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Chemometric study on the electrochemical incineration of nitrilotriacetic acid using platinum and boron-doped diamond anode

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HIGHLIGHTS

- The performances of BDD and Pt are compared through a statistical approach.
- BDD and Pt show similar patterns towards NTA mineralization.
- Fractal geometry is initially employed in the field of EAOPs.
- The oxidation of NTA results in an increase in pH and a decreased in conductivity.
- NTA oxidation pathway is proposed.

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ABSTRACT

This study investigated the electrochemical incineration of nitrilotriacetic acid (NTA) at boron-doped diamond (BDD) and platinum (Pt) anodes. Trials were performed in the presence of sulfate electrolyte media under recirculation mode. The parameters that influence the degradation efficiency were investigated, including applied current density, flow rate, supporting electrolyte concentration and reaction time. To reduce the number of experiments, the system had been managed under chemometric technique named Doehlert matrix. As a consequence, the mineralization of NTA demonstrated similar behavior upon operating parameters on these two anodes. Further kinetic study indicated that the degradations followed pseudo-first-order reactions for both BDD and Pt anodes, and the reaction rate constant of the former was found to be higher than that of the latter. Such difference could be interpreted by results from fractal analysis. In addition, a reaction sequence for NTA mineralization considering all the detected intermediates was also proposed.

1. Introduction

Synthetic chelating agents are widely employed in many industrial areas due to their excellent capability to bind and mask metal ions. Among these, nitrilotriacetic acid (NTA) is an important member whose metal binding properties are exploited in a wide range of applications (Padala et al., 2011; Njagi and Goia, 2014). Unfortunately, the extensive use of NTA has led to serious contamination of surface waters, soils and even groundwater. Moreover, codisposal of heavy metals or radionuclides along with NTA creates complex environmental problems for the latter may promote undesirable displacement of toxic heavy metals away from the primary disposal site (Sillanpaa et al., 2011). Therefore, it is desirable to remove these agents from the wastes prior to disposal. However, NTA and its metal complexes are well known for their high resistance to physical, chemical and biological degradation (Nancharaiah et al., 2006; Emilio et al., 2007; Hu et al., 2008). Thus, it is critically important to develop new and powerful alternatives for degrading NTA and its metal complexes.

In last decade, electrochemical advanced oxidation processes (EAOPs), providing versatility, energy efficiency, amenability to automation, have been the subject of intensive investigation (Comninellis and Chen, 2010). As the most popular EAOPs, anodic oxidation (AO) has been successfully applied to the degradation of various organic pollutants (Panizza and Cerisola, 2009). Specifically, one of the most important factors in AO is usually the anode material adopted, which solely determines the hydroxyl radical (·OH) generation (Brillas and Martinez-Huitle, 2011). Boron-doped

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Table 1
Coded and operating levels for the Doehlert design used for RSM analysis of the electrochemical oxidation of NTA on BDD anode (Y_1) and Pt anode (Y_2). Coordinates X_1 to X_4 correspond to the experimental variables applied current density, flow rate, supporting electrolyte concentration and reaction time, respectively.

Entry	X_1^*	X_2^*	X_3^*	X_4^*	X_1	X_2	X_3	X_4	Y_1	Y_2
1	0	0	0	0	6.4	400	5.0	90	53.9	7.6
2	1	0	0	0	9.0	400	5.0	90	66.8	13.6
3	0.5	0.866	0	0	7.7	550	5.0	90	72.5	10.6
4	0.5	0.289	0.817	0	7.7	450	9.0	90	65.6	9.7
5	0.5	0.289	0.204	0.791	7.7	450	6.0	120	77.1	12.9
6	−1	0	0	0	3.9	400	5.0	90	59.3	10.4
7	−0.5	−0.866	0	0	5.2	250	5.0	90	52.1	7.4
8	−0.5	−0.289	−0.817	0	5.2	350	1.0	90	71.0	14.4
9	−0.5	−0.289	−0.204	−0.791	5.2	350	4.0	60	44.8	7.7
10	0.5	−0.866	0	0	7.7	250	5.0	90	56.3	7.5
11	0.5	−0.289	−0.817	0	7.7	350	1.0	90	75.0	12.3
12	0.5	−0.289	−0.204	−0.791	7.7	350	4.0	60	49.1	6.4
13	−0.5	0.866	0	0	5.2	400	5.0	90	73.0	12.5
14	0	0.577	−0.817	0	6.4	550	1.0	90	78.1	17.1
15	0	0.577	−0.204	−0.791	6.4	500	4.0	60	48.7	7.5
16	−0.5	0.289	0.817	0	5.2	450	9.0	90	63.7	12.6
17	0	−0.577	0.817	0	6.4	300	9.0	90	55.0	7.8
18	0	0	0.613	−0.791	6.4	400	8.0	60	50.4	7.7
19	−0.5	0.289	0.204	0.791	5.2	450	6.0	120	65.7	12.2
20	0	−0.577	0.204	0.791	6.4	300	6.0	120	67.9	9.6
21	0	0	−0.613	0.791	6.4	400	2.0	120	84.1	16.6
22	0	0	0	0	6.4	400	5.0	90	53.6	7.5
23	0	0	0	0	6.4	400	5.0	90	53.5	7.7

diamond (BDD) and platinum (Pt) anode, one being "inert" and one being active, have been frequently employed in such studies. However, a literature review claims that no work has been done on degradation of NTA using electrochemical approaches. Furthermore, the application of response surface methodology (RSM) in comparative studies concerning the performance of different anodes has seldom been reported before. Noting that RSM is particularly useful when the levels and responses of all independent variables are not clearly known (Bezerra et al., 2008). Specifically, a very efficient RSM design called Doehlert matrix (DM) is proved to be suitable for optimizing the effective variables with a minimum number of experiments (Caldas et al., 2013).

As a result, the ability of AO to degrade NTA is not known. Hence, the purpose of this work was to cultivate AO and to evaluate its performance in treating NTA-contaminated wastewater. Four system variables, including applied current density (j_{appl}), flow rate, supporting electrolyte concentration (SEC) and reaction time, were optimized by DM-RSM for both BDD and Pt anode cells. Experiments were performed under comparable conditions in order to examine the oxidation capability of each electrolytic system. Specifically, fractal geometry was initially employed to explain the different electro-catalytic activities of these two anode materials. In addition, the reaction intermediates were properly identified by LC/MS and an oxidation pathway of NTA was proposed.

2. Experimental

2.1. Reagents and materials

HPLC-grade NTA was provided by Shanghai Jinke Chemicals (China), while Na_2SO_4 was analytical regents from Wako (Japan). Deionized water was used for all stock solutions.

2.2. Reactor and experimental procedure

Degradation experiments were performed in galvanostatic mode with NTA and deionized water containing sodium sulfate. The electrochemical reactor adopted was a one-compartment flow cell containing two parallel plate electrodes. The anode was either a Nb/BDD thin film (Condias Corporation, Germany) or a Pt sheet with a high polished surface (99.99% purity, Nanjing Tongling Jewelry limited, China), while the cathode was a stainless steel (AISI 304) plate with a high polished surface. The effective surface areas of all electrodes were 77.44 cm^2 and the electrode gap was 10 mm. The solution was stored in a 1.0 L thermo-regulated glass reservoir and circulated through the anode cells by a peristaltic pump. For all entries, the solution volume was 0.5 L and the initial concentration of NTA was 200 mg L^{-1}. Samples were taken at different time intervals to track the concentration of the reactants and intermediates.

2.3. Analytical methods and calculations

The concentration of NTA was mainly monitored from the fall of their TOC values, which were analyzed using a Shimadzu TOC-L analyzer. The observed error in the determination of TOC in duplicate tests was about 1–2%. Conductivity and pH measurements of reaction medium were followed by conductivity meter (Cyberscan300, Singapore) and portable pH analyzer (PHH5012, Taiwan), respectively.

Identification of the reaction intermediates was achieved by UPLC (Ultra Performance Liquid Chromatography) separation of the reaction medium and subsequent online detection via high resolution mass spectrometry equipped with an ESI source at positive or negative polarization and MS^n fragmentation experiments (Waters Acquity UPLC/SQD analyzer, USA). In the UPLC measurements, the mobile phase was 65:35 methanol/phosphate buffer (pH = 3.5) at 0.5 mL min^{-1}. For each trial, the injection volume was 50 μL. The identification and quantitative analyses of the inorganic ions (NH_4^+ and NO_3^-) were performed following the procedures described in our former work (Zhang et al., 2013a).

The surface morphology of the electrodes was examined in morphological mode using field emission scanning electron microscopes (Ultra Plus, Zeiss, Germany). The fractal dimension (D_f) was determined by the Triangular Prism Surface Area methodology of the Fractal Fox 2.0 program (Zhang et al., 2014b). Noting that prior to calculation of D_f values, Laplacian filter (denoising) was performed to exclude any possible influences from the noise of the SEM images (Dhillon and Kant, 2013).