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ORIGINAL PAPER

Mixed first and zero order kinetics in the electrooxidation of sulfamethoxazole at a boron-doped diamond (BDD) anode

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Abstract Pharmaceutical residues in the aquatic environment represent an emerging environmental problem, because many pharmaceuticals are refractory towards conventional waste water treatment. This study focussed on the oxidation of the sulfonamide antibiotic sulfamethoxazole (SMX) at a boron-doped diamond anode, at which reactive hydroxyl radicals are formed. Electrochemical oxidation led to mineralization with high current efficiency, but without the formation of known toxic products of partial oxidation. A "mixed" kinetic order with respect to substrate concentration was observed; the kinetics could be shifted in the direction of either diffusion control (first order in SMX) or current control (zero order in SMX) by adjusting the substrate concentration and current density. Alternatively, the electrooxidation could be described by a model, applicable to a wide range of reaction conditions, in which the kinetic orders with respect to current and initial substrate concentration were approximately 0.4 and 0.5, respectively.

Keywords Sulfamethoxazole · Boron-doped diamond anode · Electrochemical oxidation · Diffusion vs. current control · Mineralization

1 Introduction

Boron-doped diamond (BDD) has been extensively studied in electrochemical research because it is unusually stable towards both cathodic and anodic polarization [1, 2]. An important process in aqueous solution is the generation of hydroxyl radicals at anodic potentials where the evolution of molecular oxygen is inefficient. Hydroxyl radicals have been identified by "spin-trapping" a nitroxide-hydroxyl radical spin adduct, which was observed by ESR [3].

The high and indiscriminate chemical reactivity of hydroxyl radicals towards organic compounds is the basis of numerous "advanced oxidation processes". The ensuing interest in electrolysis at BDD has led to studies of remediation of matrices such as wastewater [4, 5], dye waste [6], soil [7], and removal of herbicides from waste water [8]. Some recalcitrant organics can be mineralized completely upon electrolysis at BDD anodes [4–6, 8, 9]. Some of these reactions occur with high apparent current efficiency, because attack of the hydroxyl radical on the organic substrate initiates radical chain auto-oxidation, assisted by the O_2 that is concomitantly formed at the anode [10].

The context for our investigation is environmental contamination by waste pharmaceuticals. In the US, Kolpin et al. [11] found pharmaceuticals, hormones and other organic wastewater contaminants in 80% of streams sampled. Sulfamethoxazole (SMX), the subject of this paper, was found in about one sample in six at concentrations up to 1.9 $\mu g\ L^{-1}$. SMX has also been found in the low ng L^{-1} range in drinking water [12, 13]; its principal source is human use, through excretion in urine and improper disposal of unused material to drains [14, 15]. Other sources of environmental contamination by SMX include animal husbandry [16, 17] and point discharges from pharmaceutical manufacturing plants [18], where 1–5% of the product is lost during manufacturing [16, 19, 20].

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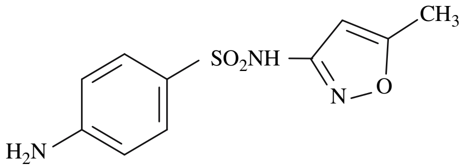

SMX is only partially degraded during sewage treatment in activated sludge systems [14, 21], especially when other carbon and nitrogen sources are plentiful [22]. Proposals have been made for oxidizing SMX and other pharmaceutical contaminants in sewage effluents with agents such as ozone [23, 24], chlorine dioxide [25], and potassium ferrate [26]. SMX in treated sewage effluents has been postulated to pose possible risks of induced bacterial resistance to SMX [27, 28] and to human health [29], although the emerging consensus is that the actual concentrations are well below those likely to harm human populations [30, 31].

In this work we report the electrochemical oxidation of SMX at BDD anodes. Most reported electro-oxidations at constant current exhibit kinetics that are first order in substrate, with the rate limited by diffusion of substrate from the bulk solution to the electrode. The electrochemical oxidation of the sulfonamide antibiotic sulfamethoxazole (SMX) at BDD exhibits mixed kinetic behaviour. The rate of oxidation is zero order in substrate at low current density, when the rate of oxidation at the anode is slower than the rate of arrival of substrate molecules (current control). The data can also be conveniently characterized as partial order in substrate and current.

2 Experimental details

2.1 Materials

Sulfamethoxazole, 4-amino-N-(5-methyl-3-isoxazolyl)-benzenesulfonamide, and sulfanilamide were supplied by Sigma-Aldrich (Oakville, ON); sulfuric acid ($d = 1.84$ g/mL) used for the pH adjustment for initial electrolysis analyte solutions, sodium sulfate used as supporting electrolyte, and HPLC grade methanol were supplied by Fisher Scientific Company (Toronto, ON). Solutions were prepared using a Millipore Milli-Q Reagent Water System with water having resistivity about 18.2 MΩ cm. Additional chemicals for the bacterial assays were 70% ethanol solution (Sigma-Aldrich) and hydrogen peroxide (Fisher) diluted to a 3% concentration with distilled water. Tripticase Soy Broth (TSB) was obtained from Becton, Dickinson Company (Franklin Lakes, NJ). Boron doped diamond electrode (BDD) was supplied by Swiss Center for Electronics and Microtechnology, Inc., Neuchâtel; cathode materials included stainless steel and nickel plate (Sigma-Aldrich).

2.2 Electrolyses

Flow electrolyses utilized a custom-made plug-flow Plexiglas electrochemical reactor, with each compartment having dimensions 58 mm × 15 mm × 4.5 mm, and separated by a Nafion-424 cation exchange membrane. The electrodes (BDD anode and Ni cathode) had outer dimensions 50 × 15 mm, with pieces of Pt wire (Sigma-Aldrich) as electrode feeders. The electrodes were configured vertically to allow the escape of gases evolved during electrolysis. Power to the electrochemical reactor was supplied by an EG&G Model 363 potentiostat/galvanostat. Separate solutions were passed through the anode and cathode compartments at equal flow rates of 1.0 mL min^{-1}, using a Masterflex C/L peristaltic pump. The anolyte (50 mL) was a solution of SMX (0.16–1.0 mM) in 0.025 M Na_2SO_4 as supporting electrolyte; this was recirculated into a reservoir of capacity 100 mL. The catholyte was 0.05 M Na_2SO_4 which was passed only once through the reactor. Electrolyses were run galvanostatically at currents of 100–800 mA (13–107 mA cm^{-2}), with total electrolysis times 200–400 min.

Batch electrolyses were performed with a custom-made Plexiglas undivided reactor, with external dimension 48 mm × 56 mm × 42 mm, internal dimension 36 mm × 50 mm × 30 mm, and the area of both stainless steel cathode and BDD anode 350 mm^2. Solutions were stirred during electrolyses using a Thermix stirrer (Fisher Scientific Model 120 MR). Power was supplied by an EG&G Model 363 potentiostat/galvanostat. Voltage was monitored using a Wavetek DM5XL voltmeter. The analyte (40 mL) was a 0.1–1.0 mM solution of SMX in 0.5 M Na_2SO_4 as supporting electrolyte. Electrolyses were run galvanostatically at currents of 5–100 mA (1.4–28.6 mA cm^{-2}) with total electrolysis times 120–360 min.

2.3 Analysis

HPLC analyses employed a Waters 600E system, equipped with Waters 2487 dual λ absorbance detector set at 254 nm and a Zorbax CN column 4.6 × 150 mm, equipped with a silica pre-column guard. The mobile phase was methanol:water (50:50) (filtered through a 0.2 μm filter) at flow rate of 1.0 mL min^{-1} (retention time of SMX ~ 3.0 min and of sulfanilic acid (SA) ~ 2.5 min). Samples were manually injected with a 150 μL syringe into a 20 μL sample loop of a Rheodyne injector and evaluated using MassLynx® Version 4.0 software.

2.4 Bacterial assays

Electrolyzed solutions were passed into sterile vials via a 0.22 μm sterile syringe driver filter unit (Millex®GS).

Equal portions of the solution (4.7 mL) were inoculated, at least in triplicate, with 100 μL of either *Eschericia coli* or *Bacillus subtilus* (obtained from Dr. H. Lee, University of Guelph), giving ~10^8 bacteria in 10 mL of solution, comprising 5 mL of electrolysate and 5 mL of Tripticase Soy Broth at a final concentration of 30 g L^{-1}. The TSB and all glassware were autoclaved prior to mixing with the electrolysate. Controls, in triplicate, comprised 100% ethyl alcohol, 3% hydrogen peroxide, and the electrolyte (0.025 M Na_2SO_4) without SMX.

The bacteria were thawed and then a small loop was used to smear the bacteria onto an agar plate. From this stock bacteria source a subculture was taken when needed and grown overnight in 5 mL TSB to create a thick bacterial slurry, 200 μL of which was added to 30 mL of TSB solution. A fresh solution was made from the stock concentrations for each set of experiments. A growth curve was obtained by measuring the increase in turbidity at 620 nm (Ultraspec 3100 pro UV/visible spectrophotometer: Amersham Biosciences, Biochrom Ltd., Cambridge England). Turbidity was measured every hour for 8 h and then at 10, 12, 16, 24 and 48 h. Logarithmic bacterial growth occurred 6–8 h after inoculation. After 7 h, enough solution to afford ~10^8 bacteria, as determined by turbidimetry, was used to inoculate the chemical assay solution. After incubation for 7 h, 100 μL of solution were smeared onto pre-prepared petri-dishes, and the colonies were counted after incubation at 30 °C for 24 h.

3 Results and discussion

Initial experiments were carried out amperostatically in the plug-flow micro-reactor operated as a divided cell in recirculation mode, with concentrations of SMX in the range 0.16–1.0 mM, and 0.05 M Na_2SO_4 as an environmentally friendly supporting electrolyte. Under our conditions, peroxodisulfate did not appear to be formed from the supporting electrolyte. During electrolysis the pH of the solution remained in the range 6–7, at which the amino group of SMX is exclusively in the $-NH_2$ form. These reactions followed conventional first order kinetics, with ln[SMX remaining] linearly dependent on the number of passes through the reactor, a proxy for time (Fig. 1). This behavior is consistent with our previous work [9, 10]. The rate of electrolysis was also first order in applied current (see insert to Fig. 1).

Conventional chemical oxidations of SMX yield the hydroxylamine or nitroso compound [32, 33]. Direct electrochemical oxidation of SMX, using a carbon paste anode, also occurs at the $-NH_2$ group, to give the azo compound [34], which may also be the coloured product having λ_{max} 460 nm, observed upon Ce(IV) oxidation of SMX [35]. No such products were seen in our work, consistent with the electro-oxidation of SMX at a BDD anode being hydroxyl radical mediated. The lack of formation of the hydroxylamine and/or the nitrosocompound is significant environmentally because these compounds—whose formation is catalyzed in vivo by cytochrome P-450 monooxygenases [36, 37]—are responsible for the development of the hypersensitivity reactions such as fever, hepatotoxicity, and skin eruptions [37] that are frequently seen when SMX is used to treat opportunistic infections in patients infected with human immunodeficiency virus (HIV) [38].

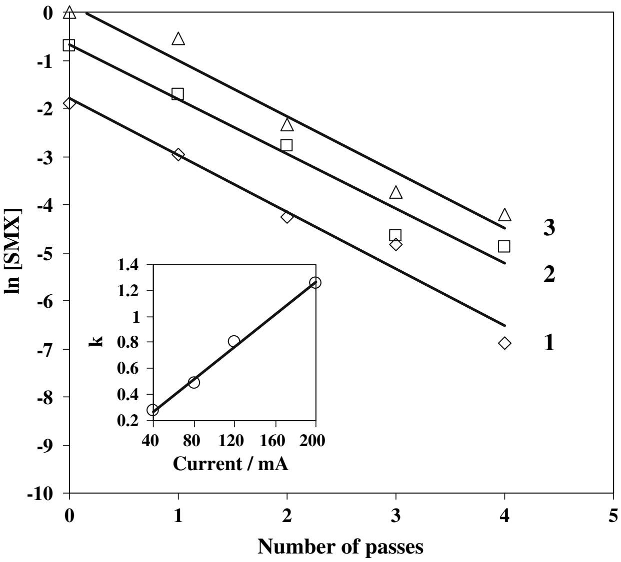

Fig. 1 Electrooxidation of SMX in a divided plug-flow microreactor operated in recirculation mode; **1**—0.15 mM; **2**—0.5 mM; **3**—1 mM

Different kinetic behaviour was seen upon electrolysis of SMX in the undivided 40 mL batch cell, using a BDD anode, a stainless steel cathode, and 0.5 M Na_2SO_4 as the supporting electrolyte (Fig. 2). In the oxidation of 1.0 mM SMX electrolysed at 20 mA, the time points in the range 0–75 min followed a linear (zero-order) relationship between SMX concentration and time (current control, Fig. 2A), but the later time points from 45 to 195 min followed first order behaviour, with a linear relationship between ln (c_t/c_0) and time (diffusion control, Figure 2B). Current control implies that the substrate arrives at the anode faster than it can be oxidized, whatever the mechanism of oxidation, whereas first-order kinetics indicates rate-limiting arrival of the substrate at the electrode [39]. In the context of waste remediation, the importance of current control is that the remediation process does not slow down as the reaction proceeds, whereas diffusion-controlled processes become slower—and at constant current, less efficient—as the substrate is consumed.

Adjustment of the experimental conditions moved the kinetic behaviour towards either current control or diffusion control. The time ranges over which current or diffusional

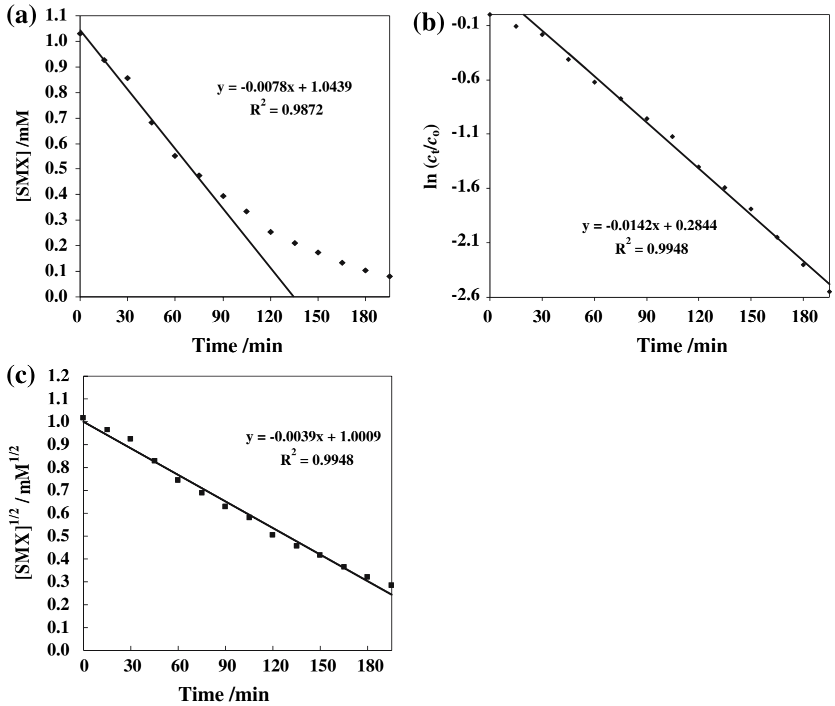

Fig. 2 (**A**) Pseudo-zero order data (0–75 min) for 1.00 mM SMX electrolysis at Si/BDD under 20 mA current in an undivided batch cell. (**B**) Pseudo-first order data (45–195 min) for 1.00 mM SMX electrolysis at Si/BDD under 20 mA current in an undivided batch cell. (**C**) Partial order data (full time range, $n = 0.5$) for 1.00 mM SMX electrolysis at Si/BDD under 20 mA current in an undivided batch cell

control were operative were selected on the basis of the highest R^2 for fitting the relevant time points. At a constant initial concentration of 1.0 mM SMX (Table 1A), pseudo first-order kinetics were followed exclusively at currents 50 mA and greater. Mixed behaviour was seen at 20 mA and below, with zero order behaviour persisting to greater substrate conversion the lower the current. In the low-current regime, the rate of reaction was proportional to the applied current. The average rates 0.0023, 0.0037 and 0.0078 mM min^{-1} observed at currents 5, 10, and 20 mA approximated the expected ratio 1:2:4.

Electrolyses at a constant current of 10 mA but different starting concentrations gave mixed zero- and first-order behaviour in all cases (Table 1B). Zero order kinetics persisted less at the lower concentrations (Fig. 3A), at which the rate of reaction was almost proportional to the initial concentration. In the pseudo first-order part of the reaction, the rate constant was almost invariant with concentration, as expected for a first order reaction (Fig. 3B).

The foregoing discussion implies that current control and diffusion control are competing processes. Under zero order conditions (low current and/or high [SMX]), SMX molecules arrive at the anode faster than the electrochemical production of hydroxyl radicals with which to react. Under first order conditions (high current and/or low [SMX]) the converse situation pertains, with the rate of oxidation limited by the rate of diffusion of SMX molecules to the electrode.

A different kinetic perspective is that the electrochemical oxidation of SMX at BDD is a partial order process with kinetic participation from both the formation of hydroxyl radicals (current) and the concentration of SMX. For a partial order rate expression (Eq. [1]), the integrated form is given by Eq. [2].

$$\text{rate} = k.[\text{SMX}]^n.i^m \quad (1)$$

$$[\text{SMX}]^{1-n}(t) - [\text{SMX}]^{1-n}(0) = k.i^m.t \quad (2)$$

Plots of $[\text{SMX}]^{1-n}$ vs. time at constant current over the whole time course of the reactions were constructed with varying values of n; the best fit was determined on the basis of the highest R^2 value. For electrolyses of 1.0 mM SMX at currents 20 mA and lower, values of n near 0.5 consistently fitted the complete kinetic run, as shown by Fig. 2C. Correspondingly, Fig. 3C shows the half order plots for electrolyses at 10 mA but different initial concentration of SMX. Figure 4, derived from Table 1A, shows the relationship between the half order $k_{\frac{1}{2}(obs)}$ and i when current was varied and $[\text{SMX}]_0$ was constant, corresponding to a 0.42 order in current.

The validity of the partial order model was tested by calculating the half-order $k = k_{\frac{1}{2}(obs)}/i^{0.42}$ for all experiments. For the data of Table 1A (1.0 mM SMX, vary i), $k = 0.017 \pm 0.002$ $\text{mM}^{0.5}$ min^{-1} $\text{A}^{-0.42}$; for the data of Table 1B ($i = 10$ mA, vary [SMX]), $k = 0.017 \pm 0.003$ $\text{mM}^{0.5}$ $\text{min}^{-1}\text{A}^{-0.42}$.

In order to probe the mechanism of oxidation, similar experiments were undertaken with sulfanilamide (SA), an analog of SMX lacking the heterocyclic substituent. Comparisons of Table 1A, B (SMX) with Table 2A, B

Table 1 (A) Degradation rates of 1.00 mM or 0.50 mM SMX at various currents at Si/BDD in an undivided batch cell. (B) Degradation rates of various concentrations of SMX at applied current of 10.0 mA at Si/BDD anode in an undivided batch cell

[SMX]/mM	*i*/mA	Reaction type	Current controlled kinetics *n* = 0			Diffusion controlled kinetics *n* = 1			Partial order kinetics *n* = 0.5		
			$v_{0\ (obs)}$ (mM min^{-1})	R^2	Time range (min)	$k_{1\ (obs)}$ (min^{-1})	R^2	Time range (min)	$k_{1/2\ (obs)}$ (mm$^{0.5}$ min^{-1})	R^2	Time range (min)
(A)											
1.00	5	Mixed	0.0023	0.990	0–330	0.011	0.995	270–360	0.0018	0.988	0–360
	10	Mixed	0.0041	0.994	0–165	0.012	0.996	75–195	0.0030	0.988	0–195
		Mixed	0.0031	0.964	0–195	0.0085	0.983	120–195	0.0020	0.971	0–195
		Mixed	0.0039	0.944	0–120	0.0081	0.982	135–210	0.0020	0.973	0–210
	20	Mixed	0.0078	0.987	0–75	0.014	0.995	45–195	0.0039	0.991	0–195
	50	First	0.0082	0.985	0–120	0.019	0.901	0–180	0.0055	0.974	0–180
		First	N/A			0.019	0.977	0–195	0.0042	0.975	0–195
	100	First	N/A			0.018	0.974	0–180	0.0048	0.968	0–180
		First	N/A			0.022	0.975	0.986	0.0060	0–120	0–120
		First	N/A			0.021	0.992	0–120	0.0057	0.972	0–120
0.50	10	Mixed	0.0034	0.996	0–90	0.014	0.993	30–195	0.0026	0.985	0–195
	10	Mixed	0.0035	0.992	0–60	0.013	0.995	60–195	0.0026	0.985	0–195
	20	First	N/A			0.016	0.994	0–195	0.0028	0.982	0–195
B											
[SMX] (mM)		Reaction type	Current controlled kinetics *n* = 0			Diffusion controlled kinetics *n* = 1			Partial order kinetics *n* = 0.5		
			$v_{0\ (obs)}$ (mM min^{-1})	R^2	Time range (min)	$k_{1\ (obs)}$ (min^{-1})	R^2	Time range (min)	$k_{1/2\ (obs)}$ (mM$^{0.5}$min^{-1})	R^2	Time range (min)
1.0		Mixed	0.0041	0.994	0–165	0.012	0.996	75–195	0.0030	0.988	0–195
1.0		Mixed	0.0031	0.964	0–195	0.0085	0.983	120–195	0.0020	0.971	0–195
1.0		Mixed	0.0039	0.944	0–120	0.0056	0.979	0–210	0.0020	0.973	0–210
0.75		Mixed	0.0036	0.996	0–150	0.013	0.991	75–195	0.0028	0.993	0–195
0.50		Mixed	0.0034	0.996	0–90	0.014	0.993	30–195	0.0026	0.985	0–195
0.50		Mixed	0.0035	0.992	0–60	0.013	0.995	60–195	0.0026	0.985	0–195
0.25		Mixed	0.0017	0.996	0–105	0.017	0.998	60–180	0.0021	0.989	0–180
0.25		Mixed	0.0016	0.994	0–120	0.013	0.994	45–195	0.0018	0.987	0–195
0.10		Mixed	0.00070	1.000	0–30	0.016	1.000	30–180	0.0013	0.982	0–180

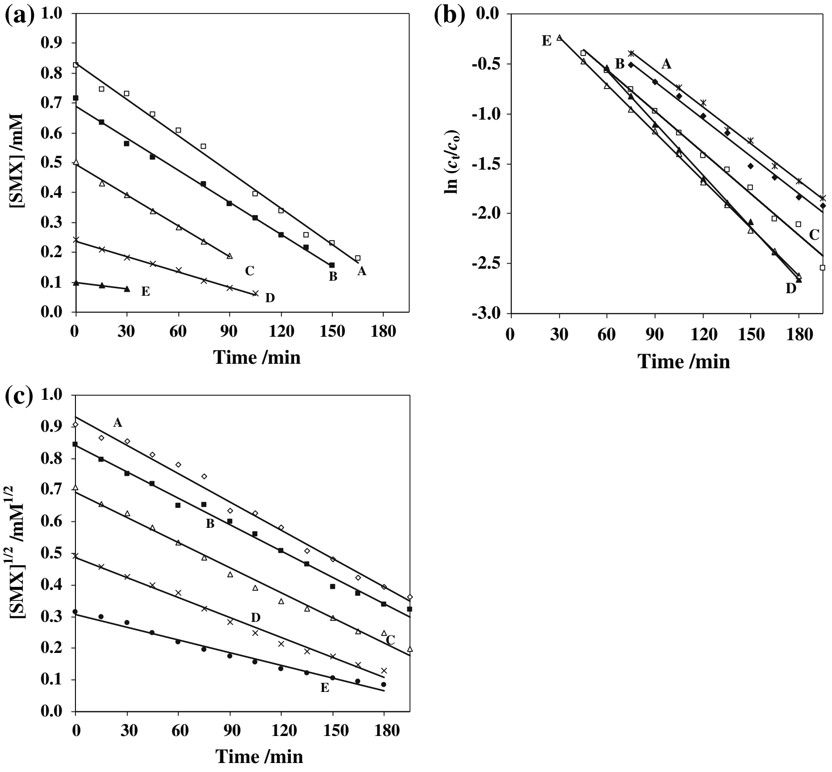

Fig. 3 (**A**) Comparison of pseudo zero order data for all SMX electrolyses at 10 mA (Curve A, squares: 1.0 mM; Curve B, solid squares: 0.75 mM; Curve C, triangles: 0.50 mM; Curve D, crosses: 0.25 mM; Curve E, solid triangles: 0.10 mM). (**B**) Comparison of pseudo first order data for all SMX electrolyses at 10 mA (Curve A, asterisks: 1.0 mM; Curve B, solid rhombi: 0.75 mM; Curve C, squares: 0.50 mM; Curve D, solid triangles: 0.25 mM; Curve E, triangles: 0.10 mM). (**C**) Comparison of partial (n = 0.5) order data for all sulfamethoxazole electrolyses under 10 mA (Curve A, rhombi: 1.0 mM; Curve B, solid squares: 0.75 mM; Curve C, triangles: 0.50 mM, Curve D, crosses: 0.25 mM; Curve E, dots: 0.10 mM)

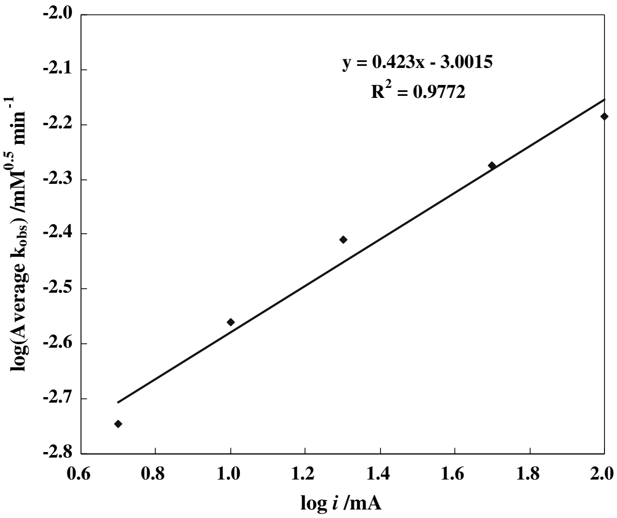

Fig. 4 Determination of the kinetic order of electrooxidation with respect to current (m) of SMX at fixed initial concentration and varied applied currents at Si/BDD anode (the units refer to those of k)

(SA) show that zero order behaviour was somewhat more prominent for SA. At variable concentrations (Tables 1B and 2B) the first order rate constants for the relevant parts of the data were closely similar. When the data were treated on a partial order basis, the best fit was to [SA]$^{0.6}$ vs. time (i.e., 0.6 order in SA) and 0.4 order in current. This similarity suggests that the amino-substituted ring is the principal site of oxidation in both molecules. An unexpected observation, recognizing the electrophilic nature of the hydroxyl radical [40], was that in acidic solution (pH = 2), at which the NH_2 group is protonated, the rate of oxidation of SA was almost the same as in neutral solution.

The electrolyses of SMX and SA in the undivided cell gave no intermediates or products observable by HPLC with UV detection at wavelengths ≥230 nm. This implies that oxidation produced small organic molecules or gave complete mineralization to $CO_2 + H_2O$. This was confirmed by TOC (total organic carbon) analysis. For the electrolysis of 1.0 mM SMX at 10 mA current after 210 min, the loss of TOC was 32% when the loss of SMX by HPLC was 73%; for the electrolysis of 0.25 mM SMX at 10 mA current after 195 min, the loss of TOC was 62% when the loss of SMX by HPLC was 90%.

Equation [3] is the hypothetical process for the complete mineralization of SMX assuming that every act of oxidation is electrochemical.

$$C_{10}H_{11}N_3O_3S + 30H_2O \rightarrow 10CO_2 + 3NO_3^- + SO_4^{2-} + 71H^+ + 66e^- \quad (3)$$

Electrolysis for 210 min at 10 mA corresponds to Q = $i.t$ = 126 C ≡ 1.31×10^{-3} mol of electrons. Considering only the SMX molecules that are mineralized completely, based on the TOC measurement, their oxidation requires

Table 2 (A) Degradation rates of 1.00 mM SA at various currents at Si/BDD in an undivided batch cell. (B) Degradation rates of various concentrations of SA at applied current of 10.0 mA at Si/BDD anode in an undivided batch cell

[SA]/mM	*i*/mA	Reaction type	Current controlled kinetics $n = 0$			Diffusion controlled kinetics $n = 1$			Partial order kinetics $n = 0.6$		
			$v_{0\ (obs)}$ (mM min^{-1})	R^2	Time range (min)	$k_{1(obs)}$ (min^{-1})	R^2	Time range (min)	$k_{0.6\ (obs)}$ (mM$^{0.4}$min^{-1})	R^2	Time range (min)
A											
1.0	2	Mixed	0.0028	0.993	0–255	0.0080	0.999	225–390	0.0016	0.998	0–390
	10	Mixed	0.0069	0.997	0–60	0.013	1.000	75–195	0.0031	0.996	0–195
	20	Mixed	0.0076	0.997	0–60	0.018	0.997	75–165	0.0037	0.999	0–165
	20	Mixed	0.0063	0.997	0–105	0.013	0.998	75–195	0.0032	0.996	0–195
	50	Mixed	0.011	0.999	0–50	0.031	0.997	60–110	0.0059	0.998	0–110
	50	Mixed	0.011	0.994	0–60	0.017	0.996	40–150	0.0045	0.994	0–150
	100	Mixed	0.013	0.999	0–50	0.044	0.997	50–90	0.0077	0.995	0–90
B											
[SA] /mM		Reaction type	Current controlled kinetics $n = 0$			Diffusion controlled kinetics $n = 1$			Partial order kinetics $n = 0.6$		
			$v_{0\ (obs)}$	R^2 (mM min^{-1})	Time range (min)	$k_{1(obs)}$ (min^{-1})	R^2	Time range (min)	$k_{0.6\ (obs)}$ (mM$^{0.4}$min^{-1})	R^2	Time range (min)
1.0		Mixed	0.0069	0.997	0–60	0.013	1.000	75–195	0.0031	0.996	0–195
0.50		Mixed	0.0038	0.995	0–60	0.016	0.999	135–195	0.0024	0.998	0–195
0.40		Mixed	0.0030	0.996	0–75	0.012	0.994	30–195	0.0022	0.991	0–195
0.25		First	N/A			0.013	0.999	0–195	0.0019	0.980	0–195
0.10		First	N/A			0.013	0.998	0–195	0.0014	0.987	0–195

Table 3 Partial order kinetics in electrochemical oxidations for various substrates

Substrate	Concentration range /mM)	Anode	Kinetic order (*n*)	Reference
Sulfide ion	15–60	BDD	0	42
Dihydroxymalonic acid	50	Pt	0	43
Phenol (+NaCl)	1–50	Carbon	0.04	44
1,2-Dichloroethane	1–4	Stainless steel	0.28	45
Sulfamethoxazole	0.1–1.0	BDD	0.5	This work
Sulfanilamide	0.1–1.0	BDD	0.6	This work

$(0.32 \times 10^{-3}$ mol SMX $L^{-1} \times 0.040$ L $\times$ (66 mol e^{-}/1 mol SMX)) = 8.4×10^{-4} mol of electrons, so the apparent current efficiency is 64%. The corresponding calculation for the 0.25 mM solution gave an apparent current efficiency of 34%.

These TOC data are minimal values, because they include only those SMX molecules that underwent complete mineralization, and also because they refer to data points at the end of the kinetic runs, when first order behaviour had become more prominent—as noted earlier, under these conditions, current efficiency falls as the reaction progresses. High apparent current efficiencies are compatible with the initial attack of hydroxyl radicals being followed by radical chain autoxidation, with participation from the molecular oxygen that is the co-product at the anode [10]. The low cost of electrons (electricity) per mole compared with chemical agents, combined with these high current efficiencies, makes this "advanced electrochemical oxidation process" an attractive possibility as a remediation technology [41].

In order to consider any remediation process as a possible technology, it is essential to know whether the process might afford byproducts more toxic than the starting material. We argue against this eventuality on two grounds. First, the electrolysis products did not include the oxidized metabolites that are considered to be the active toxic agents. Second, we compared the growth of two bacterial species (*E. coli and B. subtilis*) in the presence of electrolyzed and unelectrolyzed SMX solutions, using ethanol and hydrogen peroxide as positive bactericidal controls. In no case were partly or completely electrolyzed solutions of SMX more toxic to the bacteria than untreated solutions.

4 Conclusion

The significant results of this study are that electrochemical oxidation of SMX at a BDD anode proceeds without the formation of known toxic products of partial oxidation. The high current efficiency makes the process attractive as a practical remediation technology. The reaction follows "mixed" kinetics, which can be shifted in the direction of either diffusion control or current control by adjusting the reaction conditions (substrate concentration and current density). Alternatively, the kinetics of electrooxidation of SMX over a wide range of initial conditions can be described in terms of kinetics that are partial order with respect to both substrate (*n*) and applied current (*m*). The kinetic orders with respect to current and initial substrate concentration were approximately 0.4 and 0.5 respectively. For this model, examination of the literature suggests that the value of the order with respect to substrate depends more on the initial substrate concentration than on the identity of the anode, see Table 3.

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References

1. Swain GM, Ramesham R (1993) Anal Chem 65:345
2. Perret A, Haenni W, Niedermann P, Skinner N, Comninellis Ch, Gandini D (1998) Proc Electrochem Soc 97:275
3. Marselli B, Garcia-Gomez J, Michaud P-A, Rodrigo MA, Comninellis Ch (2003) J Electrochem Soc 150:D79
4. Rodrigo MA, Michaud PA, Duo I, Panizza M, Cerisola G, Comninellis Ch (2001) J Electrochem Soc 148:D60
5. Morao A, Lopez A, Pessou de Amorim M, Goncalves M (2004) Electrochim Acta 49:1587
6. Ammar S, Abdelhedi R, Flox C, Arias C, Brillas E (2006) Environ Chem Lett 4:229
7. Both VM, Comninellis Ch (1999) Process/System Engineering 70:165
8. Da Pozzo A, Merli C, Sirés I, Garrido JA, Rodríguez RM, Brillas E (2005) Environ Chem Lett 3:7
9. Bonin PML, Bejan D, Radovic-Hrapovic Z, Halasz H, Hawari J, Bunce NJ (2005) Environ Chem 3:125
10. Waterston K, Bejan D, Bunce NJ (2006) J Appl Electrochem 36:227
11. Kolpin D, Furlong E, Meyer M, Thurman E, Zaugg S, Barber L, Buxton H (2002) Environ Sci Technol 36:1202
12. Ternes T (2001) ACS Symp Ser 791:39
13. Heberer T (2002) Toxicol Lett 131:5
14. Carballa M, Omil F, Lema JM, Llompart M, Garcia-Jares C, Rodriguez I, Gomez M, Ternes T (2004) Water Res 38:2918
15. Miao X-S, Bishay F, Chen M, Metcalfe CD (2004) Environ Sci Technol 38:3533
16. Hirsch R, Ternes T, Haberer K, Kratz K-L (1999) Sci Total Environ 225:109
17. Sanderson H, Johnson D, Wilson C, Brain R, Solomon K (2003) Toxicol Lett 144:383

18. Ternes T, Meisenheimer M, McDowell D, Sacher F, Brauch H, Haist-Gulde B, Preuss G, Wilme U, Zulei-Seibert N (2002) Environ Sci Technol 36:3855
19. Zuccato E, Calamari D, Natangelo P, Fanelli R (2000) Lancet 355:1789
20. Kümmerer K (2001) Chemosphere 45:957
21. Perez S, Eichhorn P, Aga DS (2005) Environ Toxicol Chem 24:1361
22. Drillia P, Dokianakis SN, Fountoulakis MS, Kornaros M, Stamatelatou K, Lyberatos G (2005) J Hazard Mater 122:259
23. Huber MM, Canonica S, Park G-Y, von Gunten U (2003) Environ Sci Technol 37:1016
24. Huber MM, Korhonen S, Ternes TA, von Gunten U (2005) Water Res 39:3607
25. Huber MM, Goegel A, Joss A, Hermann N, Loeffler D, McArdell CS, Reid A, Siegrist H, Ternes TA, Von Gunten U (2005) Environ Sci Technol 39:4290
26. Sharma VK, Mishra SK, Ray AK (2006) Chemosphere 62:128
27. Jørgensen SE, Halling-Sørensen B (2000) Chemosphere 40:691
28. Ingerslev F, Halling-Sørensen B (2000) Environ Toxicol Chem 19:2467
29. Drewes JE, Shore LS (2001) ACS Symp Ser 791:206
30. Webb S, Ternes T, Gibert M, Olejniczak K (2003) Toxicol Lett 142:157
31. Schwab BW, Hayes EP, Fiori JM, Mastrocco FJ, Roden MN, Cragin D, Meyerhoff RD, D'Aco VJ, Anderson PD (2005) Regul Toxicol Pharmacol 42:296
32. De Souza A, Baylocq D, Pellerin F (1988) Talanta 35:875
33. Lovrek M, Zorc B, Butula I (1998) Acta Pharm (Zagreb) 48:31
34. Goyal RN, Srivastava RK (1990) Indian J Chem 29A:635
35. Husain S, Krishna Murty ASR, Prasad PR, Sekar R (1995) Indian Drugs 32:336
36. Cribb AE, Spielberg SP (1992) Clin Pharmacol Ther 51:522
37. Lavergne SN, Volkman EM, Maki JE, Yoder AR, Trepanier LA (2005) Toxicology 208:63
38. Lehmann DF, Liu A, Newman N, Blair DC (1999) J Clin Pharmacol 39:533
39. Bard AJ, Faulkner LR (2000) Electrochemical methods: fundamentals and applications, 2nd edn. Wiley, New York, Chapter 3
40. Marusawa H, Ichikawa K, Narita N, Murakami H, Ito K, Tezuka T (2002) Bioorg Med Chem 10:2283
41. Rajeshwar K, Ibanez JG (1997) Environmental electrochemistry. Academic Press, San Diego, CA, Chapter 2
42. Waterston K, Wang JW, Bejan D, Bunce NJ (2007) J Appl Electrochem 37:367
43. Le Naour C, Moisy P, Arpigny S, Madic C (1999) Electrochim Acta 44:3505
44. Körbahteit BK, Salih B, Tanyolac A (2001) J Chem Technol Biotechnol 77:70
45. Bejankiwar R, Lalman JA, Seth R, Biswas N (2005) Water Res 39:4715