

Electrochemical Oxidation of Sulfonamides with Boron-Doped Diamond and Pt Anodes

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Electrochemical oxidation processes usually favored specific degradation pathways depending on anode materials. In this work, a series of sulfonamides (SNs) were degraded by electrochemical oxidation. Compared to Pt anodes (0.1567–0.1795 h⁻¹), degradation rates of SNs were much higher at boron-doped diamond (BDD) anodes (2.4290–13.1950 h⁻¹). However, the same intermediates were detected in the two anode systems. Due to the strong oxidizing ability of BDD anodes, a large amount of intermediates with high toxicities

were initially generated and then finally reduced in the BDD anode systems, while the amount of intermediates continuously increased in the Pt anode systems. Additionally, SNs were degraded faster in Na₂SO₄ than NaH₂PO₄ electrolytes at BDD anodes, while they were similar at Pt anodes. This study demonstrated that the degradation pathways of SNs at BDD and Pt anodes were similar, but the evolutions of intermediate amounts and toxicities were different due to their varied oxidizing abilities.

1. Introduction

Sulfonamides (SNs) are synthetic antimicrobial agents that are widely used in the treatment of respiratory and bacterial infections for humans and animals.^[1] Sulfadiazine, one of the sulfonamides, was detected to have a concentration as high as 51 mg kg⁻¹ in chicken litter.^[2] Kumar et al. demonstrated that antibiotics were only partially metabolized in the body and a major proportion was excreted with urine and feces.^[3] Because SNs cannot be effectively eliminated by conventional biological wastewater treatment processes, the drug residues usually exit the facilities unaltered and were frequently detected in aquatic environments. It has been reported that SNs are dominant in water and the total concentration of 13 antibiotics ranges from 3.1 to 109 ng L⁻¹ in surface water.^[4] Although they are present in environments at low concentration levels, high biological activity gives rise to drug-resistant pathogenic bacteria and potential risks to human health and ecosystems.^[5]

Since SNs exhibit semi-resistance to biological degradation, a suitable technology to remove them from water is needed.^[6,7] Current techniques include chlorination,^[8] ozonation,^[9] photolysis and photocatalysis,^[10,11] Fenton degradation,^[12] and electrochemical oxidation.^[7,13,14] Among them, electrochemical oxidation is promising because it is environmentally clean, versatile, energy efficient, and can be automated.^[15,16] As an electrochemical process, organic compounds are broken down by means of hydroxyl radicals formed through water oxidation.^[14] The electrode material and its stability are usually considered to be the most important factors in implementing electrochemical oxidation for the effective degradation of organic pollutants. Boron-doped diamond (BDD) anodes have been demonstrated with superior performance in the treatment of many organic compounds, due to their extremely wide potential window, corrosion stability, inert surface, high O₂-overpotential, and strong oxidizing capacity.^[17] On the other hand, Pt anodes showed different degradation behaviors, which were attributed to the different states of hydroxyl radicals formed at Pt (adsorbed) and BDD (free) anodes.^[18,19]

A few reports have investigated the kinetics and pathways of electrochemical oxidation of SNs, including sulfa-chloropyridazine,^[7,13] sulfamethazine (SMT),^[20] sulfamethoxazole,^[21] and sulfadiazine (SDZ).^[22] Mezyk et al. indicated that hydroxyl radicals were predominantly added to the sulfanilic acid ring of different sulfa drugs, while the destruction reaction occurred at different reaction sites with these sulfa drugs, likely different heterocyclic rings.^[23] Kim et al. proposed the hydroxylation of the ring structures to be the initial step during the degradation of sulfonamides.^[24] Fabiańska et al. investigated the electrochemical oxidation of sulfonamides using BDD anodes and found the structures of the SNs had no significant effect on the degradation rates.^[20] However, our previous study demonstrated that the degradation rates of phthalates were varied at both BDD and Pt anodes due to different degradation mechanisms.^[16] In detail, the degradation rates of phthalates decreased at the BDD anode but increased at the Pt anode with increasing alkyl chain length, which

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Supporting information for this article is available on the WWW under <https://doi.org/10.1002/open.201900250>

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was attributed to the different oxidation mechanisms at the two anodes. The electrophilic attack by $\bullet\text{OH}$ was the main reaction at BDD anode, while adsorbed oxidants (PtO_{x+1}) with low oxidation ability tended to form on the surface of the active Pt anode.^[16]

Rocha et al. investigated the electrochemical degradation of Novacron Yellow C-RG using BDD and Pt anodes and came to the conclusion that fragmentation of azo dye group occurred mainly at Pt anodes, while the rupture of dye in different parts of its chemical structure was favored at BDD anodes.^[25] A detailed exploration of electrochemical oxidation systems with different anodes and electrolyte solutions to understand the essential degradation mechanism of SNs was still lacking.

In this study, electrochemical oxidation of SNs of similar chemical structures, including SDZ, sulfamerazine (SMR), sulfamonomethoxine (SMM), sulfamethoxydiazine (SMD), SMT, and sulfadimethoxypyrimidine (SDM), was investigated with BDD and Pt anodes in 0.05 M Na_2SO_4 or NaH_2PO_4 electrolytes. The degradation rates of SNs in different systems were compared as well as the removal of total organic carbon (TOC) and energy consumption. Furthermore, with SMT as a model organic, the degradation pathways at BDD and Pt anodes were elucidated by monitoring the aromatic products and inorganic ions by liquid chromatography-time of flight-mass spectrometry (LC-TOF-MS), and ion chromatography (IC). At the end, the evolution of toxicity in the different systems was determined.

2. Results and Discussion

2.1. Degradation of SNs

The degradation of the six SNs (0.02 mM) in 0.05 M Na_2SO_4 or NaH_2PO_4 electrolytes at BDD or Pt anodes was shown in Figure 1. Notably, complete disappearance of the SNs only occurred in sulfate electrolytes with BDD anodes (< 3 h). With Pt anodes, the total removal rates in 6 h were ~65%. An exponential decrease of concentration was found for all treatments and the pseudo first-order rate constant (k) values were calculated with correlation coefficients (r^2) > 0.99 (Table 1).^[7,13] The k values increased from 0.1567–0.1795 h^{-1} at Pt anodes to 2.4290–13.1950 h^{-1} at BDD anodes in Na_2SO_4 electrolytes and from 0.1601–0.21835 h^{-1} (Pt) to 0.2111–0.3908 h^{-1} (BDD) in NaH_2PO_4 electrolytes, showing greater oxidizing ability of BDD compared to Pt anodes. Moreover, it was noted that during the

Table 1. Degradation rate constants (k) of SNs with different treatments (h^{-1}).

Organics	$k_{\text{B-S}}$	$k_{\text{B-P}}$	$k_{\text{P-S}}$	$k_{\text{P-P}}$
SDZ	10.9990	0.2796	0.1666	0.2183
SMR	3.6243	0.2690	0.1567	0.1601
SMD	3.1357	0.2369	0.1795	0.1969
SMM	13.1950	0.3111	0.1672	0.2136
SMT	12.9460	0.3918	0.1634	0.1614
SDM	2.4290	0.2111	0.1695	0.1938

B–S, BDD anode in Na_2SO_4 electrolyte; B–P, BDD anode in NaH_2PO_4 electrolyte; P–S, Pt anode in Na_2SO_4 electrolyte; P–P, Pt anode in NaH_2PO_4 electrolyte.

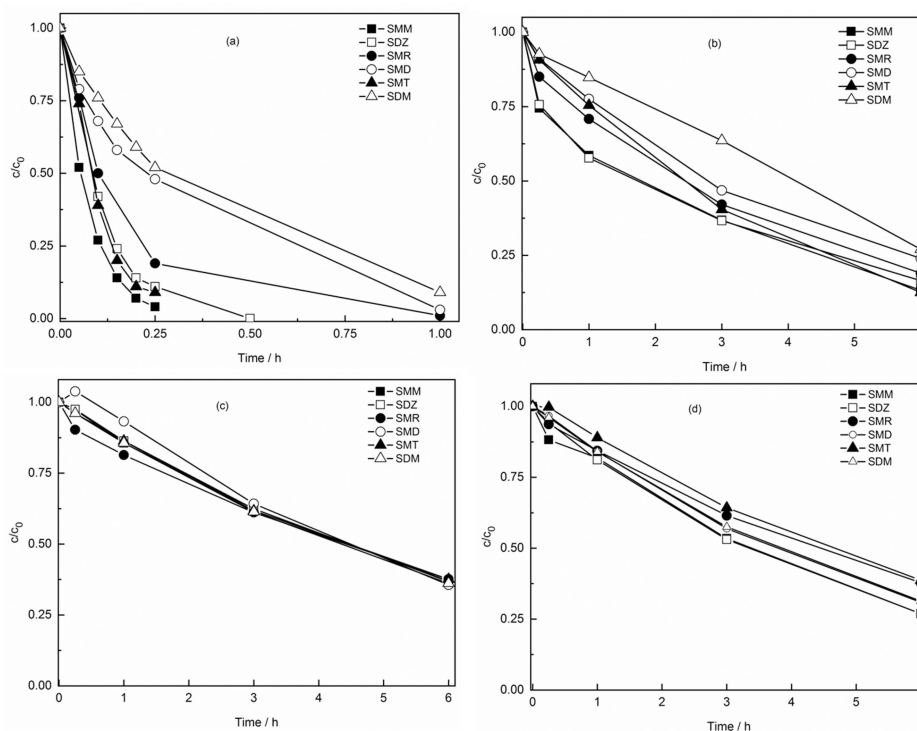
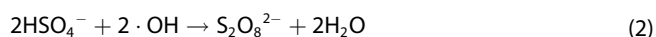


Figure 1. SNs concentration decayed with electrolysis time with 0.02 mM SNs solutions at an initial pH of 7.0 with (a) BDD anode and 0.05 M Na_2SO_4 ; (b) BDD anode and 0.05 M NaH_2PO_4 ; (c) Pt anode and 0.05 M Na_2SO_4 ; and (d) Pt anode and 0.05 M NaH_2PO_4 . Current density: 20 mA cm^{-2} .

treatment the SN solutions remained colorless in Pt anode systems, while the color changed to yellow or brown in the first 1 hour and then the color disappeared in BDD anode systems. It indicated that the degradation of SNs was faster at BDD anodes and intermediates with chromophoric groups occurred. The reasons for the much faster degradation at BDD anodes could be due to the much lower overpotential for O₂ evolution (side reactions) at Pt compared to BDD electrodes.^[26] Moreover, more active physisorbed ·OH existed at BDD anodes, while they were chemisorbed at Pt anodes.^[27]

The effect of Na₂SO₄ and NaH₂PO₄ electrolytes on the degradation of SNs differed at BDD and Pt anodes. At BDD anodes, all the SNs showed a faster degradation rate in Na₂SO₄ than in NaH₂PO₄ electrolytes. Taking SMM as an example, complete removal was achieved in ~15 min in 0.05 M Na₂SO₄, while it took >6 h to reach a removal rate of 87.2% in 0.05 M NaH₂PO₄. It has been reported that the effective decomposition of SNs was mainly mediated by the oxidants produced by the electrolysis of water (·OH, H₂O₂, O₃, and ·O₂⁻) and supporting electrolytes (S₂O₈²⁻ and SO₄^{-·}).^[20] The concentration of ·OH and other reactive oxygen species were all higher with sulfate solutions compared with other supporting electrolytes. It was detected that the amount of ·OH reached 2250 μM for sulfate electrolyte and 1750 μM for phosphate electrolyte after 3-h electrolysis with BDD anodes. The amount of the total oxidants was 5.3 mg L⁻¹ for 0.2 M Na₂SO₄ and 3.7 mg L⁻¹ for 0.2 M NaH₂PO₄ during a 30-min electrolysis with BDD anodes. Moreover, the oxidation rate was much faster in Na₂SO₄ than in NaH₂PO₄ electrolytes, even in the presence of an ·OH scavenger, which might be due to the other oxidants produced in the electrolysis of SO₄²⁻, such as peroxodisulfate (S₂O₈²⁻) (Equations 1 and 2).^[16,28] The S₂O₈²⁻ ions was a powerful oxidant that could attack organic matters.^[29,30] Therefore, SNs were degraded faster in Na₂SO₄ than in NaH₂PO₄ electrolytes at BDD anodes.



At Pt anodes, the degradation rates of SNs were similar in Na₂SO₄ and NaH₂PO₄ electrolytes. The final concentration of SNs comprised 26.9–38.7% of the initial value with NaH₂PO₄ electrolytes, and it ranged in 32.2–37.7% with Na₂SO₄ electrolytes after 6-h electrolysis. Because the oxidizing capacity of oxide sites PtO_{x+1} formed on the Pt anode was much lower than that of ·OH at the BDD anode, the Pt anode system was less able to destroy the SNs.^[18] Moreover, the transformation of sulfate ions in the electrochemical system had been reported to occur at very high potentials (Equations 1 and 2), leading to little generation of S₂O₈²⁻ in the Pt anode system.^[31] As a result, the removal of SNs in Na₂SO₄ electrolytes was similar to that in NaH₂PO₄ electrolytes at Pt anodes.

As for the effects of chemical structures on the degradation rates, similar trends of SNs degradation were observed at Pt anodes, while obvious effects were shown at BDD anodes. Among the studied SNs, SMM, SDZ, SMR, and SMD had very similar chemical structures, with a singly substituted pyrimidine

ring. As the alkyl chain changed from –OCH₃ (-meta) with a Hammett's constant of 0.115 to –H (0), –CH₃ (–0.069), –OCH₃ (-para) (–0.268), the corresponding attack by ·OH became easier and consequently the degradation rates increased (Figure S1). It is in consistent with our previous studies. Li et al. demonstrated that the electrochemical oxidation by ·OH in the BDD system was an electrophilic reaction and a positive correlation between the degradation rate constants and electronic energy was observed at BDD anodes in the degradation of phthalic acid esters with electron-withdrawing groups.^[18] Zhu et al. found that *p*-substituted phenols with electron-withdrawing groups degraded faster than those with electron-donating groups,^[27] and it was mainly conducted by indirect electrochemical oxidation with hydroxyl radicals at BDD. Since electron-withdrawing groups were easily released, the SNs with these groups were degraded faster than those with electron-donating groups. Therefore, their degradation rates rose with increasing Hammett's constants in both Na₂SO₄ (*r*²=0.76) and NaH₂PO₄ electrolytes (*r*²=0.98) (Figure S1).

2.2. Removals of Total Organic Carbon

The mineralization rates of SNs at BDD anodes were higher than those at Pt anodes (Figure 2), which was consistent with the SNs degradation rates. The mineralization was relatively fast during the early stage of the electrolysis attributed to the high reactivity of aromatic/cyclic organics with ·OH. Due to the subsequent formation of refractory compounds such as short-chain carboxylic acids, the removal of TOC became slower with prolonged reaction time. After 6-h electrolysis, the mineralization rates reached 45% for SMM, 42% for SDZ, 29% for SMR, and 29% for SMD with BDD anodes and sulfate electrolytes. When phosphate supporting electrolytes were used, the corresponding TOC removals decreased to 17–35% in the BDD anode cell. In contrast, a reduction in TOC removals was observed in the Pt anode cell: 4–18% in the Na₂SO₄ electrolyte, and 5–19% in the NaH₂PO₄ electrolyte. These differences were attributable to both the amount and the characteristics of the oxidants generated in the different electrochemical cells.^[18] The larger generation of ·OH in the vicinity of the BDD anode surface led to greater mineralization rates of SNs and their intermediates, especially in the Na₂SO₄ electrolyte.^[32]

A higher current density was beneficial for yielding large amounts of hydroxyl radicals, while suffering from a lower current efficiency due to parasitic side-reactions.^[13,33] Mineralization current efficiency (MCE) is an important factor to describe the energy efficiency. In BDD anode systems with Na₂SO₄ electrolytes, MCE decreased in the order: SMM (29.0%) > SDZ (25.0%) > SMR (19.5%) > SMD (18.7%) for the single-substituted SNs, and SMT (33.4%) > SDM (19.4%) for the disubstituted SNs. The MCE values decreased to 11.8–22.5% when using NaH₂PO₄ electrolytes. These results were consistent with the trends of SNs decays in BDD anode systems. In comparison, electrochemical oxidation of SNs at Pt anodes consumed much more energy than at BDD anodes. The MCE values were as low as 1.9–12.5% for Na₂SO₄ and 3.2–11.8% for NaH₂PO₄ electrolytes.

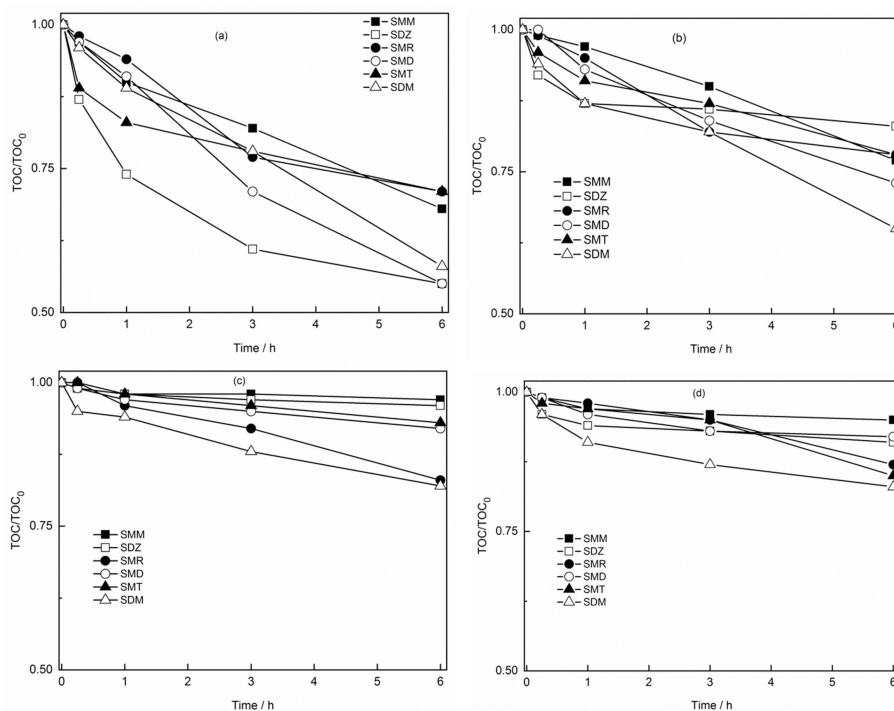


Figure 2. TOC removal for 0.02 mM SN solutions with (a) BDD anode with 0.05 M Na_2SO_4 ; (b) BDD anode with 0.05 M NaH_2PO_4 ; (c) Pt anode with 0.05 M Na_2SO_4 ; (d) Pt anode with 0.05 M NaH_2PO_4 . Current density: 20 mA cm^{-2} .

The difference was mainly attributable to the different oxidizing ability of BDD and Pt electrodes.^[33]

2.3. Degradation Pathways

While the degradation mechanisms of SNs has been reported by several authors,^[13,20,22,24,32] comparison of the degradation pathways between BDD and Pt anodes were not yet studied. Here, degradation pathways of SMT at BDD and Pt anodes were investigated as an example (Figure 3).

LC-TOF-MS analyses showed the decrease in the intensity of the peak assigned to SMT and the appearance of new peaks (M1-M5) attributed to the products of electrochemical oxidation

in both BDD and Pt anode systems. The main intermediates were listed in Table 2. Two of these intermediates (M2 and M5) had not been previously reported. The structure assignment of these intermediates was studied according to the accurate mass measures provided by the TOF analyzer, including both the elemental composition of the protonated molecules and the ion fragments with a high level of accuracy. The ion fragment at $[m + H]^+ = 216.0437$ (M1, sulfanilylurea) evidenced the attack of the hydroxyl radicals on the pyrimidine ring, identified as a urine derivative.^[20] It was confirmed by the presence of the ion in the mass spectrum of m/z 108.0869. M2 ($[m + H]^+ 173.0379$, sulfanilamide), M3 (m/z 173.0219, sulfanilic acid), and M4 (m/z 123.0869, 2-amino-4,6-dimethylpyrimidine), corresponded to the cleavage of the sulfonamide bond, in

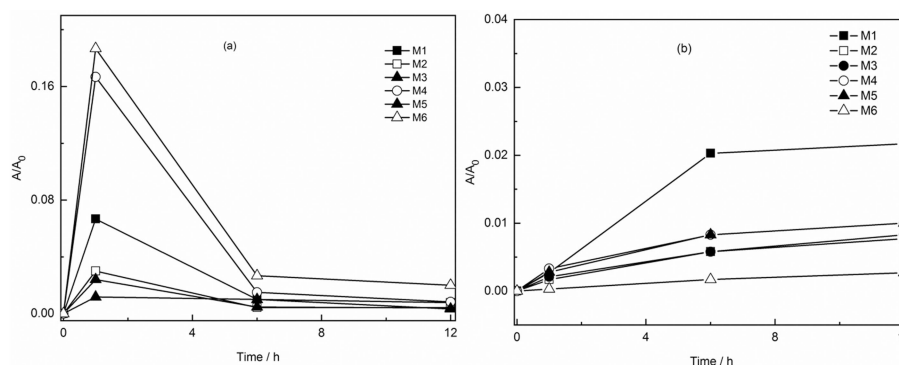


Figure 3. Formation of intermediates in electrochemical oxidation of SMT with BDD (a) and Pt (b) anodes (current density, 20 mA cm^{-2} ; SMT, 0.02 mM; pH, 7.0; Na_2SO_4 , 0.05 M)

Compound	[M + H] ⁺ / <i>m/z</i>	Identification	CAS No.	Chemical Structure
SMT	[M + H] ⁺ = 279.0910	C ₁₂ H ₁₄ N ₄ SO ₂	57-68-1	
M1 (sulfanilylurea)	[M + H] ⁺ = 216.0437	C ₇ H ₉ N ₃ SO ₃	547-44-4	
M2 (sulfanilamide)	[M + H] ⁺ = 173.0379	C ₆ H ₈ N ₂ SO ₂	63-74-1	
M3 (sulfanilic acid)	<i>m/z</i> = 173.0219	C ₆ H ₇ NSO ₃	121-57-3	
M4 (2-amino-4,6-dimethylpyrimidine)	<i>m/z</i> = 123.0869	C ₆ H ₉ N ₃	767-15-7	
M5 (2-Amino-1,3-benzenediol)	[M + H] ⁺ = 125.0628	C ₆ H ₇ NO ₂	3163-15-3	

accord with previous research.^[13,14] Moreover, an *m/z* ratio of 188.0488 was detected, and the best-fit formula was C₆H₉N₃O₂S (protonated molecule). It is indicated that both hydroxylation of the sulfonamide bond as well as decay of the heterocyclic ring were important pathways of SMT electrochemical decomposition. The hydroxyl radicals attacking on the sulfonamide moiety, resulted in the cleavage of the S–N bond and formed two aromatic intermediates with the pyrimidine (M4) and aniline rings (M2, and M3). According to our previous studies,^[34] these cyclic intermediates underwent oxidation to form polyhydroxylated and/or quinone forms, such as benzoquinone or phenol derivatives, the cleavage of which led to the formation of short-chain aliphatic carboxylic acids.^[26] Similarly, the two transformation pathways, which involved hydroxyl radicals attacking either on the benzenic or isoxazole aromatic (pyridazine) rings, had also been proposed in the photo-Fenton degradation of sulfamethoxazole, as well as in the electrochemical mineralization of sulfachloropyridazine.^[13,35]

Based on the results of LC-TOF-MS analyses, there was no difference for the intermediates regardless of the anodes used in this study. However, BDD showed the largest amount of intermediates in the first 1 hour of electrolysis, constituting 6.7% (M1), 16.7% (M4), and 18.7% (M6) of the initial SMT peak area (Figure 3). In the subsequent reaction intervals (6 h and 12 h), these intermediates were gradually degraded and the corresponding peaks diminished to 0.8% (M1), 0.8% (M4), and 2.0% (M6). In the Pt anode system, the amount of intermediates kept increasing during the 12-h electrolysis process. At the end of electrolysis, most of them showed a higher relative

abundance than those with BDD anodes. It has been reported that organic molecules containing nitrogen and sulfur were progressively mineralized with the formation of NH₄⁺ and/or NO₃⁻, and SO₄²⁻. According to Kim et al.,^[24] 3.7–14.7% of the N atoms constituting STZ, SMT, and SMZ were transformed into NO₃⁻ in a dielectric barrier discharge plasma system. Aiming to confirm this behavior, we performed IC analyses. Based on the initial concentration of SMT, the maximum theoretical concentration of nitrogen (NO₃⁻ + NH₄⁺) was 0.08 mM and of sulfur (SO₄²⁻) was 0.02 mM. The IC results demonstrated that no trace of nitrite ions was found. For electrolysis with BDD anodes, the final concentration of nitrate was 0.071 mM (Na₂SO₄) and 0.052 mM (NaH₂PO₄), while it was 0.006 mM (Na₂SO₄) and 0.026 mM (NaH₂PO₄) in the Pt anode system. It was in accord with the mineralization rates of SMT under the same conditions. Besides, the amount of SO₄²⁻ generated with BDD anodes (0.018 mM) was much greater than that with Pt anodes (0.008 mM) in the NaH₂PO₄ electrolyte. The SO₄²⁻ values were not measured considering the possible disturbance in the case of the Na₂SO₄ electrolyte.

Above all, it was not appropriate to compare the degradation pathways of SNs at different electrodes just by the quantity of the intermediates over a fixed period. Electrochemical oxidation systems with BDD and Pt anodes actually showed different oxidizing periods. In detail, hydroxyl radicals were generated more quickly and effectively in the BDD system, leading to a faster formation of intermediates. In the case of the Pt anode, the adsorbed hydroxyl radical showed weaker oxidation, causing a relatively much slower generation of

possible intermediates. As a result, it was improper to conclude that the intermediates produced by the BDD anode were much more complex than those by the Pt anode. Instead, they were at different oxidation periods.

2.4. Toxicity Evolution

Successful "remediation" of wastewater is not achieved if only the original contaminant disappeared, but the reaction intermediates are more toxic or more persistent.^[21] We compared the toxicity of solutions during the degradation of SMT to the initial SMT solution (Figure 4). The increased toxicity suggested the formation of new intermediates with high toxicities, while negative values indicated that the luminescence of *V. fischeri* was not inhibited and the light emission increased. In the first 0.25 hour of the electrolysis, the toxicity showed a decreasing trend for all the four treatments. Combined with analysis of the degradation intermediates, the LD₅₀ value of M2 and M3 was reported to be 3.8 g kg⁻¹ and 12.3 g kg⁻¹, respectively, higher than that of SMT (1.06 g kg⁻¹).^[36] It means that these intermediates would not increase the risk to a hazardous extent in the electrolysis solution. However, the further oxidation products of these intermediates, such as M5 and hydroquinone, with LD₅₀ values of 0.750 g kg⁻¹ and 0.245 g kg⁻¹, would increase the acute toxicity of the whole solution afterwards. Due to the efficient oxidation with the BDD anode, these intermediates were generated in large amounts during the study period than with the Pt anode. With a prolonged reaction time, the toxic substances were gradually removed and the total toxicity values would be reduced, as shown in the sulfate electrolyte with both BDD and Pt anodes at 12 h (Figure 4).

Generally, a high toxicity was usually observed after electrochemical treatment since benzoquinone or derivatives of phenol were potentially toxic.^[13,33] Electrochemical process showed greater toxicity with BDD anodes, irrespective of the electrolytes used, which could be due to the strong oxidative capacity of BDD compared with Pt anodes, leading to more

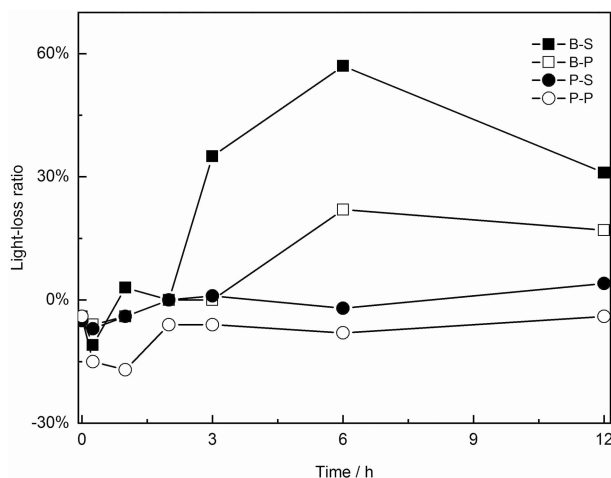


Figure 4. Acute toxicity variation during electrolysis (current density, 20 mA cm⁻²; SMT, 0.02 mM; pH, 7.0; Na₂SO₄, 0.05 M).

varieties of intermediates during electrochemical oxidation.^[33] In addition, the acute toxicity with the Na₂SO₄ electrolyte was stronger than that with the NaH₂PO₄ electrolyte as a whole. It indicated that more reactive species were generated in the former system, facilitating the formation of more intermediates, even though the trend differed from the organic degradation rates.

Toxicity evaluation gave a cautionary message that the toxicity of a solution might not be eliminated even though the SNs were completely removed. Variation of the acute toxicity showed different trends with BDD and Pt anodes. Based on the results of organic mineralization ability as well as the toxicity evolution of intermediates, the electrochemical oxidation of SNs with the BDD anode was advantageous. Electrochemical oxidation should be controlled according to the different demands for the target solutions. Meanwhile, complete mineralization is always encouraged to guarantee the final water quality, even though relatively high cost may be required.

3. Conclusions

Electrochemical oxidation of SNs was more effective at BDD than Pt anodes. The degradation rates increased from 0.1567–0.1795 h⁻¹ (Pt) to 2.4290–13.1950 h⁻¹ (BDD) in the Na₂SO₄ electrolyte. Compared to the Na₂HPO₄ electrolyte, the degradation of SNs in the Na₂SO₄ electrolyte was much faster at BDD anodes, while the degradation rates in different electrolytes were similar at Pt anodes, due to the generation of different oxidizing species at these electrodes. The degradation rates of SNs with a singly-substituted pyrimidine ring rose with the Hammett's constants for both electrolytes in the BDD anode system. Although there was no difference in the intermediates generated in the electrochemical oxidation of SMT regardless of the anodes used, the relative amount of these intermediates differed between BDD and Pt anodes. As a result, it was improper to conclude that the intermediates produced by the BDD anode were more complex than those with the Pt anode. Actually, the electrolysis with the two anodes was at different oxidation periods. In total, the electrochemical oxidation of SNs was advantageous with BDD anodes based on its mineralization ability, and more importantly, the intermediate toxicity evolution during the electrolysis.

Experimental Section

Chemicals

SDZ, SMR, SMM, SMD, SMT, and SDM were purchased from Sigma Aldrich (St. Louis, USA). Their molecular structures were shown in Figure 5. High performance liquid chromatography (HPLC) -grade acetonitrile and methanol were used for HPLC analysis. All other chemicals were analytical grade from Beijing Chemical Co. (China) and were used without further purification. Solutions were prepared using deionized Milli-Q water (Millipore, USA).

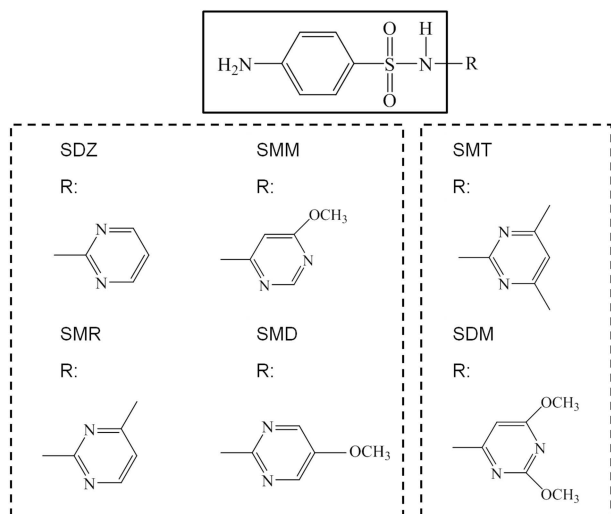


Figure 5. Molecular structures of the SNs investigated.

Electrochemical Oxidation

Electrochemical oxidation was performed under galvanostatic conditions (20 mA cm^{-2}) at room temperature (25°C). The system consisted of a BDD or Pt anode (Condias GmbH, Germany) and a stainless steel (SS) cathode, with an effective electrode area of 1 cm^2 . The electrolyte solution (250 mL) was continuously stirred by a magnetic bar throughout the process. Considering that the original pH of 0.02 mM SNs solution varied from 4.6–6.7, the initial pH for the electrolysis was adjusted to 7.0 with 1 M NaOH solution. The neutral forms of SNs existed at $\text{pH} > 5$, while protonated forms were mostly present under acidic conditions.^[7] Moreover, 0.05 M Na_2SO_4 or NaH_2PO_4 was added in order to reduce the solution resistance and investigate the influence of supporting electrolytes.^[16] Samples were collected from the cell at prescribed time intervals for chemical analysis.

Chemical Analysis

The concentrations of SNs were monitored by using HPLC (Agilent HP1100, Palo Alto, CA, USA) equipped with a diode array detector. The mobile phase comprised a mixture of acetonitrile, Milli-Q water and formic acid (25:65:10) at a flow rate of 0.5 mL min^{-1} . The separation was performed on a ZORBAX SB-C18 column at 30°C . The compounds were detected at the wavelength of 270 nm. The retention time was 8.50 min for SMR, 4.78 min for SDZ, 7.68 min for SMM, 6.99 min for SMD, 6.59 min for SMT, and 10.98 min for SDM.

The decay of TOC was monitored by using a TOC analyzer (TOC-VCSH, Shimadzu Corp., Japan). MCE indicated the efficacy of current consumed in the electrolysis system and it was calculated using Eq. (3),^[26] where $(\text{TOC})_0$ is the initial TOC (mg L^{-1}), $(\text{TOC})_t$ is the TOC at time t (h), n is the number of electrons exchanged in the mineralization process of the organic compound, F is the Faraday constant (96487 C mol^{-1}), V is the volume of electrolyte (L), 4.32×10^7 is the conversion factor for units homogenization, m is the number of carbon atoms of the molecule under study, and I is the current (A).

$$\text{MCE} = \frac{[(\text{TOC})_0 - (\text{TOC})_t]nFV}{4.32 \times 10^7 mIt} \times 100 \quad (3)$$

The intermediates were identified using a LC-TOF-MS (Agilent 6530 Q-TOF System, Agilent, USA). Detailed analytical conditions for LC-TOF-MS were previously illustrated in several reports and listed in Table S1.^[7,20,24] Intermediates were relatively quantified using the ratio of their respective peak area to the initial SMT peak area and expressed as A/A_0 . It was adopted only to investigate the relative variation trend of intermediates generated in the electrolysis process. Inorganic ions were simultaneously measured with a Dionex DX-600 IC system equipped with an Ionpac AS 19 anion-exchange column. The detailed parameters are given in a previous report and illustrated in Text S1.^[33] The concentration of total oxidizing species was determined by *N,N*-diethyl-*p*-phenylenediamine colorimetric method using a Unico (UV-4802) UV/VIS Double Beam Spectrophotometer.^[37] Hydroxyl radical was determined based on the method proposed by Tai et al. with dimethyl sulfoxide as a scavenger.^[38] The quantification of $\cdot\text{OH}$ was done by the liquid chromatography-UV of 2,4-dinitrophenylhydrazine – HCHO by an Agilent HP1100 HPLC instrument with a DAD detector and a ZORBAX SB-C18 column ($150 \times 4.6 \text{ mm}$, particle size $5 \mu\text{m}$) at 35°C .

Toxicity was evaluated based on the Microtox method using the luminescent bacterium *Vibrio fischeri* (No. 13L4152, ModernWater Inc., New Castle, DE, USA) as the model microorganism.^[39] The reduction of luminescence was measured using a Delta Tox II Analyzer (Strategic Diagnostics Inc., USA) according to the test protocol ISO 11348-3 (2007).^[40] All samples were adjusted to have a pH of 7.0 ± 0.2 prior to the assay tests. After mixing 500 μL of samples with 500 μL luminescent bacteria suspensions, the light-loss ratio after 15 min contact time was measured on the basis of a toxicant-free control. The acute toxicity of the samples was calculated by the bioluminescence intensity. The higher the acute toxicity, the greater the light-loss ratio. Negative values indicated that the luminescence of *V. fischeri* was not inhibited and the light emission increased. Residual H_2O_2 or $\text{S}_2\text{O}_8^{2-}$ in the samples was removed with sodium thiosulfate and enzyme catalase (made from *Micrococcus lysodeikticus*) to eliminate their positive effect on toxicity measurements.^[16]

Acknowledgments

This research was funded by the Young Elite Scientist Sponsorship Program by CAST (YESS) (2018QNRC001), Beijing Municipal Natural Science Foundation (Grant number 6192029), Central Public-interest Scientific Institution Basal Research Fund (Grant number BSRF201903), and the National Natural Science Foundation of China (Grant number 51308537). Dr. IC Bruce is greatly acknowledged for reading the manuscript. Dr. Yi Jiang from the Hong Kong Polytechnic University is greatly acknowledged for his diligent comments and suggestions to improve the paper.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: electrochemical oxidation · antibiotics · reaction mechanisms · anode · wastewater toxicity

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 Manuscript received: July 30, 2019

Revised manuscript received: November 9, 2019