



Degradation of creatinine using boron-doped diamond electrode: Statistical modeling and degradation mechanism



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HIGHLIGHTS

- Boron-doped diamond was initially used to degrade creatinine.
- The mineralization was favored in case of low chloride concentration.
- Supporting electrolyte concentration was a crucial parameter for BDD technology.
- Quantum chemistry calculation and LC/MS were used for mechanistic study.
- Creatinine degradation pathways in both electrolyte medium were proposed.

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ABSTRACT

This study investigated the degradation performance and mechanism of creatinine (a urine metabolite) with boron-doped diamond (BDD) anodes. Experiments were performed using a synthetic creatinine solution containing two supporting electrolytes (NaCl and Na₂SO₄). A three-level central composite design was adopted to optimize the degradation process, a mathematical model was thus constructed and used to explore the optimum operating conditions. A maximum mineralization percentage of 80% following with full creatinine removal had been achieved within 120 min of electrolysis, confirming the strong oxidation capability of BDD anodes. Moreover, the results obtained suggested that supporting electrolyte concentration should be listed as one of the most important parameters in BDD technology. Lastly, based on the results from quantum chemistry calculations and LC/MS analyses, two different reaction pathways which governed the electrocatalytic oxidation of creatinine irrespective of the supporting electrolytes were identified.

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1. Introduction

Creatinine is a product of creatine metabolism in the body, which plays vital roles in keeping the health of skeletal muscles and providing energy in mechanisms (Wyss and Kaddurah-Daouk, 2000). In clinical medicine, creatinine content in urine is widely used as a normalising parameter to reflect the specific index of renal function. The accumulation of creatinine in the body may cause acute or chronic renal inadequacy, diabetes, hypothyroidism and gigantism (Bihari et al., 2016; Cao et al., 2016). As a result,

scientific interest in this compound is intensified after its role in kidney failure has been realized.

Creatinine in the environment mostly comes from hemodialysis and urine metabolites (Kallenbach, 2012). Due to its high nitrogen content (40%, w/w), creatinine may cause environmental problems like eutrophication and perturbation in aquatic life. In this scenario, methods of removing creatinine and its behavior during various oxidation processes warrant investigation. Besides, in order to improve the ratio of water reclamation, particularly in aerospace and wearable artificial kidney, it is also necessary to employ efficient technologies for the removal of creatinine (Gura et al., 2009; Nicolau et al., 2009). Unfortunately, in the field of environmental chemistry, creatinine has not been regarded as a conventional pollutant. For this reason, till now there are only two reports available concerning its oxidative degradation (both using TiO₂

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photocatalysis (Antoniou and Dionysiou, 2007; Abdelkader et al., 2009). The major drawback of this technology lies in the low recyclability of the photocatalysts. Moreover, the possible biotoxicity of the nano-sized photocatalysts is also of particular concern since a fraction of catalysts may be released into the environment during the treatment (Friehs et al., 2016). Thus, there is an urgent need to develop more reliable and greener options for the degradation of creatinine.

Among the existing alternatives, the most promising and innovating one is the electrochemical oxidation process (Moreira et al., 2017). This is mainly due to the invention of advanced anode materials, such as boron-doped diamond (BDD). The excellent performance of BDD mainly originates from its high oxygen evolution overpotential and the quasi-free hydroxyl radicals ($\cdot\text{OH}$) generated on its surface (Garcia-Segura et al., 2015). BDD also exhibits outstanding physical and chemical stability, low background current and high surface fractal dimension (Zhang et al., 2014a, 2014b; Moreira et al., 2017). Owing to these properties, BDD appears to be more promising than other existing anodes in the development of practical decontamination technologies (Brillas and Martinez-Huitle, 2015). In the past 10 years, BDD technology has been successfully applied to the degradation and mineralization of various organic pollutants (Chatzisyameon et al., 2009; Martinez-Huitle et al., 2015; Moreira et al., 2017). Thus, it can be assumed that similar success may also be obtained in the case of creatinine.

Hence, the main objectives of the present study are to explore the feasibility of BDD technology in degrading creatinine, as well as to gain new insights into the roles of supporting electrolytes during the electrolysis. Considering that analyzing variables individually was inefficient, a response surface technique named central composite design (CCD) had been employed for optimization purposes (Ferreira et al., 2007; Mao et al., 2012). The main and interactive effects of several operating variables were accordingly assessed under a circulation flow condition. Specifically, due to the lack of comparative studies concerning reaction kinetics and pathway in the absence and presence of chlorides, a special emphasis had been put on investigating the differing roles of supporting electrolytes (Na_2SO_4 and NaCl) in BDD anode cells. The mechanisms for creatinine degradation in sulfate and chloride medium were proposed separately by considering the nature of respective reaction intermediates. As expected, BDD technology represented a powerful alternative for the degradation of creatinine.

2. Experimental section

2.1. Reagents and materials

Creatinine (99.95% purity, $\text{C}_4\text{H}_7\text{N}_3\text{O}$, MW 113.1) was provided by Aladdin (Shanghai, China), while reagent-grade NaCl and Na_2SO_4 were obtained from Nanjing Chemical Corporation (Nanjing, China). Planar film BDD and Pt (both deposited on Nb substrate) were purchased from Condias Corporation (Germany). Stock solutions of 1.0 g L^{-1} creatinine were prepared with ultra-pure water in advance and were kept in a dark bottle.

2.2. Degradation procedure and analytical apparatus

The degradation experiments of creatinine were performed in a recirculation flow cell, which was composed of Nb/Pt cathode and Nb/BDD anode. Fig. SM-1 presented a schematic representation of the apparatus employed. The effective surface areas of both electrodes were 77.44 cm^2 , and the electrode spacing was 10 mm. In each run, $0.50 \text{ L } 100 \text{ mg L}^{-1}$ (0.88 mM) creatinine solution was degraded in aqueous medium containing Na_2SO_4 and/or NaCl as

supporting electrolytes. Note that 0.88 mM was a usual creatinine concentration found in hemodialysis wastes (Kallenbach, 2012). The whole system was operated in batch and galvanostatic mode, with 5 mL sample taken at preset time intervals. The creatinine concentration was then determined using an Agilent 1200 HPLC, which was fitted with a Krosasil C_{18} column ($18 \mu\text{m}$, $4.6 \text{ mm} \times 250 \text{ mm}$) and coupled with a photodiode array detector (set at 210 nm). Analysis was conducted by using methanol/water (65:35, v:v) as mobile phase, at 0.50 mL min^{-1} flow rate. Under these conditions, creatinine eluted at retention time of 8.2 min. The total organic carbon (TOC) of reaction medium was measured with a Shimadzu TOC-L analyzer based on combustion infrared method (the TOC value of 100 mg L^{-1} creatinine aqueous solution was $41.95 \pm 0.07 \text{ mg L}^{-1}$). A MERCK NOVA 60 spectroquant (Germany) was used to determine the concentrations of NH_4^+ and NO_3^- (following 114544 and 114563 cell tests described in the user manual, respectively). Besides, the variations of solution pH and electrical conductivity were monitored by a PPH5012 pH analyzer (Taiwan) and a SANXIN200 conductivity meter (China), respectively.

Identification of degradation products was achieved with a Waters Acquity UPLC/SQD analyzer (LC/MS). For this analysis, $50 \mu\text{L}$ sample was injected into the apparatus, and a mixture of methanol and phosphate buffer (pH = 3.5) (65:35 v/v) was passed at a flow rate of 0.45 mL min^{-1} as mobile phase. The MS operated with electrospray source ionization by applying an interface voltage of -4.0 V and 40 V Q-array RF voltage (in negative mode). The carrier and nebulizing gas was pure nitrogen, and the DL temperature was $300 \text{ }^\circ\text{C}$. Mass spectra were obtained over an m/z range of 80–300.

According to the previous work (Tissot et al., 2012), the initial limiting current density ($j_{\text{lim},0}$) could be defined as follows:

$$j_{\text{lim},0} = 4Fk_m\text{COD}_0 \quad (1)$$

where F was the Faraday constant; k_m was the average mass transfer coefficient (m s^{-1}), which was calculated using the ferric/ferrocyanide couple (Wragg et al., 1980); and COD_0 was the initial chemical oxygen demand of the reaction medium ($4.65 \text{ mol O}_2 \text{ m}^{-3}$ for 100 mg L^{-1} creatinine). Note that to guarantee efficient oxidations, all experiments were performed considering j_{appl} higher than $j_{\text{lim},0}$ (i.e. under mass-transfer control regime).

The mineralization current efficiency (MCE, in %) was assessed by Eq. (2) (Brillas and Martinez-Huitle, 2015):

$$\text{MCE} = \frac{nFV\Delta(\text{TOC})_{\text{exp}}}{4.32 \times 10^7 mIt} \times 100 \quad (2)$$

where n was the number of electrons consumed per creatinine molecule, V was the solution volume (L), $\Delta(\text{TOC})_{\text{exp}}$ was the experimental TOC decay (mg L^{-1}), m was the number of carbon atoms in creatinine, I was the current (A) and t was the electrolysis time (h).

2.3. Experiment design and analysis

In this work, a three-level CCD had been adopted to examine the role of main variables during the electrolysis, as well as to determine optimal operating conditions to maximize the degradation percentage. Four operating variables including initial NaCl concentration ($[\text{NaCl}]$, X_1), initial Na_2SO_4 concentration ($[\text{Na}_2\text{SO}_4]$, X_2), applied current density (j_{appl} , X_3) and flow rate (X_4) were selected for investigation. The corresponding range and level adopted were given in Table SM-1. Note that these operating levels were made according to the results from preliminary experiments and two

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