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Definitive screening design applied to electrochemical degradation of Chromotrope 2R with BDD anodes

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HIGHLIGHTS

- A novel definitive screening design was used for optimization of BDD technology.
- The differing and peculiar roles of five anions were identified and interpreted.
- Supporting electrolyte nature and concentration play vital roles in BDD technology.
- Chromotrope 2R degradation pathway in BDD anode cell was proposed.
- The strategy (DSD plus CCRD) was recommended for optimization processes.

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ABSTRACT

Here, a novel three-level definitive screening design (DSD) was initially employed to investigate the electrochemical degradation of Chromotrope 2R (C2R) with boron-doped diamond (BDD) anodes. Experiments were performed using a synthetic C2R solution containing five supporting electrolytes (Na_2SO_4, NaCl, Na_3PO_4, $NaNO_3$ and Na_2CO_3). The effects of nine quantitative parameters on C2R removal rate: initial C2R concentration (50–100 mg L^{-1}), applied current density (1.29–3.87 mA cm^{-2}), Na_2SO_4 concentration (0–10 mM), NaCl concentration (0–10 mM), Na_3PO_4 concentration (0–10 mM), $NaNO_3$ concentration (0–10 mM), Na_2CO_3 concentration (0–10 mM), flow rate (300–500 mL min^{-1}) and temperature (10–50 °C), were investigated. The model obtained was validated and used to select three most significant variables for further investigation. Interestingly, the differing roles of electrolytes during the electrolysis revealed the ion-selective nature of BDD anode system. A five-level central composite rotatable design (CCRD) was then employed to describe the C2R conversion as a function of applied current density, NaCl concentration and temperature. The results obtained confirmed the strong capability of DSD to separate and identify the significant variables in BDD technology. Moreover, the strategy (DSD plus CCRD) employed here enabled a significant reduction in the number of experiments (from over 500 to only 38) compared to traditional screening methods. The possible degradation mechanism of C2R in BDD anode cells was also proposed.

1. Introduction

Chromotrope 2R (C2R) is a kind of monoazo dye which has found wide applications in textile, paper and dyeing industry (Goscianska et al., 2015). In universities, it is often employed for plasma staining and counterstaining in animal histology, and as an indicator for complexometry (Salem et al., 2015). As a consequence, there is a high possibility of releasing C2R into the aquatic environment. Being concerned with its serious menace to the environment and human health, research efforts have been directed toward the development of efficient treatment techniques including adsorption (Goscianska et al., 2015), wet air oxidation (Gomes et al., 2011), TiO_2 photocatalysis (Qamar et al., 2005; Silva et al., 2006; Wang et al., 2007), chemical oxidation (Salem et al., 2015; Santana and Aguiar, 2015) and photoelectro-Fenton

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oxidation (Almeida et al., 2012). Unfortunately, the extreme promises of these options for real applications are tempered by various technological defects, such as secondary pollution, release of toxic metal ions, and low recyclability of the employed catalysts. In this context, there is still an enormous interest in developing more efficient and reliable options for the removal and degradation of C2R.

In recent years, electrochemical oxidation over boron-doped diamond (BDD) seems to have interesting potentialities for emerging pollutants remediation (Moreira et al., 2017). Efficient degradation of organics can be achieved with BDD electrode because of its unique properties such as wide potential window and excellent electrochemical stability, as well as the generation of quasi-free hydroxyl radicals (•OH) on the anode surface (Martinez-Huitle et al., 2015). However, the performance of BDD technology is strongly dependent on the adopted operating variables, such as initial substrate content, the type and concentration of supporting electrolytes, applied current density, temperature, flow rate, initial solution pH, electrolysis time, and et al. (Panizza and Cerisola, 2009). For this reason, it is a daunting task to optimize the process if a large number of variables are taken into account simultaneously.

It is generally accepted that the design of experiment (DOE) is a powerful tool for the optimization of degradation processes (Ferreira et al., 2007). Such tool can take into account the variable interactions, while the number of experiments is limited. However, for most DOE methodologies, the number of operating variables adopted is usually limited to 5 or less (Chatzisymeon et al., 2009; Zhang et al., 2010; Nam et al., 2015). This is because the number of experiments increases quickly when more variables are included in the experimental design. In this scenario, it is necessary to employ statistical screening methods to identify the significant variables while to eliminate the irrelevant ones (Georgiou et al., 2014). Thereafter, the significant variables are examined by applying experimental designs of higher sensitivity (e.g., five-level designs).

In traditional screening designs, each variable is usually set at two levels (−1, +1). Hence, they cannot offer information on possible curvature or on active pure-quadratic effects (Georgiou et al., 2014). One solution to this problem is to employ three-level (−1, 0, +1) design. Recently, a novel three-level DOE named definitive screening design (DSD) has been developed (Jones and Nachtsheim, 2013). The construction of DSD is accomplished by using a numerical algorithm that maximize the determinant of the main effect model matrix while enforcing this structure (Meyer and Nachtsheim, 1995). Moreover, the rows of DSD are randomly shuffled to create a random design. As a consequence, DSD is capable of assess significant variables, two-variable interaction and pure quadratic effects in the presence of effect sparsity (Erler et al., 2013). More importantly, the number of experiments required for k variables is only $2k + 1$ or $2k + 3$ (for an odd number of variables) (Fidaleo et al., 2016). This strategy leads to a dramatic reduction in the number of experiments to be performed, compared to traditional screening methods, thus enabling a significant saving in time and reagent costs (Libbrecht et al., 2015).

However, to our best knowledge, there is still a few literature available considering the employment of DSD approach in various experimental studies (Olsen et al., 2014; Hecht et al., 2015; Kauffman et al., 2015). Thus, it is necessary to undertake further validation studies so as to confirm the usefulness of the methodology.

In this contribution, a DSD approach was initially employed to investigate the electrochemical degradation of C2R by BDD technology. This study was novel, because nine operating variables of BDD technology were included in one single experimental design. Specifically, the roles of five representative supporting electrolytes (Na_2SO_4, NaCl, Na_3PO_4, $NaNO_3$ and Na_2CO_3) during the oxidations have been examined. This is because each anion may present its unique behavior (promotive, inhibitive or unobvious) during the electrolysis, and the coexistence of these anions may result in synergistic or antagonistic effects (Akrout and Bousselmi, 2012). To our knowledge, this was also the first investigation that examined the effects involved in BDD anode cells when five different supporting electrolytes were present in the bulk solution. As expected, some novel results were obtained and were properly interpreted. Lastly, LC/MS analysis was also employed to investigate the degradation pathway of C2R in BDD anode cells.

2. Experimental materials and methods

2.1. Reagents and materials

Chromotrope 2R (C2R, 99.9% purity, $C_{16}H_{10}N_2Na_2S_2O_8$, MW468.37) was obtained from Sinopharm Chemicals (China), while $NaSO_4$, NaCl, Na_3PO_4, $NaNO_3$ and Na_2CO_3 (99% purity) were obtained from Wako (Japan). Solutions and electrolytes were prepared using deionized water. BDD anode and Pt cathode, both deposited on Nb substrates, were obtained from Condias Corporation (Germany).

2.2. Experimental procedure and analytical methods

Degradation experiments were mainly carried out in an undivided recirculation flow cell which consisted of BDD anode of the geometric area exposed to the solution of 77.44 cm^2 (8.8 cm × 8.8 cm), a Pt cathode of the same size and with the electrode gap of 10 mm. The processed solution volume for all entries was 500 mL. All experiments were performed at constant current mode using a RXN-602D DC power supply (Shenzhen, China). Fig. SM-1 gives a schematic representation of the experimental setup adopted.

The color decay of C2R was monitored by using a Shimadzu UV-1800 spectrophotometer (λ_{max} 508 nm). Accordingly, the color removal percentage (η) was assessed by Eq. (1):

$$\eta(\%) = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

where A_0 and A_t, respectively, were the initial and final absorbances of the reaction medium measured at 508 nm.

The TOC values of the reaction medium were determined with a Shimadzu TOC-L analyzer (the TOC value of 100 mg L^{-1} C2R aqueous solution was 32.05 ± 0.05 mg L^{-1}). Identification of the reaction intermediates was achieved by the LC/MS analysis (Waters Acquity UPLC/SQD analyzer, USA). The separation column was reversed-phase CSH C_{18} column (2.1 mm × 50 mm, 1.7 μm), USA, and the mobile phase was a mixture of methanol and phosphate buffer (pH = 3.5) (65:35 v/v) with a flow rate of 0.45 mL min^{-1}. The injection volume was 50 μL for each trial. The MS operated in negative mode with electrospray source ionization by applying an interface voltage of −4.0 V and 40 V Q-array RF voltage. The DL temperature was 300 °C and pure nitrogen gas was used as carrier and nebulizing gas. Mass spectra were acquired over an m/z range of 80–500.

The initial limiting current density ($j_{lim,0}$) was determined as follows (Panizza and Cerisola, 2009):

$$j_{lim,0} = 4Fk_mCOD_0 \quad (2)$$