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Research Paper

# New insights into the relationship between anode material, supporting electrolyte and applied current density in anodic oxidation processes

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ABSTRACT

Taking Acid orange-II (AO II) as pollutant model, the relationship between anode material, supporting electrolyte and applied current density was quantitatively investigated with the aid of a statistical tool, factorial design methodology. Boron-doped diamond (BDD), mixed metal oxide (MMO) and platinum (Pt) used as anode materials were examined with $Na_2SO_4$ and NaCl as supporting electrolytes. Analysis of result showed that AO II degradation efficiency was strongly linked to the anode-electrolyte-current interaction. The differing performances recorded in these anode/electrolyte systems could be explained in terms of oxygen evolution over-potential and electro-generated oxidants, and BDD/NaCl system outperformed other systems in terms of decolorization and mineralization efficiency. Further kinetic study indicated that the electrochemical degradation of AO II might follow different reaction orders, depending on the anode material and supporting electrolytes adopted. As a consequence, the new results recorded above were mainly consistent with the low electrolyte concentrations employed (1.0 ~ 10.0 mM). Thus, we highlighted the importance of operating level selections in anodic oxidation processes, especially when different concentrations of supporting electrolytes were present in the reaction system.

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## 1. Introduction

In recent years, anodic oxidation (AO) has demonstrated to be an excellent option for the treatment of various wastewaters [1,2]. However, the efficiency of AO depends dramatically on the employed operating parameters, such as anode material, supporting electrolyte, applied current, flow rate, reaction temperature, initial solution pH, and et al. Among them, the first three have been regarded as the most important parameters that governing the efficiency of AO [3]. Firstly, the nature of anode material significantly influences the stability, electrocatalytic activity and performance. Specifically, boron-doped diamond (BDD), mixed metal oxide (MMO) and platinum (Pt) anodes are all ideal candidates for such studies [4]. Next, the nature of supporting electrolyte is also of vital importance for the involvement of various electro-generated oxidants (e.g., hydroxyl radicals ($^{\bullet}OH$) and $Cl_2$). $Na_2SO_4$ and NaCl, one being "inert" and one being active, have been widely adopted in AO [5]. Lastly, different operating regime may be obtained when the applied current density ($j_{appl}$) employed is higher or lower than the initial limiting current density ($j_{lim,0}$). As is known, the pollutant degradation may be ruled by charge transfer and mass transfer when $j_{appl} < j_{lim,0}$ and $j_{appl} > j_{lim,0}$, respectively [6].

Here, it should be mentioned that there exists a strong relation between anode material, supporting electrolyte and applied current density (i.e. anode-electrolyte-current relation, AEC relation), which exhibits vital implication in understanding electrochemical oxidation processes [2,7]. Despite the numerous works concerning AO, the AEC relation is far from been established. Up to now, there was only one recent report available regarding this topic [7]. Briefly, it was found that BDD/$Na_2SO_4$ and MMO/NaCl were the best systems in removing the pollutant (crystal violet), and the degradation with these two systems was favored at lower and higher $j_{appl}$, respectively. It is interesting to note that crystal violet molecule contains free chloride ions, which may participate in the electrolytic oxidations (thus it is not an ideal pollutant model). Moreover, this study only offers some qualitative information on the AEC relation. Hence, it may be speculated that a quantitative study will surely offer more accurate information on this relationship.

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To achieve this goal, the most common strategy used is to develop theoretical models for prediction purposes. Some kinetic models, including those by Comninellis, Polcaro and Scialdone, have been proposed during the past decade [8]. As a consequence, each model has its advantages and disadvantages when used in real cases. Another effective strategy is to employ the design of experiment (DOE) method. It is well known that DOE is able to create a quantitative relationship between input and output variables [9]. Among the DOE, factorial design methodology (FDM) allows the development of mathematical models which can describe the interactive effect of key operating parameters [10,11]. Considering the complexicity of the reactions in AO, the employment of FDM in such studies is quite appropriate.

In this light, the main objective of this study is to evaluate the AEC relation quantitatively, with the aid of FDM. Here, the combination of three anode materials and two supporting electrolytes results in six different reaction systems (BDD/$Na_2SO_4$, BDD/NaCl, MMO/$Na_2SO_4$, MMO/NaCl, Pt/$Na_2SO_4$ and Pt/NaCl). Please consider, if degradation efficiency is considered as the output variable whereas, $j_{appl}$, reaction time and concentration of supporting electrolyte are chosen as the input variables. Operating conditions being equal, six mathematical models will be obtained and used to demonstrate the quantitative ACE relation. Acid orange-II (AO II), a common azo dye, was chosen as a model pollutant because of its nice structure and bio-refractory nature (see Fig. 1). As expected, achieved results deepen our understanding of the AEC relation in AO.

## 2. Experimental materials and methods

### 2.1. Reagents and materials

Reagent-grade AO II, $Na_2SO_4$ and NaCl were all supplied by Wako (Japan). Nb/BDD electrode was purchased from Condias Corporation (Germany), while MMO electrode (Ti/$(IrO_2)_{0.35}(RuO_2)_{0.65}$), Pt electrode (of 99.99% purity) and stainless steel electrode (AISI 304 grade) were provided by Zhuhai Linai Corporation (China).

### 2.2. Reactor and experimental procedure

Degradation experiments were performed in galvanostatic mode with AO II and deionized water containing $Na_2SO_4$ or NaCl. For all entries, the solution volume was 500 ml and the initial concentration of AO II was 200 mg $dm^{-3}$. In these anode cells, BDD, MMO and Pt plates were used as anode while a stainless steel sheet acted as cathode. The effective surface areas of all electrodes were 77.44 $cm^2$, and the electrode spacing was 10 mm. The solution was pumped through each anode cell and then returned to reservoir for recycling. Samples were taken at preset intervals to track the substrate concentration. All entries were performed in duplicate and the average data were reported. Fig. SM-1 presents a schematic representation of the experimental setup employed.

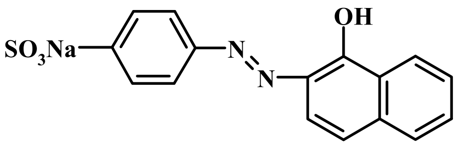

Fig. 1. Molecular structure of Acid Orange-II (AO II).

### 2.3. Analytical methods and calculations

AO II concentration was analyzed by recording the UV–vis spectrum from 200 to 800 nm using a Shimadzu UV-1800 spectrophotometer ($\lambda_{max}$ 482 nm). The corresponding mineralization efficiency (TOC abatement) was determined with a Shimadzu TOC-L total organic carbon analyzer.

According to the Comminellis model, $j_{lim,0}$ could be expressed by Eq. (1): [2].

$$j_{lim,0} = 4Fk_mCOD_0 \tag{1}$$

where F was the Faraday constant, $k_m$ was the average mass transport coefficient (m $s^{-1}$) [12], $COD_0$ was the original chemical oxygen demand value of the solution (10.56 mol $O_2$ $m^{-3}$ for 200 mg $dm^{-3}$ AO II).

Electrochemical measurements (cyclic voltammetry and linear sweep voltammetry) were performed in a traditional three-electrode cell powered by a CHI660E electrochemical workstation (Shanghai, China). The working electrode was a BDD, a MMO or a Pt plate (all with effective surface area of 5.0 $mm^2$), while a Pt plate and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. All measurements were made at 20 ± 1 °C and under nitrogen atmosphere.

### 2.4. Experimental design and analysis

As mentioned above, the FDM model was able to create a quantitative relation between dependent and independent variables, helping us to screen their effects on final response of a reaction system. Briefly, this model was composed of employed variables multiplied by the associated coefficients (see Eq (2)).

$$Y = b_0 + \sum b_iX_i + \sum b_{ij}X_iX_j \tag{2}$$

where Y was the response factor, $b_0$ was the constant, $b_i$ was the coefficient associated with each factor, $X_i$ was the employed variable and $b_{ij}$ represented the coefficient of two-factor interactions.

In this study, FDM was implemented on the basis of four operating parameters for the six reaction systems: supporting electrolyte concentration (SEC, $X_1$), applied current density ($j_{appl}$, $X_2$), flow rate ($X_3$) and reaction time ($X_4$). The variable ranges chosen were: SEC (1.0 ~ 10.0 mM), $j_{appl}$ (2.58 ~ 10.33 mA $cm^{-2}$), flow rate (200 ~ 400 ml $min^{-1}$) and reaction time (20 ~ 40 min) (see Table 1). It was to be noted that low SEC values (1.0 and 10.0 mM) were chosen for the exclusion of side reactions of $S_2O_8{}^{2-}$, $ClO_3{}^-$ and $ClO_4{}^-$ formation [13–15]. Besides, the two $j_{appl}$ values employed (2.58 and 10.33 mA $cm^{-2}$) were lower and higher than $j_{lim,0}$, respectively. Clearly, this strategy allowed us to harvest important information on the role of $j_{appl}$. In addition, the removal rate of AO II (in %) was adopted as the response factor (Y) since the initial concentration of AO II was a constant. As a result, the above combinations guaranteed the Y value ranging from 20 ~ 99% within 40 min of electrolysis. The experimental plan involved 16 entries for each anode/electrolyte system. Statistical examination of the results and generation of contour plots were supported by means of a SPSS 17.0 program.

**Table 1**
Independent variables of the $2^4$ factorial design of experiments.

| Level | $X_1$ | $X_2$ | $X_3$ | $X_4$ |
|---|---|---|---|---|
| - | 1.0 | 2.58 | 200 | 20 |
| + | 10.0 | 10.33 | 400 | 40 |

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