



Response surface methodology as a tool to optimize the electrochemical incineration of bromophenol blue on boron-doped diamond anode



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ABSTRACT

This study investigated the electrochemical incineration of bromophenol blue (BPB) at boron-doped diamond (BDD) anode. The individual and interaction effects of three control parameters (applied current density, flow rate and supporting electrolyte concentration) on process efficiency were estimated by central composite rotatable design. Among the independent variables, supporting electrolyte concentration displayed the most interesting roles on BPB degradation. The optimal conditions obtained by response surface methodology were: applied current density of 7.36 mA cm^{-2} , $2.6 \text{ mM Na}_2\text{SO}_4$ and flow rate of 568 ml min^{-1} , which gave a decolorization rate of 91.7% and a mineralization rate of 47.3%, as well as an energy consumption of $3518.89 \text{ kWh kg}^{-1} \text{ TOC}$ (7.0 kWh m^{-3}) and a mineralization current efficiency of 15.1% at 120 min of electrolysis. The results presented here demonstrated the high efficiency of BDD technology in mineralizing BPB under mild conditions, as well as the usefulness and capability of the experimental design strategy for successful investigation and modeling of the electrocatalytic processes.

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1. Introduction

In the past decades, dyeing wastewater has been one of the major concerns in environmental protection for its severe color, high toxicity and low biodegradability. As an important member of dye family, bromophenol blue (BPB) has been widely used in many industrial areas for various purposes [1] (see Fig. 1). In universities, it is employed as an acid–base indicator, as well as a color marker to monitor the process of agarose gel electrophoresis and polyacrylamide gel electrophoresis [2]. Unfortunately, most of aqueous BPB consumed are usually disposed without any treatment. Since BPB is highly soluble and stable in aqueous medium, it can easily migrate through aquifers and cause widespread contamination of surface waters. In this scenario, many options have been developed for the in situ and ex situ treatment of BPB [3–5]. Current technologies, like adsorption, photocatalysis, biotic and biomediated degradation, possess disadvantages such as poor treatment efficiency, harsh operating conditions, and difficulty in large-scale applications. Thus, it is critically important to develop new and reliable options for the treatment of BPB-contaminated wastewater.

Recently, oxidative electrochemical technologies, providing versatility, energy efficiency, amenability to automation, have reached a promising stage to effectively degrade biorefractory dye pollutants

[6–8]. However, effective electrochemical oxidation is strongly dependent on the employed anode materials [9–12]. Research into this area has primarily focused on a “non-active” anode called boron-doped diamond (BDD), which exhibits high oxygen overpotential and can produce large amount of quasi free hydroxyl radicals ($\cdot\text{OH}$). Nowadays, BDD technology is well established as one of the most effective options in the areas of wastewater treatment [10]. However, the electrochemical oxidation of BPB has not been addressed yet. For this reason, it is valuable to find that the work related to BPB degradation is extremely significant.

In this study, we examined the electrochemical incineration of BPB through a statistical approach. The objectives of the investigation were: (i) to examine the individual and interaction effects of three variables employed, namely flow rate, applied current density (j_{appl}) and supporting electrolyte concentration, (ii) to optimize these parameters through central composite rotatable design (CCRD), and finally, (iii) to examine the reaction kinetics involved. As a result, electrochemical treatment of BPB offers one possible answer to the problem of their disposal into environment.

2. Experimental

2.1. Reagents and materials

Pure bromophenol blue (BPB) was purchased from Alfa Aesar and used as received. Na_2SO_4 was reagent grade supplied by Wako

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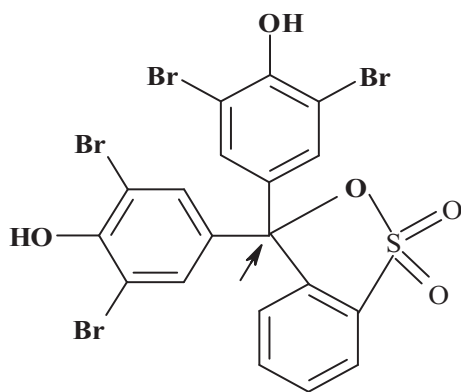


Fig. 1. Molecular structure of bromophenol blue (BPB, $C_{19}H_{10}Br_4O_5S$, MW669.99).

(Japan). All stock solutions were carefully prepared with deionized water. Nb/BDD anode and Nb/Pt cathode were commercial products of Condias Corporation (Germany).

2.2. Analytical apparatus and calculations

The concentration of BPB dye was mainly monitored by measuring absorbance decrease (at wavelength of 592 nm), using a UV-1800 Shimadzu spectrophotometer. In addition, the mineralization of BPB was monitored from the abatement of their TOC values, determined on a Shimadzu TOC-L analyzer.

The energy consumption (EC , in $kWh\ kg^{-1}TOC$) of the process was calculated from Eq. (1) [13]:

$$EC = \frac{1000E_{cell}It}{V\Delta(TOC)_{exp}} \quad (1)$$

where E_{cell} was the average applied potential to the cell (V), I was the current (A), t was the electrolysis time (h), V was the treated solution volume (dm^3) and $\Delta(TOC)_{exp}$ was the experimental TOC decay ($mg\ dm^{-3}$).

The mineralization current efficiency (MCE , in %) was assessed by Eq. (2) [13]:

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

where n was the number of electrons consumed per BPB molecule, F was the Faraday constant, and m was the number of carbon atoms of BPB.

According to the Cominellis model, the relationship between the initial limiting current density ($j_{lim,0}$) and chemical oxygen demand (COD) could be expressed by Eq. (3): [10]

$$j_{lim,0} = 4 F k_m COD_0 \quad (3)$$

where k_m was the average mass transport coefficient ($m\ s^{-1}$), which was determined following the diffusion limiting current technique [14]; COD_0 was the original COD value of the solution ($1.455\ mol\ O_2\ m^{-3}$ for $50\ mg\ dm^{-3}$ BPB).

As is well known, the degradation of organics on BDD may be ruled by charge transfer and mass transport when $j_{appl} < j_{lim,0}$ and $j_{appl} > j_{lim,0}$, respectively [15]. For instance, for entries with a flow rate of $400\ ml\ min^{-1}$ and a sulfate concentration of $5.0\ mM$, the k_m values were $1.267 \times 10^{-5}\ m\ s^{-1}$ and $j_{lim,0}$ resulted in values of $0.712\ mA\ cm^{-2}$ for j_{appl} of $2.970\ mA\ cm^{-2}$. Following this analysis, the BPB degradation in all entries might be considered as under mass-transfer control.

2.3. Degradation experiments

Degradation experiments were performed in galvanostatic mode with BPB and deionized water containing sodium sulfate. The electrolytic systems employed, as well as the experimental procedures, were similar to those of our recent work [8]. The electrochemical reactor adopted was a one-compartment flow cell containing Nb/BDD anode and Nb/Pt cathode. The effective surface areas of both electrodes were $77.44\ cm^2$ and the electrode gap was $10\ mm$. The solution was stored in a $1000\ ml$ thermo-regulated glass reservoir and circulated through the BDD anode cell by a centrifugal pump. For all entries, the solution volume was $500\ ml$ and the initial concentration of BPB was $50\ mg\ dm^{-3}$. Most of the water samples were collected at $60\ min$ for analysis.

2.4. Experimental design and analysis

Response surface methodology (RSM) based on the central composite rotatable design (CCRD) has been widely employed to investigate the effect of variables and to seek the optimum conditions for a multi-variable system [13,16,17]. A three-variable CCRD coupled with RSM was then applied to the optimization of the electrochemical oxidation of BPB on BDD anode. In this study, three control parameters, including flow rate (X_1 , $ml\ min^{-1}$), applied current density (X_2 , $mA\ cm^{-2}$) and supporting electrolyte concentration (X_3 , mM), each in five levels, were investigated. The operating levels adopted were given in Table 1. Note that this selection had considered the results of our former work [16], and preliminary experiments were carried out to limit the extreme values of the variables. Specifically, sodium sulfate was chosen as supporting electrolyte owing to its low reactivity on either anode or cathode. Furthermore, the electrolyte concentrations were set as low as 2.6 – $9.4\ mM$ in order to exclude the undesired side reactions (i.e. the $S_2O_8^{2-}$ formation in sulfate media).

The quadratic equation used to model the responses was $Y = b_0 + \sum b_i X_i + \sum b_{ii} X_i^2 + \sum b_{ij} X_i X_j$, where b_0, i, ii, ij were the model coefficients and X_i, j independent variables [17]. The experiments were randomly conducted to minimize the effect of unexplained variability on the observed responses due to systematic errors. Statistical examination of the results and generation of response surfaces were performed by a SPSS 17.0 program.

3. Results and discussion

3.1. UV-vis spectra changes during electrolysis

Prior to the development of experimental design, a set of representative UV-vis spectra during the electrolysis are recorded to obtain qualitative information on the changes in the molecule of BPB.

As shown in Fig. 2, the UV-vis spectrum of BPB before the treatment presents four well-defined absorption bands, two in the visible region (440 and $592\ nm$) and another two in the UV region (283 and $310\ nm$). The former is directly linked to the chromophore of BPB, while the latter is due to the $\pi \rightarrow \pi^*$ transition in aromatic rings [18]. The insert of Fig. 2 shows the variation of the ratio (A/A_0) at four different wavelengths. A quicker decrease of the band at $592\ nm$, when compared to those of other wavelengths, indicates that the decolorization of

Table 1
Independent variables of the experiments.

Level	X_1	X_2	X_3
–1.68	232	2.97	2.6
–1	300	3.87	4.0
0	400	5.16	6.0
+1	500	6.46	8.0
+1.68	568	7.36	9.4

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