 0.5 M NaOH aqueous solution was used as the anode in order to provide a harmless counter reaction (20H⁻-2e⁻ \rightarrow (1/2O₂)+H₂O). The catholyte was stirred during the electrolysis process. All electrochemical experiments were carried out at 298±1 K, and all potentials are reported as relative to SCE.

2.4. Analytical methods

Quantitative analysis of the dechlorinated products and the remaining 2,4-D was performed at room temperature by using a Waters HPLC system with a symmetry column (250 mm length \times 4.6 mm i.d., 5 μ m particle size), an injection valve fitted with 20 μ L sample loop, and a Waters 2996 Photodiode Array Detector (λ 270 nm). Isocratic elution was used with a mobile phase of acetonitrile/methanol/H₂O (1:3:6, v/v) containing 30 mM H₃PO₄ at a flow rate of 1 mL min⁻¹. Product concentrations were determined by using calibration curves of standards. The precision of the PAA mass balance in the measurement was ca. 95–105% of the nominal value.

The conversion of 2,4-D was calculated as the ratio of the amount of 2,4-D eliminated to the initial amount prepared. The yield of PAA was determined as the molar ratio of PAA produced to the initial amount of 2,4-D. The CE of dechlorination 2,4-D was calculated from the following equation:

$$CE = \frac{(n_1 \Delta C_{PAA} + n_2 (\Delta C_{2-CIPAA} + \Delta C_{4-CIPAA}))FV}{I \times \Delta t}$$

where n_1 and n_2 are the electron transfer numbers per molecule of PAA (n_1 = 4) and CIPAA (n_2 = 2), respectively; ΔC_{PAA} , $\Delta C_{2-\text{CIPAA}}$, and $\Delta C_{4-\text{CIPAA}}$ are the concentration differentials (M) of PAA, 2-CIPAA, and 4-CIPAA, respectively, during Δt ; F is Faraday's constant (96,500 A s mol⁻¹); V is the volume of the total catholyte (0.04 L); and I is the applied current density.

3. Results and discussion

3.1. Effect of preparation conditions

3.1.1. Effect of GRR time

A series of Pd/Ag(r) cathodes were prepared using GRR with Ag(r) electrodes and a solution of $PdCl_2$ for different GRR times. As shown in Fig. 1A, Pd loading of the Pd/Ag(r) cathodes rapidly increased during the initial 30 min, before reaching a quasi-steady-state value. Figs. 1B–D illustrates the effect of GRR time on the dechlorination rate, as evaluated by 2,4-D conversion, PAA yield, and the CE of the Pd/Ag(r) cathodes. As GRR time increased to 60 min, a notable increase in the dechlorination rate and CE was observed. The values then reached a plateau, before slightly decreasing after 90 min. These results imply that the catalytic activity of the Pd/Ag(r) cathodes strongly depend on Pd loading, with moderate loading favouring the catalytic activity.

3.1.2. Reactivation of Pd/Ag(r) electrode

In general, the activity of a catalytic material decreases over the course of the reaction. Therefore, a preliminarily evaluation of the stability of the prepared Pd/Ag(r) electrode towards ECH dechlorination of 2,4-D was carried out by a prolonged electrolysis



Fig. 1. Effect of GRR time on Pd loading and ECH chlorination of 2,4-D. Cathode: Pd/Ag(r) mesh (GRR temperature = 298 ± 1 K); anode: Pt sheet; catholyte: 0.5 M NaOH + 25 mM 2,4-D; and anolyte: 0.5 M NaOH solution. Applied current density: 4.2 mA cm⁻² (50 mA); time of electrolysis: 3 h; temperature: 298 ± 1 K.

experiment. As shown in Fig. 2A, during the initial 2 h, the concentration (c) of 2,4-D decreased linearly with electrolysis time, while that of CIPAA and PAA showed the opposite behaviour. At longer times, especially after 3 h, the concentration of 2,4-D, CIPAA, and PAA remained almost unchanged.



Fig. 2. Effect of reactivation on the electrocatalytic activity of a Pd/Ag(r) cathode during ECH dechlorination of 2,4-D. Cathode: Pd/Ag(r) mesh (GRR temperature = 298 ± 1 K, GRR time = 60 min). (A) The Pd/Ag(r) cathode was not reactivated. (B) The Pd/Ag(r) cathode was bihourly reactivated in the catholyte. Time of electrolysis is 6 h and all other electrolysis conditions were the same as those in Fig. 1.

Highly similar results were previously observed for the electrocatalytic reduction of 2,4-D on a Pd-modified glassy carbon electrode by the Casella group [11], with the results attributed to the strong adsorption of the reaction products such as chloride species, which gradually poison the catalyst. On the basis of this deactivation hypothesis, a convenient surface-cleaning process (which polarised the Pd/Ag(r) electrode with an anode current of 5 mA for 100 s) was used to reactivate the Pd/Ag(r) electrode. Fig. 2B shows the results of an electrolysis experiment in which the Pd/Ag(r) cathode was bihourly reactivated by the surfacecleaning process. It can be seen that almost 100% conversion of 2,4-D was achieved, with an 85% yield of PAA after 6 h electrolysis. This result indicates that the catalytic activity of the Pd/Ag(r) cathode can be kept constant using this surface-cleaning process.

3.1.3. Effect of GRR temperature

Twelve electrolysis experiments using three Pd/Ag(r) cathodes (GRR temperature = 283, 298, 313 K) were carried out to assess the effect of GRR temperature on the electrocatalytic activity and stability of Pd/Ag(r) cathodes. As shown in Fig. 3, the two Pd/Ag(r)cathodes with lower GRR temperature (283, 298 K) gave excellent catalytic stability in four sequent electrolysis experiments, whereas Pd/Ag(r) cathode with the highest GRR temperature (313 K) lost its electrocatalytic activity in last three electrolysis experiments though it exhibited the best electrocatalytic activity in its first electrolysis experiment. Generally, increasing GRR temperature not only accelerates the rate of a GRR but also changes surface characteristics (morphology, phase state and elements) of a bimetallic catalyst [33,34], therefore the great difference of catalytic capability between three Pd/Ag(r) cathodes probably were caused by the changes of surface characteristics of them. The dependence between catalytic capability of a Pd/Ag(r) cathode and its surface characteristics is an interesting topic, however it is not possible to analyses it on the basis of the data so far available.



Fig. 3. Effect of GRR temperature on the electrocatalytic activity and stability of Pd/Ag(r) cathodes. Cathode: (A) Pd/Ag(r) mesh (GRR temperature = 283 ± 1 K, GRR time = 300 min); (B) Pd/Ag(r) mesh (GRR temperature = 298 ± 1 K, GRR time = 60 min); (C) Pd/Ag(r) mesh (GRR temperature = 313 ± 1 K, GRR time = 20 min). All other conditions were the same as those in Fig. 2B.

3.2. Effect of operating parameters

3.2.1. Effect of electrolyte composition

Among the various operating parameters, the electrolyte composition showed the most obvious effect on the dechlorination efficiency of the Pd/Ag(r) cathode towards the ECH dechlorination of 2,4-D. Table 1 shows the results of the reduction process carried out in seven different electrolytes. By assessing the dechlorination rate and CE, the following conclusions were drawn:

- 1. Cl[–] is detrimental to the ECH dechlorination. Na₂SO₄ enhanced the dechlorination rate by increasing the conductivity of the electrolyte solution, while NaCl did not have a similar positive effect on the process.
- 2. OH⁻ can drastically promote the ECH process when ethanol is absent from the electrolyte solutions. This positive effect of OH⁻ probably originates from its neutralisation towards the adsorbed HCl produced by a catalytic hydrogenation step between adsorbed 2,4-D and chemisorbed hydrogen [32]. The adsorbed HCl would block the reaction sites if it was not quickly removed from the cathode surface.
- 3. Ethanol deactivates the Pd/Ag(r) cathode if an aqueous alkaline solution is used for the ECH dechlorination of 2,4-D. It has been previously reported that ethanol can dissociatively chemisorb on Ag to form Ag ethoxide at room temperature [35]. Because an aqueous alkaline solution favours the production of an ethoxide ion, the poisonous effect of ethanol is attributed to its substantial adsorption on Ag in the form of Ag ethoxide.

Table 2

Effect of 2,4-D initial concentration on ECH dechlorination of 2,4-D. Cathode: Pd/Ag(r) mesh (GRR temperature = 298 \pm 1 K, GRR time = 60 min). Catholyte: 40 mL solution of 0.5 M NaOH + X mM 2,4-D. All other electrolysis conditions were the same as those in Fig. 1.

Initial concentration (mmol L ⁻¹)	Conversion of 2.4-D (%)	Yield of PAA (%)	CE (%)
5	99.0	60.3	11.4
10	95.8	51.7	21.1
25	92.3	40.8	47.6
30	90.2	37.7	54.8
40	84.4	28.4	64.5

3.2.2. Effect of 2,4-D initial concentration

LSVs obtained using Pd/Ag(r) as the working electrode show the influence of 2,4-D concentration on current–potential data in 0.5 M NaOH aqueous solution (Fig. 4A). Herein, the working electrode was prepared by immersing a Ag(r) electrode into 50 mL solution of 2.0 mM PdCl₂ + 0.1 M HCl for 60 min. As can be seen in the figure, a current plateau located between -0.6 and -1.3 V, which evidently originated from the reduction of 2,4-D, steadily increased in current density with increasing 2,4-D concentration. This indicates that a higher initial concentration (<40 mM) is favourable for the reduction of 2,4-D. In addition, the peak at approximately -1.17 V was used to assess the dependence of peak current on the concentration of 2,4-D (Fig. 4B). It is clear that these two parameters are not proportional to each other, thereby indicating that the reduction process is not under complete diffusion control.

In order to evaluate the effect of 2,4-D concentration on the reduction process in more detail, five electrolysis experiments with different initial concentrations of reactant (5, 10, 25, 30, and 40 mM) were carried out. As shown in Table 2, the increase in the initial concentration of 2,4-D from 5 to 40 mM led to an increase in CE from 11.4% to 64.5% as well as an increase in dechlorination rate. This result provided further evidence to support the findings of the LSV experiments, where a similar improvement in dechlorination efficiency was found at higher 2,4-D concentrations.

3.2.3. Effect of current density

Fig. 5A–C shows the effect of current density on the dechlorination efficiency, as evaluated from the conversion of 2,4-D, PAA yield, and CE, during the ECH dechlorination of 2,4-D. The best performance was achieved in the current density range $2.1-4.2 \text{ mA cm}^{-2}$ (geometric area), especially during the middle and later periods of electrolysis. An increase to a higher current density (6.3 or 8.3 mA cm⁻²) caused a rapid drop in dechlorination rate. Similar results were observed for the ECH dechlorination of chlorinated phenols using a Pd-modified Ti cathode by the Scott group [18]. They attributed this phenomenon to higher H₂ gas generation in the electrode structure, restricting the access of the liquid, and thus limiting mass transport of the reactant (H₂ gas isolation effect).

In order to confirm this hypothesis, the potentials of the Pd/Ag(r) electrode under different current densities were compared during

Table 1

Effect of electrolyte composition on the ECH dechlorination of 2,4-D. Cathode: Pd/Ag(r) mesh (GRR temperature = 298 ± 1 K, GRR time = 60 min). All other electrolysis conditions were the same as those in Fig. 1.

Entry	Catholyte	рН	Conversion of 2,4-D (%)	Yield of PAA (%)	CE (%)
1	25 mM 2,4-D + 0.5 M NaOH + 0.5 M Na ₂ SO ₄	13.3-13.4	96.9	49.1	52.0
2	25 mM 2,4-D + 0.5 M NaOH	13.3-13.4	91.3	42.8	47.8
3	25 mM 2,4-D + 0.5 M NaOH + 0.5 M NaCl	13.3-13.4	90.3	37.5	45.6
4	25 mM 2,4-D + 0.5 M NaOH + 0.5 M K ₂ HPO ₄	8.3-12.5	68.3	17.5	30.6
5	25 mM 2,4-D + 0.5 M KH ₂ PO ₄ + M NaOH + 0.5 M ethanol	6.1-6.5	42.8	1.9	16.0
6	25 mM 2,4-D + 0.5 M NaOH + 0.5 M ethanol	13.4-13.4	31.3	1.2	11.6
7	25 mM 2,4-D + 0.5 M H ₂ SO ₄ + 0.5 M ethanol	0.2-0.3	17.6	0.5	6.5



Fig. 4. LSVs of the Pd/Ag(r) electrode (\emptyset 2 mm, GRR temperature = 298 ± 1 K, GRR time = 60 min) in 0.5 M NaOH aqueous solutions, V = 50 mV s⁻¹, with various concentrations of 2,4-D: (1) 5 mM, (2) 10 mM, (3) 20 mM, (4) 30 mM, and (5) 40 mM (A), and the fitted peak current for 2,4-D on a Pd/Ag(r) electrode vs. the concentrations (B).

the entire electrolysis process. As shown in Fig. 5D, an increasing current density resulted in progressive negative shift of the potential of Pd/Ag(r) electrode and it went beyond -1.4 V during last 5 h of electrolysis when applied current density was 6.3 or 8.3 mA cm⁻². According to the LSVs of 2,4-D on the Pd/Ag(r) electrode (Fig. 4), H₂ evolution is dominant at potentials more negative than -1.30 V. Therefore, it is reasonable to attribute the decrease in dechlorination rate at higher current density to H₂ gas isolation effect. However, an important finding shown in Fig. 5 contradicts this interpretation: the dechlorination rate was almost constant on increasing the current density from 6.3 to 8.3 mA cm⁻². This current density increase would have resulted in a considerable increase in H₂-gas generation over the cathode. Therefore, the dechlorination rate should deteriorate further if the H₂ gas isolation effect was the main reason for the observed decrease in dechlorination efficiency.

It is well known that potential-driven desorption of halide ions [36] and organic compound anions [37] occurs on Ag electrodes in the potential region more negative than the potential of zero charge and the potential of zero charge of Ag locate at approximately -0.9 V in basic aqueous solutions containing Cl⁻ [38]. So, we propose that the desorption of 2,4-D on the Pd/Ag(r) electrode in

sufficiently negative potential region (the potential-driven desorption effect) is the main reason of the decrease of dechlorination rate at higher current density.

3.3. ECH dechlorination mechanism

The mechanism of ECH dechlorination of 2,4-D on the Pd/Ag(r) cathode can be described by Eqs. (1)-(4) [32]. First, adsorbed 2,4-D is formed on pure Ag and/or Ag of the Pd–Ag alloy (Eq. (1)) followed by the generation of chemisorbed hydrogen on the Pd of the Pd–Ag alloy (Eq. (2)). Hydrogenolysis of 2,4-D then proceeds as in catalytic hydrogenation (Eq. (3)) by reaction of the adsorbed 2,4-D with chemisorbed hydrogen followed by desorption of the product (Eq. (4)).

$$R-Cl + Ag \leftrightarrow (R-Cl)_{ads}Ag \tag{1}$$

$$2H_2O + 2e^- + Pd \rightarrow 2(H)_{ads}Pd + 2OH^-$$

$$\tag{2}$$

$$(R-Cl)_{ads}Ag + 2(H)_{ads}Pd \rightarrow (R-H)_{ads}Ag + HCl + Pd$$
(3)

$$(R-H)_{ads}Ag \leftrightarrow R-H + Ag \tag{4}$$



Fig. 5. Effect of current density on ECH chlorination of 2,4-D. Cathode: Pd/Ag(r) mesh (GRR temperature = 298 ± 1 K, GRR time = 60 min). All other conditions were the same as those in Fig. 2B.

$$(H)_{ads}Pd + H_2O + e^- + Pd \rightarrow H_2 + 2OH^-$$
(5)
(H)_{ads}Pd + (H)_{ads}Pd \leftrightarrow H₂ (6)

A very similar reaction mechanism has been previously reported for the chemical hydrodechlorination of 1,2-dichloroethane on Pd–Ag catalysts by the Heinrich group [39]. They found that the main role played by Ag in the catalytic process was dissociative adsorption of 1,2-dichloroethane and successive breaking of the two C–Cl bonds, with Pd present in the alloy supplying H atoms for the regeneration of the chlorinated Ag surface into metallic Ag. According to this mechanism, the dechlorination efficiency of Pd/Ag(r) cathode depends on the relative rates of the hydrogenolysis step and H₂ desorption (Eqs. (5) and (6)), and hence the factors that affect these two steps would influence the dechlorination efficiency.

The electrolyte composition and the concentration of 2,4-D in the bulk solution may influence the adsorption of 2,4-D (Eq. (1)), therefore these are important factors that could significantly change the rate of the hydrogenolysis step. The effects of OH-, Cl⁻, and ethanol were discussed in Section 3.2.1, where it was shown that Cl⁻ was detrimental to the ECH dechlorination while OH⁻ could promote the process. These results strongly suggest that the adsorbed HCl formed by the catalytic hydrogenation between adsorbed 2,4-D and chemisorbed hydrogen is fairly stable on the Pd/Ag(r) cathode. On the other hand, the fact that ethanol in a basic aqueous solution poisons the Pd/Ag(r) cathode confirms the adsorption step (Eq. (1)). A high 2,4-D concentration in the bulk solution inevitably resulted in a high concentration of adsorbed 2,4-D on the cathode, which is favourable for the hydrogenolysis step. In addition, a fast hydrogenolysis step would immediately consume chemisorbed hydrogen and thus restrict the H₂ desorption step (Eqs. (5) and (6)). Therefore, high dechlorination efficiency can be obtained at high 2,4-D concentrations, which agrees with the results discussed in Section 3.2.2 about the effects of concentration.

The current density and the electrode potential not only influence the hydrogenolysis step but can also adjust the rate of H₂ desorption, mainly by controlling the concentration of chemisorbed hydrogen. According to Eq. (3) (hydrogenolysis step), the concentration of chemisorbed hydrogen could drop to zero if a very low current density was applied. In other words, the dechlorination process would be kinetically controlled by the rate of generation of chemisorbed hydrogen (Eq. (2)) under such a condition. Conversely, if a high current density was used, a high concentration of chemisorbed hydrogen would occur, thereby accelerating the rate of H₂ desorption. Consequently, the maximum dechlorination efficiency is most likely to be achieved under moderate current densities, because a low current density gives a low dechlorination rate and a high CE, while a high current density gives a high dechlorination rate and a low CE. The results discussed in Section 3.2.3 comply with this hypothesis, except for the observation that increasing the current density over a certain value decreases the rate of the dechlorination reaction. This phenomenon was attributed to the potential-driven desorption effect.

3.4. Product selectivity and equilibrium analysis

The product selectivity and the carbon mass balance during the reductive electrolysis of 2,4-D at the Pd/Ag(r) cathode is illustrated in Fig. 6. The 2,4-D concentration decreased with the increasing electrolysis time, with the main intermediate product during the reaction and the main product after 10 h electrolysis being 2-CIPAA and PAA, respectively. In addition, the total carbon mass balance recorded was ~100%, with the HPLC data revealing no trace amounts of chlorophenols or phenol produced during the electrolysis. These results suggest that the electrocatalytic dechlorination of 2,4-D was performed in a highly selective manner by the method



Fig. 6. The product selectivity and carbon mass balance during the ECH dechlorination of 2,4-D. Cathode: Pd/Ag(r) mesh (GRR temperature = 298 ± 1 K, GRR time = 60 min). Applied current density: 2.1 mA cm⁻² (25 mA), time of electrolysis: 10 h, and all other conditions were the same as those in Fig. 2B.

described in this work, and 2,4-D \rightarrow 2-CIPAA \rightarrow PAA was the main dechlorination reaction pathway.

4. Conclusions

We have investigated various factors that might affect the electrocatalytic activity and stability of a Pd/Ag(r) cathode and the rate and CE of the dechlorination reaction of 2,4-D. The main findings are as follows:

- (I) Pd loading of a Pd/Ag(r) cathode could be controlled by GRR time and volcano-shape relation between the dechlorination efficiency and Pd loading was observed. The maximum dechlorination efficiency was obtained when the Pd/Ag(r) cathode was used with moderate Pd loading $(0.91-0.99 \text{ mg cm}^{-2})$.
- (II) The Pd/Ag(r) cathode prepared at moderate GRR temperature showed excellent catalytic activity and stability and its electrocatalytic activity could be maintained by employing a convenient surface-cleaning process.
- (III) Cl⁻ was detrimental to the ECH dechlorination, whereas OH⁻ was able to drastically promote the dechlorination of 2,4-D. Ethanol deactivated the Pd/Ag(r) cathode if an aqueous alkaline solution was used for the reaction.
- (IV) The dechlorination efficiency increased on increasing the initial concentration of 2,4-D (from 5 to 40 mM), indicating that higher initial concentrations (<40 mM) were favourable for the ECH dechlorination of 2,4-D on Pd/Ag(r) cathodes. Current density strongly influenced the dechlorination efficiency of 2,4-D, with a moderate current density (2.1–4.2 mA cm⁻²) having the most beneficial effect on the ECH dechlorination process.
- (V) The mechanism of ECH dechlorination of 2,4-D on the Pd/Ag(r) electrode has been revised as follows: (1) HCl formed by the catalytic hydrogenation is steadily adsorbed on the Pd/Ag(r) electrode, and (2) the amount of adsorbed 2,4-D on the Pd/Ag(r) electrode may rapidly decrease in a sufficiently negative potential region owing to the potential-driven desorption effect.

For future studies, such a system could be adjusted for selective removal of Cl from other chloroaromatic compounds, which are known as priority pollutants in the environment.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (21106133) and the National Basic Research Program of China (973 Program) (2012CB722604) and the Zhejiang Provincial Natural Science Foundation of China (LQ12B03003).

Appendix A. Nomenclature

- CE current efficiency of 2,4-D dechlorination Ag(r) roughened silver cathode
- Pd/Ag(r) roughened silver-palladium cathode
- CACs chlorinated aromatic compounds
- 2,4-D 2,4-dichlorophenpoxyacetic acid
- CIPAA 2-chlorophenoxyacetic acid and 4-chlorophenoxyacetic acid
- 2-ClPAA 2-chlorophenoxyacetic acid
- 4-CIPAA 4-chlorophenoxyacetic acid
- PAA phenoxyacetic acid
- ECH electrocatalytic hydrogenolysis
- GRR galvanic replacement reaction
- GRR time time of a galvanic replacement reaction

GRR temperature temperature of a galvanic replacement reaction

References

- J. Peller, O. Wiest, P.V. Kamat, Synergy of combining sonolysis and photocatalysis in the degradation and mineralization of chlorinated aromatic compounds, Environmental Science and Technology 37 (2003) 1926.
- [2] Y. Fan, X.B. Lu, Y.W. Ni, H.J. Zhang, M.W. Zhu, Y. Li, J.P. Chen, Catalytic destruction of chlorinated aromatic pollutants over mesoporous Cu_xMg_{1-x}Al₂O₄ spinel oxides, Applied Catalysis B: Environmental 101 (2011) 606.
- [3] J. Gao, G.H. Zhao, W. Shi, D.M. Li, Microwave activated electrochemical degradation of 2,4-dichlorophenoxyacetic acid at boron-doped diamond electrode, Chemosphere 75 (2009) 519.
- [4] J.M. Fontmorin, S. Huguet, F. Fourcade, F. Geneste, D. Floner, A. Amrane, Electrochemical oxidation of 2,4-Dichlorophenoxyacetic acid: Analysis of byproducts and improvement of the biodegradability, Chemical Engineering Journal 195–196 (2012) 208.
- [5] B.B. Huang, A.A. Isse, C. Durante, C.H. Wei, A. Gennaro, Electrocatalytic properties of transition metals toward reductive dechlorination of polychloroethanes, Electrochimica Acta 70 (2012) 50.
- [6] M.D. Esclapez, M.I. Diez-Garcia, V. Saez, I. Tudela, J.M. Perez, J. Gonzalez-Garcia, P. Bonete, Spectroelectrochemical study of trichloroacetic acid reduction at copper electrodes in an aqueous sodium sulfate medium, Electrochimica Acta 56 (2011) 8138.
- [7] C.Y. Cui, X. Quan, S. Chen, H.M. Zhao, Adsorption and electrocatalytic dechlorination of pentachlorophenol on palladium-loaded activated carbon fibers, Separation and Purification Technology 47 (2005) 73.
- [8] A.I. Tsyganok, K. Otsuka, Selective dechlorination of chlorinated phenoxy herbicides in aqueous medium by electrocatalytic reduction over palladium-loaded carbon felt, Applied Catalysis B: Environmental 22 (1999) 15.
- [9] B. Yang, G. Yu, D.M. Shuai, Electrocatalytic hydrodechlorination of 4chlorobiphenyl in aqueous solution using palladized nickel foam cathode, Chemosphere 67 (2007) 1361.
- [10] A.I. Tsyganok, Selective removal of chlorine from chloroaromatic pollutants by electrocatalytic reduction over palladium-loaded carbon felt, Research on Chemical Intermediates 32 (2006) 357.
- [11] I.G. Casella, M. Contursi, Electrocatalytic reduction of chlorophenoxy acids at palladium-modified glassy carbon electrodes, Electrochimica Acta 52 (2007) 7028.
- [12] K.R. Zhu, S.A. Bajg, J. Xu, T.T. Sheng, X.H. Xu, Electrochemical reductive dechlorination of 2,4-dichlorophenoxyacetic acid using a palladium/nickel foam electrode, Electrochimica Acta 69 (2012) 389.
- [13] P. Dabo, A. Cyr, F. Laplante, F. Jean, H. Menard, J. Lessard, Electrocatalytic dehydrochlorination of pentachlorophenol to phenol or cyclohexanol, Environmental Science and Technology 34 (2000) 1265.
- [14] Ge Chen, Z.Y. Wang, D.G. Xia, Electrochemically codeposited palladium/molybdenum oxide electrode for electrocatalytic reductive dechlorination of 4-chlorophenol, Electrochemistry Communications 6 (2004) 268.

- [15] Y.X. Fang, S.R. Al-Abed, Electrocatalytic dechlorination of a PCB congener at a palladized granular-graphite-packed electrode: Reaction equilibrium and mechanism, Applied Catalysis B: Environmental 80 (2008) 327.
- [16] C.Y. Cui, X. Quan, H.T. Yu, Y.H. Han, Electrocatalytic hydrodehalogenation of pentachlorophenol at palladized multiwalled carbon nanotubes electrode, Applied Catalysis B: Environmental 80 (2008) 122.
- [17] K. Miyoshi, Y. Kamegaya, M. Matsumura, Electrochemical reduction of organohalogen compound by noble metal sintered electrode, Chemosphere 56 (2004) 187.
- [18] H. Cheng, K. Scott, P.A. Christensen, Electrochemical hydrodehalogenation of chlorinated phenols in aqueous solutions II. effect of operating parameters, Journal of the Electrochemical Society 150 (2003) 25.
- [19] B. Yang, G. Yu, J. Huang, Electrocatalytic hydrodechlorination of 2,4,5trichlorobiphenyl on a palladium-modified nickel foam cathode, Environmental Science and Technology 41 (2007) 7503.
- [20] G. Chen, Z.Y. Wang, T. Yang, D.D. Huang, D.G. Xia, Electrocatalytic hydrogenation of 4-chlorophenol on the glassy carbon electrode modified by composite polypyrrole/palladium film, Journal of Physical Chemistry B 110 (2006) 4863.
- [21] Z.R. Sun, H. Ge, X. Hu, Y.Z. Peng, Preparation of foam-nickel composite electrode and its application to 2,4-dichlorophenol dechlorination in aqueous solution, Separation and Purification Technology 72 (2010) 133.
- [22] Z.R. Sun, X.F. Wei, X. Hu, K. Wang, J.T. Shen, Electrocatalytic dechlorination of 2,4-dichlorophenol in aqueous solution on palladium loaded meshed titanium electrode modified with polymeric pyrrole and surfactant, Colloids and Surfaces A: Physicochemical and Engineering Aspects 414 (2012) 314.
- [23] Y.H. Xu, Y.H. Zhu, F.M. Zhao, C.A. Ma, Electrocatalytic reductive dehalogenation of polyhalogenated phenols in aqueous solution on Ag electrodes, Applied Catalysis A: General 324 (2007) 83.
- [24] Y.H. Xu, H. Zhang, C.P. Chu, C.A. Ma, Dechlorination of chloroacetic acids by electrocatalytic reduction using activated silver electrodes in aqueous solutions of different pH, Journal of Electroanalytical Chemistry 664 (2012) 39.
- [25] A.A. Isse, S. Gottardello, C. Durante, A. Gennaro, Dissociative electron transfer to organic chlorides: Electrocatalysis at metal cathodes, Physical Chemistry Chemical Physics 10 (2008) 2409.
- [26] A.A. Isse, S. Gottardello, C. Durante, A. Gennaro, Voltammetric investigation of the dissociative electron transfer to polychloromethanes at catalytic and non-catalytic electrodes, Electrochimica Acta 54 (2009) 3235.
- [27] C. Durante, A.A. Isse, S. Gottardello, A. Gennaro, Electrochemical hydrodehalogenation of polychloromethanes at silver and carbon electrodes, Applied Catalysis B: Environmental 88 (2009) 479.
- [28] P. Poizot, L.L. Dantras, J. Simonet, Why a cathodic activation by silver interface? Facile reductive homocoupling of 1-iodoalkanes, Electrochemistry Communications 10 (2008) 864867.
- [29] P. Poizot, LL. Dantras, J. Simonet, Palladized silver as new cathode material: Evidence of a one-electron scission for primary alkyl iodides, Journal of Electroanalytical Chemistry 622 (2008) 204.
- [30] P. Poizot, L.L. Dantras, J. Simonet, The one-electron cleavage and reductive homo-coupling of alkyl bromides at silver-palladium cathodes, Journal of Electroanalytical Chemistry 624 (2008) 52.
- [31] Z.Q. He, L.Y. Zhan, Q. Wang, S. Song, J.M. Chen, K.R. Zhu, X.H. Xu, W.P. Liu, Increasing the activity and stability of chemi-deposited palladium catalysts on nickel foam substrate by electrochemical deposition of a middle coating of silver, Separation and Purification Technology 80 (2011) 526.
- [32] C.A. Ma, H. Ma, Y.H. Xu, Y.Q. Chu, F.M. Zhao, The roughened silverpalladium cathode for electrocatalytic reductive dechlorination of 2,4-Dichlorophenoxyacetic acid, Electrochemistry Communications 11 (2009) 2133.
- [33] Y. Ridelman, G. Singh, R. Popovitz-Biro, S.G. Wolf, S. Das, R. Klajn, Metallic nanobowls by galvanic replacement reaction on heterodimeric nanoparticles, Small 8 (2012) 654.
- [34] W.C. Lo, Y.T. Hsieh, I.W. Sun, Chronopotentiometric investigation of the formation of nanoporous bimetallic Pd-Ag by galvanic replacement of nanoporous Ag with Pd, Journal of the Electrochemical Society 159 (2012) D282.
- [35] H.E. Evans, W.M. Bowser, W.H. Weinberg, The adsorption of ethanol on silver clusters supported on alumina, Surface Science 85 (1979) L497.
- [36] A.A. Isse, A.D. Giusti, A. Gennaro, L. Falciola, P.R. Mussini, Electrochemical reduction of benzyl halides at a silver electrode, Electrochimica Acta 51 (2006) 4956.
- [37] R. Wen, Y. Fang, Adsorption of pyridine carboxylic acids on silver surface investigated by potential-dependent SERS, Vibrational Spectroscopy 39 (2005) 106.
- [38] D.D. Bode, J.T.N. Andersen, H. Eyring, Anion and pH effects on the potentials of zero charge of gold and silver electrodes, Journal of Physical Chemistry 71 (1967) 792.
- [39] B. Heinrichs, J.P. Schoebrechts, J.P. Pirard, Palladium-silver sol-gel catalysts for selective hydrodechlorination of 1,2-dichloroethane into ethylene: III. Kinetics and reaction mechanism, Journal of Catalysis 200 (2001) 309.