Chemometric study on the electrochemical incineration of diethylenetriaminepentaacetic acid using boron-doped diamond anode

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HIGHLIGHTS

- Boron-doped diamond was initially used to degrade DTPA.
- DM and CCRD were employed for optimization and comparison purposes.
- DM model was more accurate than CCRD model in process optimizations.
- Quantum chemistry calculation and LC/MS were used for mechanistic study.
- DTPA degradation pathway was proposed.

ARTICLE INFO

ABSTRACT

The electrochemical incineration of diethylenetriaminepentaacetic acid (DTPA) with boron-doped diamond (BDD) anode had been initially performed under galvanostatic conditions. The main and interaction effects of four operating parameters (flow rate, applied current density, sulfate concentration and initial DTPA concentration) on mineralization performance were investigated. Under similar experimental conditions, Doehlert matrix (DM) and central composite rotatable design (CCRD) were used as statistical multivariate methods in the optimization of the anodic oxidation processes. A comparison between DM model and CCRD model revealed that the former was more accurate, possibly due to its higher operating level numbers employed (7 levels for two variables). Despite this, these two models resulted in quite similar optimum operating conditions. The maximum TOC removal percentages at 180 min were 76.2% and 73.8% for case of DM and CCRD, respectively. In addition, with the aid of quantum chemistry calculation and LC/MS analysis, a plausible degradation sequence of DTPA on BDD anode was also proposed.

1. Introduction

Diethylenetriaminepentaacetic acid (DTPA), a conventional chelating agent, has been extensively utilized in pulp and paper industries. This is mainly due to its strong capabilities to sequester metal cations and to form stable metal complexes which prevent the contact of transition metals and peroxygen chemicals (Nowack, 2003; Sillanpää et al., 2011). Considering that DTPA may be disposed out in the industrial effluents with a remarkable spent of water, there will be seriously environmental contaminations of surface waters, soils and sediments (Sillanpää and Rämo, 2011). In this scenario, several approaches had been employed to remove DTPA from various wastewaters, such as ozonation (Sillanpää et al., 2011), adsorption (Knepper, 2003), Fenton's oxidation (Pirkanniemi et al., 2007), and biological and photochemical degradation (Metsärinne et al., 2004). Unfortunately, these options possess major disadvantages such as inefficient mass transfer, poor separation or degradation performance, secondary pollution, and harsh treatment conditions. Thus, there is great interest in developing more efficient alternatives for destructing DTPA so as to minimize its environmental impacts.

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Over the past decade, anodic oxidation with boron-doped diamond (BDD), providing environmental compatibility and energy efficiency, has been regarded as one of the most promising options in wastewater treatment (Panizza and Cerisola, 2009; Moreira et al., 2017). The course of this option can be initiated by direct electron transfer (on the anode surface), or the organics may be oxidized indirectly by the electro-generated oxidants (mainly the quasi free hydroxyl radicals (•OH)) (Garcia-Segura et al., 2015). As a consequence, BDD technology has been successfully applied to the destruction of a large variety of organic pollutants (Murugananthan et al., 2008; Brillas and Martinez-Huitle, 2015; Jarrah and Muazu, 2016; Salazar et al., 2016; Du et al., 2017). To our knowledge, the electrochemical degradation of DTPA has not been addressed yet.

The current work thus aims at the preliminary evaluation of the viability of BDD technology for the mineralization of DTPA. Two important chemometric techniques, Doehlert matrix (DM) and central composite rotatable design (CCRD), have been employed here for optimization and comparison purposes. It is to be noted that the main difference between DM and CCRD lies in the number of operating levels adopted (Ferreira et al., 2007). For instance, in the four-variable DM, the variables are studied at 5, 7, 7 and 3 levels, respectively. While in the case of CCRD, all variables are studied at the same 5 levels. So far, a correlative work is still lacking in clarifying their similarities and differences in process optimizations. For this reason, it is valuable to find that the work related to comparison between DM and CCRD is very significant. In addition, the main degradation intermediates of DTPA were identified by LC/MS analysis and a possible mineralization sequence was proposed.

2. Experimental section

2.1. Reagents and materials

DTPA ($C_{14}H_{23}N_3O_{10}$, MW 393.35) of 99.9% purity was obtained from Aladdin Industrial Corporation (Shanghai, China). Reagent-grade Na_2SO_4 were purchased from Nanjing Chemical Corporation (China). All solutions were carefully prepared with high-purity water. Planar film Nb/BDD and Nb/Pt electrodes were both commercial products from Condias Corporation (Germany).

2.2. Analytical methods and calculations

The mineralization percentage of DTPA was monitored by the decay of TOC values, which were determined with a Shimadzu TOC-L analyzer (the TOC value of 100 mg L^{-1} DTPA aqueous solution was 39.8 ± 0.2 mg L^{-1}). Identification of the intermediates was achieved by the LC/MS analysis (Waters Acquity UPLC/SQD, USA), and the operating details had been discribed in our recent report (Du et al., 2017). Conductivity and pH of reaction medium were measured by conductivity meter (TDS-SX713, Shanghai) and portable pH analyzer (PH-SX-620, Shanghai), respectively. The quantitative analyses of NH_4^+ and NO_3^- were performed according to cell test methods 114544 and 114563 described in the user manual, respectively (NOVA 60 Spectroquant, Merck, Germany).

The initial limiting current density ($j_{lim,0}$) for electrochemical mineralization of pollutants was defined by the Comninellis model (Eq. (1)) (Tissot et al., 2012):

$$j_{lim,0} = 4 F k_m COD_0 \tag{1}$$

where F was Faraday's constants (96,485 C mol^{-1}); k_m was the average mass transport coefficient (in m s^{-1}) (Wragg et al., 1980); and COD_0 was the original COD value of the solution (1.875 mol O_2 m^{-3} for 50 mg L^{-1} DTPA). Note that the degradation of organics on BDD anode might be subjected to charge transfer and mass-transfer

when $j_{appl} < j_{lim,0}$ and $j_{appl} > j_{lim,0}$, respectively (Tissot et al., 2012). For example, for entry with j_{appl} of 4.52 mA cm^{-2}, the corresponding $j_{lim,0}$ resulted in a value of 0.72 mA cm^{-2}. As a result, all entries in our work could be considered as under mass-transfer control since the j_{appl} values adopted were always higher than the limiting one.

The specific energy consumption (SEC, in kWh kg^{-1}TOC) of the process was calculated by Eq. (2) (Panizza and Cerisola, 2009):

$$SEC = \frac{1000 E_{cell} I t}{V \Delta (TOC)_{exp}} \tag{2}$$

where E_{cell} was the average applied potential (V), I was the applied current (A), t was the reaction time (1 h), V was the solution volume (0.25 L) and $\Delta(TOC)_{exp}$ was the TOC decay (mg L^{-1}).

Accordingly, the mineralization current efficiency (MCE, in %) was estimated by Eq. (3): (Panizza and Cerisola, 2009):

$$MCE = \frac{nFV \Delta (TOC)_{exp}}{4.32 \times 10^7 m I t} \times 100 \tag{3}$$

where n was the number of electrons consumed per DTPA molecule (50), and m was the carbon atom numbers in DTPA (14).

2.3. Degradation experiments

Degradation experiments were conducted at galvanostatic conditions in batch mode (see Fig. SM-1). In the electrochemical cell, Nb/BDD and Nb/Pt were used as anode and cathode, respectively. Both electrodes exhibited an effective surface area of 77.44 cm^2 (8.8 cm × 8.8 cm), and with an electrode gap of 1.0 cm. For each entry, the feed solution (250 mL, containing DTPA and sulfate electrolytes) was stored in a reservoir and circulated continuously through the BDD anode cell via a peristaltic pump. The samples were collected at preset time intervals to track the degree of incineration.

2.4. Experimental design and analysis

In this work, the four-variable DM and CCRD had both been employed to optimize the BDD anodic oxidation processes. Four operating parameters including flow rate (X_1, mL min^{-1}), applied current density (j_{appl}, X_2, mA cm^{-2}), sulfate concentration ([Na_2SO_4], X_3, mM) and initial concentration of DTPA ([DTPA]$_0$, X_4, mg dm^{-3}) were selected for investigation. A literature review (plus the results from preliminary experiments) allowed defining the suitable range of variation for these parameters (Martinez-Huitle and Brillas, 2009). Moreover, the variable levels were chosen by considering the limits of the experimental design, as well as by guaranteeing a proper distribution of the responses (which played a vital role in determining the accuracy of regression models). All entries involved were randomly carried out to prevent biases. The design and analysis of experiments were performed with the statistical software SPSS 17.0 program.

3. Results and discussion

3.1. Process optimization by DM & CCRD

Tables 1 and 2 show the DM and CCRD matrices used in this work, respectively. The corresponding operating levels, as well as the TOC removed (Y_{DM} and Y_{CCRD}, in mg L^{-1}) and TOC removal percentages (R_{DM} and R_{CCRD}, in %) recorded at 60 min, are also presented in these two tables. Noting that for the sake of comparison, the ranges of operating levels employed in these two matrices