Journal of the Taiwan Institute of Chemical Engineers 000 (2015) 1–7

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

# Doehlert experimental design applied to electrochemical incineration of methyl green using boron-doped diamond anode

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ARTICLE INFO

*Article history:*
Received 20 March 2015
Revised 24 April 2015
Accepted 3 May 2015
Available online xxx

*Keywords:*
Boron-doped diamond
Doehlert design
Methyl green
Mineralization

ABSTRACT

Here, the electrochemical incineration of methyl green (MG), a toxic triarylmethane dye, had been initially performed using boron-doped diamond anode under galvanostatic conditions. The individual and interaction effects of four operating variables (flow rate, applied current density, sulfate concentration and initial MG concentration) on mineralization efficiency were investigated with the aid of Doehlert experimental design. Among the independent variables, sulfate concentration displayed the most interesting roles on MG degradation. Optimum MG degradation was achieved by applying a flow rate of 350 ml/min, applied current density of 7.75 mA/cm$^2$, 5.0 mM $Na_2SO_4$, and initial MG concentration of 200 mg/dm$^3$ at 120 min of electrolysis, being reduced color by 100% and TOC by 80.1%. In addition, the reaction intermediates were properly identified by LC/MS analysis and a plausible reaction sequence was proposed.



## 1. Introduction

Nowadays, synthetic dyes are extensively used in textile colorant, food and drug additives, mordants, cosmetics and so on [1]. Every year, billions of tons of dye-containing wastewater are produced, but only a small proportion is recycled and disposed. Besides the unpleasant appearance of the wastewater, most dyes and their potential breakdown products are toxic, carcinogenic and mutagentic. As a consequence, dye wastewater treatment is the most difficult pollution control task in textile and dyeing industry [2]. Among the dye family, methyl green (MG) is known to has high potential for endocrine disruption of organisms in the aquatic ecosystem [3]. Noting that this dye has been widely used for staining of solutions in medicine and biology, and as a photochromophore to sensitize gelatinous films [4]. Consequently, there is a high risk of releasing MG into the surrounding environment. However, a literature review claimed that only a little number of studies was devoted to the degradation of MG [5,6]. Moreover, the existing options including physical and chemical methods were all ineffective in removing MG because of its high aqueous solubility and resistance to biodegradation. Thus, there is an urgent need for the development of some powerful alternatives.

Over the past decade, electrochemical advanced oxidation processes (EAOPs) and in particular anodic oxidations with boron-doped diamond (BDD) are now considered as true competitors to the classical techniques of water treatment [7,8]. The course of BDD anodic oxidations may be initiated by direct electron transfer from the substrate to the anode surface, or the substrate may be oxidized indirectly by the oxidizing agents (*e.g.*, •OH, $H_2O_2$ and $O_3$) formed through water oxidation [9]. As a result, a large variety of organic pollutants, including dyes, phenols and pharmaceuticals, may be totally mineralized by anodic oxidation with BDD electrodes [10–13]. Hence, it is expected that similar results may also be obtained in the case of MG.

In this scenario, the electrochemical incineration of MG was initially performed in the current study. The main objectives are: (1) to evaluate the effectiveness of BDD technology in the degradation of MG; (2) to establish the correlation between the main operating variables with the aid of Doehlert matrix (DM); (3) to investigate the major factors influencing the degradation efficiency and their capability to remove MG; and (4) to examine the reaction kinetics and mechanism involved. Noting that DM presents some advantages over other experimental designs (*e.g.*, Box–Behnken), such as the highest efficiency and the lowest number of experiments required to complete the optimization process. Thus, the employment of DM is becoming widespread for the optimization of various procedures in recent years [14].

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http://dx.doi.org/10.1016/j.jtice.2015.05.009
1876-1070/

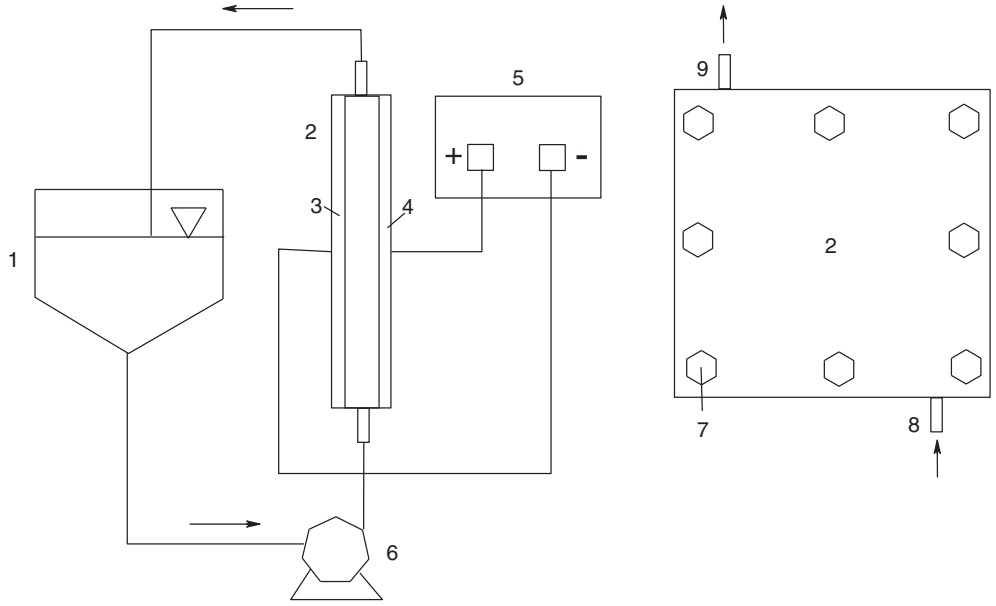


**Fig. 1.** Experimental setup and electrochemical cell for bulk oxidation of MG on BDD anode. **1**: thermo-regulated reservoir; **2**: electrochemical cell; **3**: cathode; **4**: anode; **5**: power supply; **6**: peristaltic pump; **7**: screw; **8**: inlet; **9**: outlet.

## 2. Experimental materials and methods

### 2.1. Materials and chemicals

Methyl green dye (MG, $C_{27}H_{35}Cl_2N_3$) with an appearance of green acicular crystal was purchased from Dankong Industry & Trade Company (Taizhou, China). $Na_2SO_4$ was reagent grade supplied by Wako (Japan). All stock solutions were carefully prepared with high-purity water. Diachem single-side Nb/BDD anode and Nb/Pt cathode were both from Condias Corporation (Germany).

### 2.2. Analyses and analytical methods

It should be noted that UV-vis analysis was unsuitable for determining the concentrations of MG, due to the high initial substrate concentrations employed (100 –200 mg/dm$^3$). Thus, the decay of MG was mainly monitored from the abatement of their TOC values, which were determined on a Shimadzu TOC-L analyzer (the TOC value of 100 mg/dm$^3$ MG solution was 33.91 ± 0.04 mg/dm$^3$). pH measurements of reaction medium were followed by a portable pH analyzer (PHH5012, Taiwan).

Identification of the reaction intermediates was achieved by the LC/MS analysis (Waters Acquity UPLC/SQD, USA) [15]. Note that although this measurement was effective for the identification of reaction intermediates, it was unsuitable for their quantitative analyses. Thus, carboxylic acids generated during the electrolytic oxidations were determined by the ion-exclusion HPLC, and the detailed procedures had been described elsewhere [16].

### 2.3. Degradation experiments

Electrolyses were conducted in a single-compartment electrochemical flow cell containing solutions of 500 mL, with $Na_2SO_4$ used as the supporting electrolyte. The effective surface areas of both electrodes were 77.44 cm$^2$ and the electrode gap was 10 mm. For all entries, the MG solution was pumped continuously from the reservoir to the anode cell by a peristaltic pump, and the samples were collected at 120 min for analysis (see Fig. 1). All experiments were carried out at least in duplicate, and the reported TOC values were within the experimental error of ±2%. This is not surprising since the BDD anode employed retained its original quality throughout all the entries performed in this study. As a result, this anode had maintained a nice serve record of 5 years without any special pretreatment and refreshment [17].

### 2.4. Experimental design and analysis

As mentioned previously, Doehlert matrix has been widely used in optimization processes, for it offers a uniform distribution of points over the whole experimental region [18]. Note that in this matrix, the number of levels is not the same for all parameters: in a four-factor case, the factors are studied at 5, 7, 7 and 3 levels, respectively [19]. Thus, it allows selecting the order of the parameters, and studying the most critical ones at more intense levels. However, the application of DM in the field of EAOPs has seldom been reported before.

A four-variable DM was thus employed to optimize the electrochemical incineration of MG on BDD anode. The operating parameters considered for this study were flow rate ($X_1$, ml/min), applied current density ($X_2$, $j_{appl}$, mA/cm$^2$), sulfate concentration ($X_3$, mM) and initial MG concentration ($X_4$, $[MG]_0$, mg/dm$^3$). These parameters were chosen because they typically play key roles in dictating the performance of BDD technology [7]. The matrix and corresponding code were given in Table 1. Note that some preliminary experiments had been carried out to identify the suitable region for the multivariate optimization. In addition, for practical purposes natural pH and ambient temperature were selected, so as to best simulate actual wastewater conditions prior to and during the electrolytic treatment. More specifically, all entries were performed considering the $j_{appl}$ values above the limiting one (otherwise the efficient electrocatalytic oxidation will not happen [7]). As a result, all the oxidation processes in the present study may be subjected to mass transfer control [11].

According to the methodology of DM, a second-order polynomial response equation (Eq. (1)) was adopted to correlate the response and independent variables:

$$Y = b_0 + \sum b_i X_i + \sum b_{ii} X_i^2 + \sum b_{ij} X_i X_j \quad (1)$$

where $Y$ was the amount of TOC removed (in mg/dm$^3$), $b_{0,i,ii,ij}$ were the constant coefficients and $X_{i,j}$ independent variables [16]. Statistical analyses were performed using SPSS 17.0 program.

Please cite this article as: Z. He et al., Doehlert experimental design applied to electrochemical incineration of methyl green using boron-doped diamond anode, Journal of the Taiwan Institute of Chemical Engineers (2015), http://dx.doi.org/10.1016/j.jtice.2015.05.009