Short Communication

Kinetic Model for Electrochemical Hydrodechlorination of 2-chlorobiphenyl on a Palladium-Modified Nickel Foam Electrode in a Plug Flow Reactor

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A reactor model was established to describe the electrochemical hydrodechlorination of 2-chlorobiphenyl (2-ClBP) in a plug flow reactor. This model was based on the pseudo-first-order reaction rate constants obtained under various temperatures (T), current densities (J), initial concentrations of 2-ClBP ($C_{2\text{-ClBP},0}$), and Pd loadings (M). The simple global power-law rate ($r_{2\text{-ClBP}}$) equation, with Arrhenius dependency, was determined to be $r_{2\text{-ClBP}} = -1.0982 \times 10^6 \, C_{2\text{-ClBP},0}^{0.0141} \, M^{0.9307} \, J^{1.3461} \, e^{-34615/RT} \, C_{2\text{-ClBP}}$. Results predicted by using the model are in good agreement with experimental values, showing deviation of <8.9%.

Keywords: electrochemical hydrodechlorination; palladium-modified nickel foam; 2-chlorobiphenyl; plug flow reactor

1. INTRODUCTION

Polychlorinated biphenyls (PCBs) are a class of chemical compounds comprising 209 individual congeners [1]. PCBs have recalcitrance, high toxicity, and physical and chemical stability. They can be transported over long distances in the atmosphere and can be deposited in the environment and be bioaccumulated. They can therefore cause serious harm to the environment and to human health [2]. Soil has been considered as a storage reservoir for PCBs in the environment because of its high affinity to organic matter [3,4]. Traditional methods for soil remediation include contaminant-destruction technologies and physical separation technologies. Of these, soil washing and

solvent extraction are promising alternatives for reducing the concentrations of PCBs to acceptable levels [5]. However, the process usually produces significant amounts of wastewater or waste liquids, which must be disposed of, treated, or both [4].

Because of the highly electronegativity of the chlorine atom, PCBs are generally susceptible to reduction, which involves removal of chlorine atom(s) from the PCB ring [6]. Among the various reduction techniques, electrochemically reductive dechlorination has been shown to be effective in detoxification of halogenated wastes because of its high reaction rate, low cost of apparatus, mild reaction conditions, high selectivity, and low tendency for environmental contamination [7-9]. Previous works have focused on development of electrodic materials with high catalytic activities and long working life, optimization of operating conditions (electrolyte composition, current density, temperature, initial concentration of target PCBs, catalyst loading, etc.), as well as exploration of reaction mechanism [10-15]. However, apart from our previous studies focusing on continuous stirred-tank reactor [16], few studies in this area pay attention to the chemical-reactor kinetics of electrochemical dechlorination.

Plug flow reactor (PFR) is one of the reactor types used most commonly in wastewater treatment. It is essential to predict the behavior of chemical reactors in continuous, flowing systems of cylindrical geometry, and thus in estimating key reactor variables such as the reactor dimensions.

In this work, dechlorination of 2-chlorobiphenyl (2-ClBP) to biphenyl at a palladium-modified nickel foam (Pd/Ni foam) cathode in a PFR is presented. A power-law rate equation having several operating parameters (temperature, current density, initial concentration of 2-ClBP, and Pd loading) and expressing Arrhenius dependency was developed to describe and predict reactor performance at steady-state conditions. The kinetics model was verified by comparing predictions with the experimental data.

2. EXPERIMENTAL PART

Chemical reagents and preparation of Pd/Ni foam cathode were similar to those described in our previous study [16]. Electrochemical dechlorination of 2-ClBP was conducted in a PFR (10 mm in diameter, 300 mm in length) fabricated in-house. It consisted of a centrally located stainless-steel anode (1 mm in diameter, 300 mm in length) surrounded with a Pd/Ni foam cathode (300 mm × 40 mm × 1 mm). The electrolyte was prepared by dissolving 2-ClBP in aqueous surfactant stock solution (0.5 M NaOH and 4 g L^{-1} Brij-35) with the aid of sonication, and was continuously pumped upward through the PFR by a peristaltic pump (BT200-2J, Baoding Longer Precision Pump Co., Ltd., China) at a flow rate of 1.4 to 5.5 mL min^{-1} (detention time of 154 to 600 s). Electric power (SK 1760SL, Sanke Electrical Co., Ltd., China) was supplied until the outlet concentration of 2-ClBP reached at least 90% of the inlet concentration. The reaction temperature was controlled by a thermostatic water bath. To investigate the effect of operating variables on the performance and to establish the kinetic model, a series of operating conditions were adopted, as listed in Table 1.

Table 1. Experimental results and model prediction of 2-ClBP conversion under various temperatures (T), initial concentrations of 2-ClBP ($C_{2\text{-ClBP},0}$), palladium loadings (M), current densities (J), and detention times (τ).

Run	$C_{2\text{-ClBP},0}$ (mmol L^{-1})	M (mg cm^{-2})	J (mA cm^{-2})	T (K)	τ (s)	k_{ap} (min^{-1})	X_{mod} (%)	X_{exp} (%)
1	0.031	0.5	0.5	293	600	0.153	76.7	78.5
2	0.041	0.5	0.5	293	600	0.155	76.8	78.8
3	0.086	0.5	0.5	293	600	0.156	77.1	78.9
4	0.148	0.5	0.5	293	600	0.158	77.4	79.3
5	0.086	0.5	0.25	293	600	0.053	44.0	41.1
6	0.086	0.5	0.75	293	600	0.213	92.2	88.1
7	0.086	0.5	1	293	600	0.367	97.7	97.5
8	0.086	0.05	0.5	293	600	0.019	15.9	17.0
9	0.086	0.125	0.5	293	600	0.051	33.4	40.0
10	0.086	0.25	0.5	293	600	0.099	53.9	62.8
11	0.086	0.5	0.5	273	600	0.056	40.6	42.9
12	0.086	0.5	0.5	283	600	0.101	59.1	63.7
13	0.086	0.5	0.5	303	600	0.260	90.6	92.6
14	0.025	0.5	0.5	293	600	0.140	76.6	75.4
15	0.056	0.5	0.5	293	600	0.152	76.9	78.1
16	0.202	0.5	0.5	293	600	0.156	77.6	79.0
17	0.086	0.5	0.05	293	600	0.012	6.4	11.3
18	0.086	0.5	0.8	293	600	0.236	93.8	90.6
19	0.086	0.5	1.5	293	600	0.264	99.9	92.8
20	0.086	0.02	0.5	293	600	0.006	7.1	5.7
21	0.086	0.2	0.5	293	600	0.073	46.7	51.9
22	0.086	1	0.5	293	600	0.229	94.0	89.9
23	0.086	0.5	0.5	273	600	0.055	40.6	42.4
24	0.086	0.5	0.5	288	600	0.107	68.4	65.7
25	0.086	0.5	0.5	313	600	0.266	97.4	93.0
26	0.086	0.5	0.5	293	154	0.107	31.5	24.0
27	0.086	0.5	0.5	293	255	0.127	46.6	41.8

Samples withdrawn from the effluent at steady state were analyzed by high-performance liquid chromatography (HPLC) in the same mode described elsewhere [16]. Brij-35 was selected as the surfactant because it favorably adsorbs to soil via electrostatic attraction, thereby creating a sink for retaining more PCB in the soil [17].

The dechlorination efficiency ($X_{2\text{-ClBP}}$) of 2-ClBP was calculated as the ratio of 2-ClBP that was removed to the initial quantity of 2-ClBP.

$$X_{2\text{-ClBP}} = (C_{2\text{-ClBP},0} - C_{2\text{-ClBP}})/C_{2\text{-ClBP},0} \qquad (1)$$

where $C_{2\text{-ClBP},0}$ and $C_{2\text{-ClBP}}$ are the initial concentration of 2-ClBP and concentration of 2-ClBP in the PFR outlet at a given time, respectively.

Current efficiencies (CEs) of the electrochemical dechlorination of 2-ClBP were calculated from the quantities of products formed and the charge passed by assuming that two electrons and two protons were required for the removal of one chlorine atom as hydrogen chloride.

$$CE = nFN_{BP}/tI \qquad (2)$$

where F (C mol^{-1}) is the Faraday constant, n denotes the number of electrons transferred from 2-ClBP to biphenyl (BP) (here it is equal to 2), N_{BP} (mol) is the amount of BP produced from 2-ClBP, I (A) represents the applied current, and t (s) is the time required to reach steady state.

3. RESULTS AND DISCUSSION

3.1. Confirmation of the plug flow mode of the reactor

Tracer response curves have been proven to be an effective tool for assessing the degree to which the prepared PFR has been achieved [18]. In our study, the reactor was initially filled with 22 mg L^{-1} 2-ClBP solution before it was subjected to a continuous input of clear water. As shown in Figure 1, the time that the 2-ClBP concentration declined markedly was the measured detention time (t). For practical purposes, the dispersion number (d) was used to estimate the degree of axial dispersion in the dechlorination reactor. The dispersion number can be obtained as follows:

$$d \approx \sigma_{\Delta c}^2/(2\tau^2) \qquad (3)$$

where τ denotes the theoretical detention time. $\sigma_{\Delta c}^2$, which represents the variance based on discrete time measurements, is defined as

$$\sigma_{\Delta c}{}^2 \approx \sum t_i{}^2 C_i \Delta t_i / \sum C_i \Delta t_i - (\sum t_i C_i \Delta t_i / \sum C_i \Delta t_i)^2 \qquad (4)$$

where t_i is the time at ith measurement, C_i is the concentration at ith measurement, and Δt_i is the time increment about C_i. The variable Δt_i can be omitted because it appears in both numerator and denominator. Thus, eq 4 can be written as

$$\sigma_{\Delta c}{}^2 \approx \sum t_i{}^2 C_i / \sum C_i - (\sum t_i C_i / \sum C_i)^2 \qquad (5)$$

In the case of $d < 0.05$, the chemical reactor may be regarded as a PFR. As depicted in Figure 1, when the flow rate varied between 1.4 and 5.5 mL min^{-1}, the reactor operated in plug flow mode.
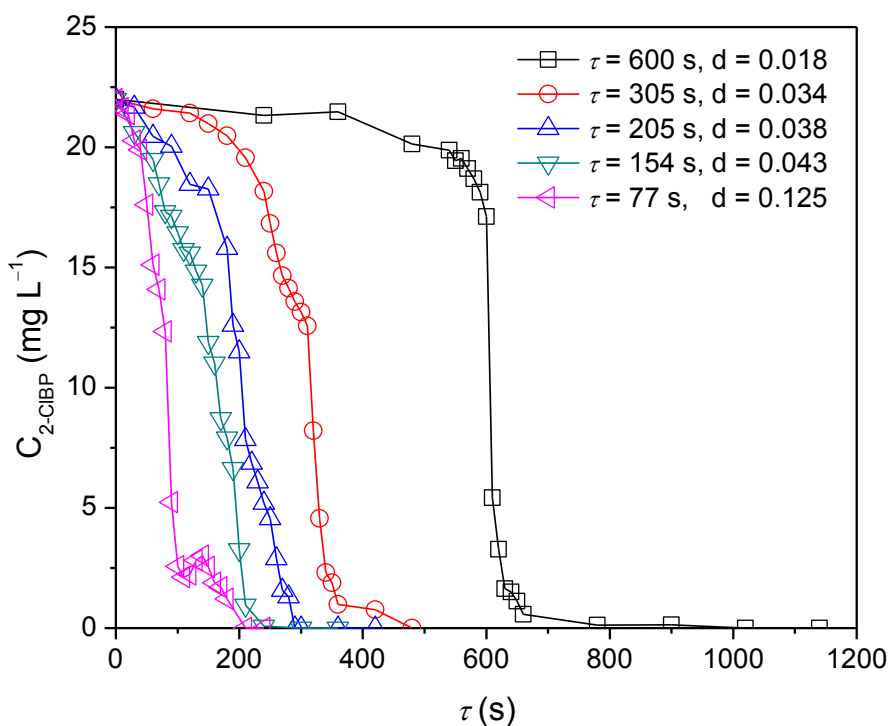
Figure 1. Nonideal response curves for the PFR reactor.

3.2. Evaluation of carbon mass balance

To verify mass balances in the reactor, we attempted to account for total masses of 2-ClBP and BP under conditions in which the reaction was in its intermediate stages and under conditions of near-complete dechlorination. A typical result of electrochemical dechlorination of 2-ClBP in the PFR as a function of time is presented in the inset of Figure 2. The initial rapid drop in 2-ClBP concentration is not matched by a BP increase. This suggests initial electrostatic sorption of the parent congener to the

Pd/Ni foam electrode and to the glassware [16]. In addition, the dechlorination system produced a lower amount of total effluent carbon than did the feed, with less than 12% mass loss.

Cyclohexylbenzene has been reported to be one of the final products during electrocatalytic hydrogenolysis of 2-ClBP on Pd/Ni foam electrode [10]. However, cyclohexylbenzene in the samples was not identified by HPLC above the detection limit of 10 μg L^{-1}. Additionally, attempts using gas chromatography–mass spectrometry could not identify BP in effluent samples. Consequently, loss of carbon mass may be attributed to irreversible adsorption in the electrolytic system. As previously demonstrated [16], direct or indirect electrochemical oxidation of 2-ClBP on stainless steel in basic electrolyte could be neglected; therefore, BP was the major product of the electrochemical process, and the predominant reaction in the present study was the catalytic hydrodechlorination of 2-ClBP to BP (eq 6). In this reaction, active hydrogen ([H]) is formed via electrochemical reduction of H_2O (Volmer reaction, eq 7) [8,9,12,19].

$$2\text{-ClBP} + 2[\text{H}] \rightarrow \text{BP} + \text{HCl} \tag{6}$$

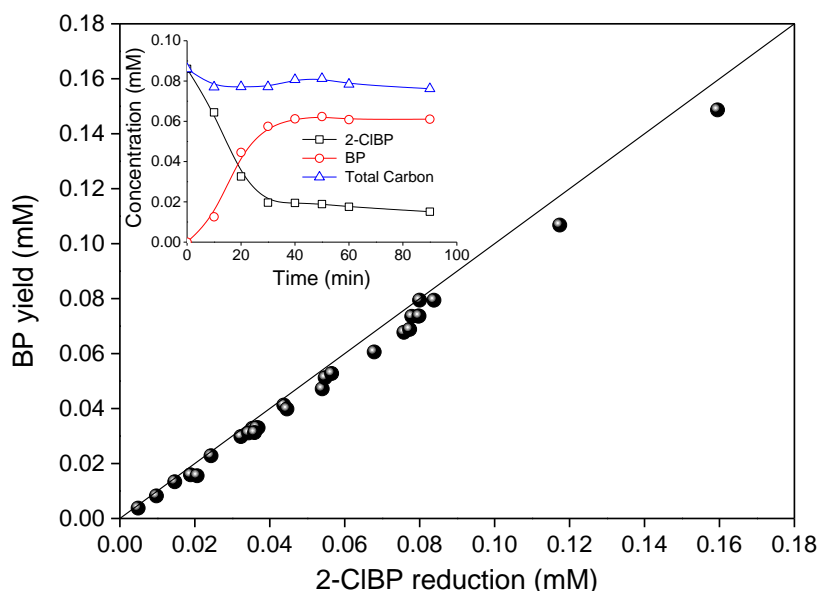$$H_2O + e^- \rightarrow [\text{H}] + OH^- \tag{7}$$

Figure 2. Correlation between the concentrations of 2-ClBP reduction and BP yields from all runs at steady state. The inset is a typical time curve for the electrocatalytic reduction of 2-ClBP in the PFR: $C_{\text{2-ClBP,0}}$, 0.086 mmol L^{-1}; M, 0.5 mg cm^{-2}; J, 0.5 mA cm^{-2}; T, 293 K; τ, 600 s.

3.3. Rate equation for the dechlorination of 2-ClBP in a PFR

The characteristic equation of electrochemical dechlorination of 2-ClBP in a PFR, is [18]

$$r_{2\text{-ClBP}} = -\mathrm{d}F_{2\text{-ClBP}}/\mathrm{d}V \tag{8}$$

where $r_{2\text{-ClBP}}$ represents the rate of electrochemical dechlorination of 2-ClBP, $F_{2\text{-ClBP}}$ denotes molar flow of 2-ClBP in PFR, and V is the volume of the PFR.

In our study, the CEs in all runs were consistently lower than 1%. As previously demonstrated [16], a pseudo-first-order expression could be used to describe the dechlorination kinetics:

$$r_{2\text{-ClBP}} = -k_{ap}C_{2\text{-ClBP}} = -k_{ap}C_{2\text{-ClBP},0}\,(1 - X_{2\text{-ClBP}}) \tag{9}$$

where k_{ap} is the apparent pseudo-first-order kinetic constant.

Combining eqs 8 and 9 yields

$$\tau = V/v_0 = \ln(1/(1 - X_{2\text{-ClBP}}))/k_{ap} \tag{10}$$

where v_0 is the volumetric flow rate through the PFR.

Notably, k_{ap} is related to the concentration of [H]. Thus, it can be regarded as a function of several variables such as $C_{2\text{-ClBP},0}$, Pd loading (M), current density (J), and temperature (T):

$$k_{ap} = \mathrm{f}(C_{2\text{-ClBP},0}, M, J, T) \tag{11}$$

Therefore, k_{ap} can be described as

$$k_{ap} = \mathrm{A}\, C_{2\text{-ClBP},0}{}^{a}\, M^{b}\, J^{c}\, \mathrm{e}^{-Ea/RT} \tag{12}$$

where the exponents a, b and c are the apparent reaction orders for $C_{2\text{-ClBP},0}$, M, and J, respectively, in the PFR; Ea is the activation energy (J mol^{-1}); A is a pre-exponential factor; and R is the universal gas constant (8.314 J mol^{-1} K^{-1}).

The effect of $C_{2\text{-ClBP},0}$, M, J, and T on the electrochemical hydrodechlorination of 2-ClBP in the PFR are listed in Table 1. k_{ap} did not vary with $C_{2\text{-ClBP},0}$ in the range 0.031–0.148 mM. That is, the initial concentration of 2-ClBP is not a significant factor in the rate equation. In addition, $X_{2\text{-ClBP}}$ and the k_{ap} increased with the increase in M (from 0.05 to 0.5 mg cm^{-2}) and J (from 0.25 to 1 mA cm^{-2}). By using eq 12, the apparent reaction orders a, b, and c can be obtained from the plots of ln k_{ap} vs. ln $C_{2\text{-ClBP},0}$, ln k_{ap} vs. ln M, and ln k_{ap} vs. ln J, respectively (Figure 3). In runs 1–13 in Table 1, the values of a, b, and c with respect to $C_{2\text{-ClBP},0}$, M, and J are 0.0141, 0.9307, and 1.3461, respectively. Upon application of the Arrhenius law, the activation energy of 2-ClBP dechlorination on Pd/Ni foam

electrode was found to be 34615 J mol^{-1} by fitting ln k_{ap} and $1/T$ between 0 and 30 °C. As $Ea > 29$ kJ mol^{-1}, the dechlorination process was limited by the chemical reaction at the electrode surface [20]. The value of A calculated by regression, minimizing the sum of squares of the residuals among k_{ap} data presented in Table 1 was found to be 1.0982×10^6. As a result, a power-law equation for the apparent rate constant for the electrochemical dechlorination of 2-ClBP in PFR can be expressed as

$$k_{ap} = 1.0982 \times 10^6 \, C_{2\text{-ClBP},0}^{0.0141} \, M^{0.9307} \, J^{1.3461} \, e^{-34615/RT} \tag{13}$$

To verify the accuracy of the model, a series of additional experiments were performed under conditions different from those used for derivation of eq 13, in particular, in a wider range of operating conditions. The deviation between experimental and model data based on Table 1 was found to be <8.9%, which is an acceptable value considering the high complexity of the electrochemical system.
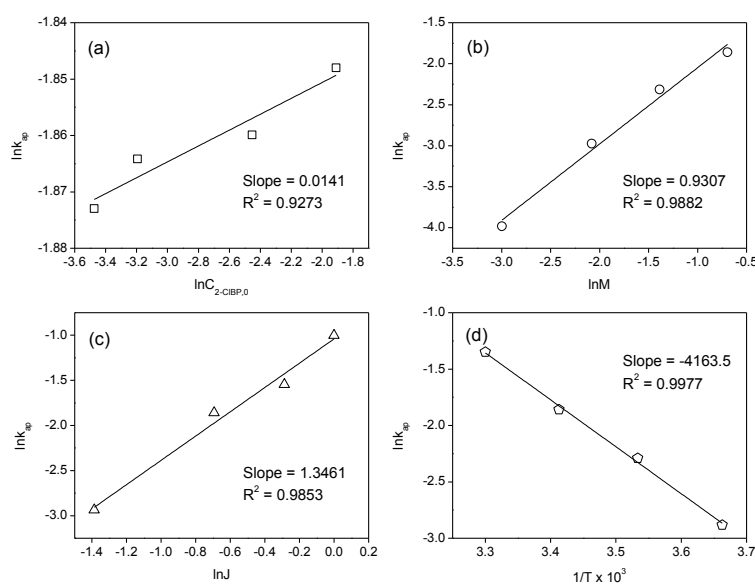

Figure 3. Relationship between ln k_{ap} and ln $C_{2\text{-ClBP},0}$ (M, 0.5 mg cm^{-2}; J, 0.5 mA cm^{-2}; T, 293 K; τ, 600 s), ln k_{ap} and ln M ($C_{2\text{-ClBP},0}$, 0.086 mmol L^{-1}; J, 0.5 mA cm^{-2}; T, 293 K; τ, 600 s), ln k_{ap} and ln J ($C_{2\text{-ClBP},0}$, 0.086 mmol L^{-1}; M, 0.5 mg cm^{-2}; T, 293 K; τ, 600 s), as well as ln k_{ap} and $1/T$ ($C_{2\text{-ClBP},0}$, 0.086 mmol L^{-1}; M, 0.5 mg cm^{-2}; J, 0.5 mA cm^{-2}; τ, 600 s).

4. CONCLUSIONS

Herein, a model for electrochemical hydrodechlorination of 2-ClBP in alkaline solution on a Pd/Ni foam electrode under various operating conditions was established on the basis of a pseudo-first-order rate constant. The rate of 2-ClBP dechlorination producing BP in the PFR can thus be described as $r_{2\text{-ClBP}} = -1.0982 \times 10^6 \, C_{2\text{-ClBP},0}^{0.0141} \, M^{0.9307} \, J^{1.3461} \, e^{-34615/RT} \, C_{2\text{-ClBP}}$. This result lays the groundwork for the design and optimization of chemical reactors for electrochemical dechlorination.

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