



Electrochemical oxidation of phenol at boron-doped diamond electrode in pulse current mode

Junjun Wei*, Xiuping Zhu, Jinren Ni

Department of Environmental Engineering, Peking University, The Key Laboratory of Water and Sediment Sciences, Ministry of Education, Beijing 100871, China

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ABSTRACT

In this study, a pulse current supply was initially used in a BDD anode system (pulse-BDD anode system) for electrochemical oxidation of phenol. The influences of operative parameters (current density, retention time, pulse duty cycle, power frequency) on the system performances were examined by response surface methodology (RSM). As for COD degradation efficiency (D_{COD}) and specific energy consumption (E_s), the influence of retention time was more important than current density and pulse duty cycle, while power frequency hardly presented significant influence. By the comparison with constant current mode, an obvious specific energy consumption reduction was achieved in the pulse-BDD anode system, though the D_{COD} was slightly lower. The significant E_s decrease might be attributed to the reduction of side reactions and concentration polarization in pulse current mode. The pulse-BDD anode system demonstrated an efficient technology to simultaneously obtain high pollutant degradation efficiency and low energy consumption.

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1. Introduction

Electrochemical oxidation is a promising technology to treat bio-refractory wastewaters [1,2]. The degradation effectiveness mainly relies on the nature of the electrodes, as well as reactor construction, electrolysis conditions, etc. Boron-doped diamond (BDD) anodic oxidation demonstrates many attractive electrochemical performances, such as strong oxidation stability, high current efficiency, weak electrode fouling, and long service life [3–6]. However, the BDD anode system is still not applied extensively. It is clear that a technically efficient process must also be economically feasible with regard to its initial capital and operating costs. Energy consumption is a very important economical parameter in electrochemical oxidation process like all other electrolytic processes.

Conventional BDD anode oxidation systems usually run in the constant current condition [7–10]. For the sake of satisfied COD degradation efficiency (D_{COD}) and no anode passivation, relatively high constant current density is required [9–12]. In such a case, side reactions (e.g., oxygen evolution, H_2O_2 and O_3 generation) were strengthened and resulted high specific energy consumption (E_s) and operating costs [13]. Enhancement of mass transport was proven to be efficient to optimize the electrochemical oxidation process. For example, ultrasound enhance will signifi-

cantly improve electrochemical oxidation and decrease the specific energy consumption [14]. However, the additional energy consumption of ultrasound system is high and the reactor is not easy to scale up.

Improvement of the power supplement seems an alternate reasonable approach to reduce the E_s . Panizza et al. [15] applied multiple current steps electrolysis and a semi-continuous current control mode in the BDD electrolysis and achieved the mineralization of organic pollutants with high reaction rate and current efficiency and low energy consumption, but this technology is too complex to be applied extensively. Therefore, we proposed a pulse mode for the electrochemical anode oxidation system.

In this study, a pulse current supply was initially used in a BDD anode system (pulse-BDD anode system) for electrochemical oxidation of phenol. The influences of the operative parameters (current density (j), retention time (t), power frequency (f), pulse duty cycle (x)) on COD degradation efficiency (D_{COD}) and specific energy consumption (E_s) were investigated and optimized by response surface methodology (RSM). Furthermore, the pulse and constant current modes were compared according to the response functions to evaluate the superiority of pulse-BDD anode system.

2. Experimental

2.1. Electrolytic cell and power supply

The electrolytic experiments were performed in a cell with two parallel planar electrodes. A Nb/BDD (boron-doped diamond film

* Corresponding author. Tel.: +86 10 6275 4290; fax: +86 10 6275 6526.

E-mail addresses: weijun81@yahoo.com.cn (J. Wei), nijinren@iee.pku.edu.cn (J. Ni).

on niobium substrate) plate with a working area of 24 cm² (CONDIAS GmbH, Germany) was used as the anode. The boron-doped diamond film (BDD) was synthesized by the hot filament chemical vapor deposition technique (HFCVD) on niobium substrate. The doping level of boron in the diamond layer expressed as B/C ration was about 3500 ppm and the obtained diamond film thickness was about 2 μm with a resistivity of 10–30 mΩ cm. A stainless steel piece with the same size was as the cathode. The interelectrode distance was 1.55 cm. Thus, the working volume of this cell was 37.2 cm³.

Pulse electrolysis was performed using a Pulse Current Supply (DH2002, Beijing Dahua Electron Co. Ltd., China) as power source in a BDD anode system. The output current wave of this power supply was square pulses wave. A pulse cycle T is comprised of T_{on} and T_{off} , which is defined as turn-on period and turn-off period, respectively. At the T_{on} period, current supplied as constant amplitude; while at T_{off} period, the current supply was intermitted. In this study, the power frequency is equal to $1/T$ in the range of 10 Hz to 500 Hz, and the pulse duty cycle is determined by T_{on}/T in the range of 0–100%.

2.2. Electrolysis experiment

Phenol was chosen as the studied object, because it is a common and typical organic pollutant in many industrial effluents. The initial COD concentration was maintained the value of 500 mg/L. Na₂SO₄ was used as the supporting electrolyte and the concentration was 0.05 M. Electrolysis experiments were conducted at different current density (j), retention time (t), power frequency (f), and pulse duty cycle (x). During electrochemical oxidation process, phenol simulated wastewater was continuously pumped through the electrolytic cell at a certain flow rate (determined by retention time).

2.3. Experiment design and analysis

Design of experiments (DOE) is a powerful tool to study the effect of variables and their responses with minimum number of experiments. Response surface methodology (RSM) is one of DOEs which can be a useful tool to examine the influence of operative parameters on system performances and to determine the optimum conditions. The most popular class of second order designs called central composite design (CCD) was used for RSM. Because the CCD is ideal for sequential experimentation and allows a reasonable amount of information for testing lack of fit while not involving an unusually large number of design point.

In this study, RSM was initially used to describe and optimize the electrochemical oxidation process of Pulse-BDD anode system. The CCD with four factors at five levels was applied for the experimental design. The current density (coded as X_1), retention time (coded as X_2), power frequency (coded as X_3) and pulse duty cycle (coded as X_4) were chosen as independent variables. Each variable was coded at five levels between –2 and 2 at the range determined by the preliminary experiments and changed in the ranges of 6–38 mA cm^{–2}, 15–75 min, 10–210 Hz, and 10–90%, respectively. The variables design was shown in Table 1. According to the design of RSM in terms of Minitab 15 software, thirty-one experiments were augmented with seven replications at the design center to evaluate the pure error.

For statistical calculations, the variables X_i were coded as x_i according to the following relationship:

$$x_i = \frac{X_i - X_0}{\delta X} \quad (1)$$

Table 1
Experimental range and levels of the process independent variables.

	Factor	Range and levels				
Independent variable	X_i	–2	–1	0	1	2
Current density (mA cm ^{–2})	X_1	6	14	22	30	38
Retention time (min)	X_2	15	30	45	60	75
Power frequency (Hz)	X_3	10	60	110	160	210
Pulse duty cycle (%)	X_4	10	30	50	70	90

where X_0 is value of the X_i at the center point, and δX presents the step change. Each response Y can be represented by a mathematical equation that correlates the response surface.

$$Y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2 + b_{44}x_4^2 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{14}x_1x_4 + b_{23}x_2x_3 + b_{24}x_2x_4 + b_{34}x_3x_4 \quad (2)$$

where Y is the predicted response, b_0 is constant, b_1 , b_2 , b_3 , and b_4 are the linear effects, b_{11} , b_{22} , b_{33} , and b_{44} are quadratic coefficients, and b_{12} , b_{13} , b_{14} , b_{23} , b_{24} , and b_{34} are interaction coefficients. In this context, D_{COD} and E_s were as the responses.

The COD (in mg L^{–1}) of the solutions were measured by a titrimetric method using dichromate as the oxidant in acidic solution at 150 °C for 2 h (Hachi, USA). For pulse current mode, the E_s (in kWh kgCOD^{–1}) was calculated using the following equation:

$$E_s = \frac{1000UItx}{(\text{COD}_{\text{in}} - \text{COD}_{\text{out}})V} \quad (3)$$

where U is the cell potential (in V), I is the applied current, (in A), t is the retention time (in h), x is the pulse duty cycle of applied current supply, (in %), COD_{in} and COD_{out} are the input and output COD concentration, respectively, (in mg L^{–1}), and V is the cell volume (in mL).

3. Results and discussion

3.1. Influences of operative parameters

Thirty-one CCD designed batch runs were conducted to visualize the effects of independent factors (j , t , f and x) on Pulse-BDD anode system responses (D_{COD} and E_s). The results along with the experimental conditions were presented in Table 2. The D_{COD} was in the range of 33.72–81.82% and the E_s was in 23.2–277 kWh kgCOD^{–1}.

Application of RSM offers, the relationships of D_{COD} and E_s with independent studied variables were obtained as shown in Eqs. (4) and (5), respectively.

$$Y(D_{\text{COD}}) = 70.7171 + 4.8125x_1 + 11.3975x_2 + 1.3208x_3 + 3.9175x_4 - 2.2999x_1^2 - 2.764x_2^2 - 0.2574x_3^2 - 3.4499x_4^2 - 0.4788x_1x_2 - 0.2825x_1x_3 + 2.1875x_1x_4 - 0.3088x_2x_3 + 0.2088x_2x_4 - 0.135x_3x_4 \quad (R^2 = 0.9407) \quad (4)$$

$$Y(E_s) = 110.224 + 41.8152x_1 + 19.0435x_2 + 1.07x_3 + 51.3014x_4 + 0.1347x_1^2 + 2.1642x_2^2 - 1.198x_3^2 + 3.342x_4^2 + 8.8574x_1x_2 + 0.2283x_1x_3 + 20.5113x_1x_4 + 1.2404x_2x_3 + 9.24x_2x_4 - 0.4015x_3x_4 \quad (R^2 = 0.9920) \quad (5)$$

The correlation factors (R^2) were respectively equal to 0.9407 and 0.9920 indicating a good fit for the dependent variables.

The residuals were the deviations of the experimental data value from the predicted values and were estimates of the error terms in

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