



Kinetic models for the oxidation of organic substrates at boron-doped diamond anodes



Rachel Hems, Charles Gauthier-Signore, Dorin Bejan, Nigel J. Bunce*

Electrochemical Technology Centre, Chemistry Department, University of Guelph, 50 Stone Road East, Guelph, Ontario N1G 2W1, Canada

HIGHLIGHTS

- Three kinetic models for the mineralization of organic substrates are presented.
- Models are fitted to the electrochemical oxidation of model substrates and authentic waste materials.
- Proposals are made for the application of these laboratory results to field conditions.

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ABSTRACT

We have studied electrochemical advanced oxidation of three single substrates (oxalic acid, maleic acid, and 2-naphthol) and real wastes (primary sewage, automotive wastewater, and composting leachate), at boron doped diamond, at which anode organic substrates undergo electrochemical mineralization by reactive hydroxyl species. Experimental data obtained under batch conditions at laboratory scale were fitted to three kinetic models under various conditions of current density and substrate concentration. The optimum kinetic regime of linear loss of substrate with time at constant current density can be achieved for almost all substrates to high conversion, except under extreme conditions of low substrate concentration and high current density. Proposals are made for optimizing this kinetic regime to the treatment of real wastes under flow conditions.

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1. Introduction

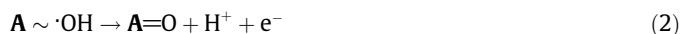
Electrochemical oxidation (EO), especially the variant known as an electrochemical advanced oxidation process (EAOP), is the target of extensive research for the remediation of waste water [1–7]. EAOP is an indirect process in which solvent water is oxidized to anode-bound hydroxyl radicals $\mathbf{A} \sim \cdot\text{OH}$ that act as chemical oxidants: Eq. (1), where \mathbf{A} represents the anode surface [8–13].



EAOP is promoted at ‘non-active’ anodes such as lead dioxide (either $\beta\text{-PbO}_2$ or Ti/PbO_2), ‘dimensionally stable anodes’ (DSAs) based on tin dioxide (e.g., $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_5$), and boron-doped diamond (BDD), all of which have high over-potentials for O_2 formation of $>1.3\text{ V}$ [14]. At these anodes, $\mathbf{A} \sim \cdot\text{OH}$ reacts directly with organic substrates S , initiating free radical oxidation, often leading to complete mineralization. BDD, which is the subject of this com-

munication, has a wide potential window (up to $+2.5\text{ V}$ vs SHE), because its surface sp^3 carbon atoms are highly resistant to oxidation. This gives BDD greater anodic stability than graphite.

EAOP is inefficient or absent at ‘active’ anodes such as DSAs based on noble metal oxides (e.g., $\text{Ti/IrO}_2\text{-Ta}_2\text{O}_5$ and Ti/RuO_2), where $\mathbf{A} \sim \cdot\text{OH}$ is further oxidized to a covalently bound surface layer of ‘higher oxide’ $\mathbf{A}=\text{O}$ (Eq. (2)). At active anodes, EO generally affords partly oxidized substrates (‘electrochemical conversion’) rather than complete mineralization. As an example, acetaminophen is converted in high yield to *p*-benzoquinone at $\text{IrO}_2\text{-Ta}_2\text{O}_5$, but negligible amounts of benzoquinone are formed at BDD, where mineralization predominates [15].



Parasitic evolution of O_2 lowers the current efficiency (CE) for substrate oxidation at both active and non-active anodes. CE, the fraction (or percentage) of all charges passed through the solution that achieve contaminant oxidation, is the ratio $Q_{\text{theor}}/Q_{\text{actual}}$ between the theoretical charge in the absence of side reactions, and the experimental charge needed for remediation.

* Corresponding author.

E-mail address: nbunce@uoguelph.ca (N.J. Bunce).

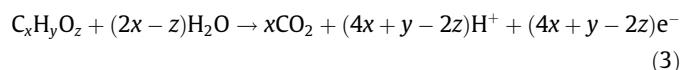
Nomenclature

List of symbols and units

[S]	concentration in mol m ⁻³ or mol L ⁻¹
<i>I</i>	current, A or mA;
<i>J</i>	current density, in this work mA cm ⁻²
<i>t</i>	time, s
<i>A</i>	anode area, m ² or cm ² depending on the context
<i>V</i>	solution volume, m ³ (or L if [S] is in mol L ⁻¹)
<i>k_m</i>	mass transfer coefficient, usually assumed to have the value 2 × 10 ⁻⁵ m s ⁻¹ for small molecules in aqueous solution;

α	I_{app}/I_{lim} (or j_{app}/j_{lim})
<i>F</i>	Faraday constant (96485 C mol ⁻¹).
<i>n</i>	number of electrons used in the oxidation;
<i>p</i>	partial order of concentration
COD	Chemical Oxygen Demand, reported as either mol O ₂ m ⁻³ or as mg O ₂ L ⁻¹
α	I_{app}/I_{lim} (or j_{app}/j_{lim})

Eq. (3) describes electrochemical mineralization of a substrate or a waste C_xH_yO_z. Its progress can be monitored by following changes in substrate concentration, Chemical Oxygen Demand (COD, conventionally based on dichromate oxidation), or Total Organic Carbon (TOC, usually based on combustion).



Loss of substrate is impractical for monitoring multi-component waste streams; also, it cannot assess whether EO led to mineralization because it does not analyze products. COD and TOC are more satisfactory for multi-component waste streams; they are 'global' analyses that do not focus on individual components. TOC measures the organic carbon content unambiguously; however, most regulatory agencies set discharge limits for aqueous wastes based on COD. In the context of EAOP, COD has the advantage that it can be related easily to current efficiency through Eqs. (4) and (5), which give the instantaneous (ICE) and average (ACE) (or cumulative) current efficiencies in terms of Δ COD [14]. A minor caveat is that CE is overestimated for chemically recalcitrant compounds whose COD is significantly lower than the theoretical oxygen demand for complete mineralization [16].

$$ICE_{COD} = F \cdot V \cdot (COD_t - COD_{t+\Delta t}) / 8I \cdot \Delta t \quad (4)$$

$$ACE_{COD} = F \cdot V \cdot (COD_0 - COD_t) / 8I \cdot t \quad (5)$$

Conventional COD analysis using Cr(VI) is time-consuming and costly. A photoelectrochemical method (PeCOD) [17] will probably displace conventional COD analysis in the future. PeCOD is based on substrate mineralization by hydroxyl radicals, which are generated upon UV photon absorption by semiconductor TiO₂ (Eqs. (6) and (7)). The analytical output is the anode current from Eq. (6), net of electron-hole recombination, which makes PeCOD compatible with on-line monitoring. Moreover, the European Union plans to restrict the use of carcinogenic Cr(VI) compounds, though not yet in scientific research and analysis [18].



COD and TOC data are often linked via Eq. (8), where the factor 2.67 is the ratio of the relative molar masses of O₂ and carbon. In practice, this factor is variable because the number of electrons (or HO radicals) needed to oxidize each carbon atom depends on the hydrogen and oxygen content of C_xH_yO_z (Eq. (3)) – and also whether oxidizable heteroatoms (N, P, S) are present.

$$COD \text{ (mg O}_2 \text{ L}^{-1}\text{)} = 2.67 \times TOC \text{ (mg C L}^{-1}\text{)} \quad (8)$$

2. Kinetic models

The extremes of kinetic behavior in an EAOP reactor operated at constant current are mass transport control and current control (the latter also called reaction oxidation control) [19].

Current control requires high substrate concentration and/or low current density. Under 'pure' current control, every A ~ ·OH is trapped by substrate, and the CE for substrate loss approaches 100%. The rate of oxidation scales with the applied current (density) and is independent of [S], whose loss proceeds linearly with charge (Eq. (9)). However, the 'price' paid for high CE is that oxidation is slow; also, mineralization lags behind substrate loss because partly oxidized intermediates are released back into the bulk solution.

$$[S]_t = [S]_0 - (It/nFV) \quad (9)$$

Mass transport control is promoted at low [S]/high *j*; oxidation is limited by the rate of arrival of substrate molecules into the reactive zone at or near the anode. The kinetics are first order in [S], with *k_{obs}* independent of *j* (Eq. (10)); the CE is low due to parasitic evolution of O₂ at the anode, but the plentiful supply of A ~ ·OH at the anode permits multiple acts of oxidation of complex organic molecules before intermediates are released to the bulk solution [20]. As a result, TOC or COD data can appear to be consistent with current control (linear loss with time or charge; CE close to 100%) even when the initial loss of substrate is mass transport controlled [8,21].

$$[S]_t = [S]_0 \exp(-k_m A t / V) \quad (10)$$

Practical remediation strategies compromise between fast remediation (mass transport control) and high CE (current control). Comminellis and his school defined a limiting current (*I_{lim}*) (or limiting current density *j_{lim}*) to achieve that kinetic compromise [14,20]. *I(j)_{lim}* approximates the low current limit of mass transport control (Eq. (11), or Eq. (11a)). High concentrations of simple substrates or small concentrations of complex substrates afford similar values of *j_{lim}*, which depends on (*n* × [S]). Current control and mass transport control are followed when *I_{app}* ≪ *I_{lim}* and *I_{app}* ≫ *I_{lim}*, shown as Eqs. (12) and (13) respectively for COD analysis [14,20].

$$J_{lim} = nFk_m[S] \quad (11)$$

$$J_{lim} = 4Fk_m[COD] \quad (11a)$$

$$[COD]_t = COD_0(1 - \alpha k_m t / V) \quad (12)$$

$$[COD]_t = \alpha [COD]_0 \exp[-Ak_m t / V + (1 - \alpha) / \alpha] \quad (13)$$

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