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Electrolyte Selection and Microbial Toxicity for Electrochemical Oxidative Water Treatment Using a Boron-Doped Diamond Anode to Support Site Specific Contamination Incident Response

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Abstract

Intentional and unintentional contamination incidents, such as terrorist attacks, natural disasters, and accidental spills, can result in large volumes of contaminated water. These waters may require pre-treatment before disposal and assurances that treated waters will not adversely impact biological processes at wastewater treatment facilities, or receiving waters. Based on recommendations of an industrial workgroup, this study addresses such concerns by studying electrochemical advanced oxidation process (EAOP) pre-treatment for contaminated waters, using a boron-doped diamond (BDD) anode, prior to discharge to wastewater treatment facilities. Reaction conditions were investigated, and microbial toxicity was assessed using the Microtox[®] toxicity assay and the Nitrification Inhibition test. A range of contaminants were studied including herbicides, pesticides, pharmaceuticals and flame retardants. Resulting toxicities varied with supporting electrolyte from 5%–92%, often increasing, indicating that microbial toxicity, in addition to parent compound degradation, should be monitored during treatment. These toxicity results are particularly novel because they systematically compare the microbial toxicity effects of a variety of supporting electrolytes, indicating some electrolytes may not be appropriate in certain applications. Further, these results are the first known report of the use of the Nitrification Inhibition test for this application. Overall, these results systematically demonstrate that anodic oxidation using the BDD anode is useful for addressing water contaminated with refractory organic contaminants, while minimizing impacts to wastewater plants or receiving waters accepting EAOP-treated effluent. The results of this study indicate nitrate can be a suitable electrolyte for incident response and, more importantly, serve as a baseline for site specific EAOP usage.

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Supplementary Material

Selected physicochemical properties and LC-MS/MS conditions for target contaminants

Keywords

Boron-Doped Diamond Anode; Nitrification Inhibition; **Microtox® Toxicity**; Electrochemical Advanced Oxidation Process

1. Introduction

Effectively managing water contamination, resulting from intentional/unintentional events such as terrorist attacks, natural disasters, or accidental spills, continues to be a primary objective for the water industry. Water contamination also arises from firefighting or decontamination activities, including washing of contaminated infrastructure and equipment following an indoor or outdoor contamination incident. These incidents can produce large volumes of contaminated water, which can pose pre-treatment, treatment, and disposal concerns for wastewater treatment works (WWTWs) and receiving waters.

Advanced oxidation processes (AOPs) can be effective at pre-treating contaminated water because they produce hydroxyl radicals, highly reactive and non-selective oxidants that exhibit higher oxidation potentials than chlorine or ozone. This chemical oxidation allows AOPs to degrade, and potentially mineralize, contaminants without the use of reagents like chlorine, reducing the potential reagent handling concerns and the formation of chlorinated byproducts (Sirés et al., 2014). These advantages make AOPs appropriate for pre-treatment of contaminated waters, especially where onsite treatment is necessary. However, the use of AOPs in this application has knowledge gaps related to the potential to produce oxidation byproducts and effluents that may stress the biological treatment processes at WWTWs or result in the discharge of toxic contaminants into the receiving waters. Wastewater utilities and related stakeholders discussed these knowledge gaps at a workshop hosted by the Water Environment Research Foundation (currently known as Water Environment & Reuse Foundation), where “participants agreed that various bench-scale studies to develop information on the treatability of contaminants by AOP (such as rate constants) and toxicity testing are needed to demonstrate an acceptable quality of AOP-treated water” (Striano et al., 2011).

Electrochemical advanced oxidation processes (EAOPs) pose advantages over some other types of AOP treatment. One main advantage associated with the EAOP approach is that it does not require reagents with handling concerns, thereby reducing the design, operation, and maintenance considerations. EAOPs may require an electrolyte, which may not be present in sufficient quantities for the types of contaminated waters generated from contamination incident response scenarios. Many electrolytes have been proposed and the literature demonstrates that each may participate in reactions to produce a variety of secondary oxidants (Martínez-Huitle and Brillas, 2009; Anglada et al., 2011; Kornienko et al., 2011; Sirés et al., 2014; Brillas and Martínez-Huitle, 2015; Jalife-Jacobo et al., 2016). These electrolyte and source-water specific oxidants and their reaction products may pose toxicity concerns. To the authors' knowledge, there are presently no systematic studies assessing the microbial toxicity produced across a range of contaminants and electrolytes upon EAOP treatment using BDD anodes.

The boron-doped diamond (BDD) anode, in particular, is ideal for EAOP treatment because it is able to attain a higher range of working potentials and is more stable to corrosion than other electrodes, resulting in higher overall performance (Kornienko et al., 2011). Moreover, the BDD anode is non-active, meaning it has an inert surface, reducing concerns about adsorption and deactivation due to fouling (Saylor et al., 2012). In electro-oxidation with BDD anodes, contaminants can be degraded either through direct anodic oxidation, or, more likely, through mediated reactions with adsorbed hydroxyl radicals produced from the electrolysis of water (Eq. 1). A variety of other side reactions are possible, some of which consume hydroxyl radicals, leading to contaminant degradation via other reactive oxygen species and secondary oxidants (Sirés et al., 2014; Uranga-Flores et al., 2015; Jalife-Jacobo et al., 2016). The BDD literature covers a wide range of reaction conditions such as pH values, electrolytes, current densities, and contaminant/electrolyte combinations and concentrations. To the authors' knowledge, few studies explore contaminant degradation in un-buffered solutions at natural solution pH, as are often found in real-world contaminated waters.

The effluent toxicity was a major concern to the WERF expert workgroup for ultimate disposal of contaminated waters treated in emergency response scenarios (Striano et al., 2011). Limited studies have reported that AOP treatments yield degradation intermediates that can be more toxic than the parent compound (Saylor et al., 2012; Haidar et al., 2013). A variety of microbial toxicity assays demonstrate potential eco-toxicity, as well as toxicity to activated sludge from WWTWs. These assays indicate that various waters are unlikely to harm WWTW processes or receiving waters (Striano et al., 2011). The Microtox® toxicity assay, a widely used and standardized test, uses *Vibrio fischeri*, luminescent marine bacteria, to indicate toxicity and is often utilized as a receiving water toxicity surrogate (Montalbán et al., 2016). This assay is sensitive, time-efficient, and low cost, making it a good screening test, especially if coupled with another toxicity assay (Dalzell et al., 2002). The Nitrification Inhibition (NI) toxicity assay is ideal to couple with the Microtox® toxicity assay for disposal of contaminated waters because, in spite of its high cost/sample, the NI test provides data directly applicable for determining toxicity to WWTW biological processes (Dalzell et al., 2002). The NI test utilizes activated sludge from local WWTWs to determine the response of nitrifying bacteria to contaminants/sample waters. Nitrifying bacteria are often considered to be the most sensitive bacteria in the WWTW processes due to their slow specific growth rates and sensitivity to toxic compounds. Thus, the nitrifying bacteria serve as an indicator of the worst case scenario for WWTW biological processes (Fox et al., 2006; Pagga et al., 2006).

The goal of this study is to systematically investigate factors affecting microbial toxicity arising from contaminant degradation using a BDD anode for electro-oxidation treatment following response activities for a variety of contamination scenarios. This study examines the efficacy of electrochemical oxidation using a BDD anode, while varying conditions including current densities, reaction times, and electrolyte composition and concentration.

Further, it includes a novel and diverse range of contaminants of emerging interest with chemical structures spanning a variety of reaction mechanisms and reported hydroxyl radical reaction rates. To address treatment and toxicity concerns raised by wastewater utilities and stakeholders at a Water Environment Research Foundation workshop (Striano et al., 2011), electrochemical oxidation is assessed using both contaminant destruction and resulting microbial toxicity, indicated by the Microtox® toxicity assay and the NI test. Microbial toxicity is a parameter not often reported in conjunction with the EAOP literature utilizing BDD anodes, with only a few studies reporting Microtox® toxicity. To the authors' knowledge, this is the first study to utilize the NI toxicity assay to assess toxic effects of waters treated with electro-oxidation using BDD anodes on WWTW biological processes. Further, this study uniquely reports directly comparable toxicities resulting not only from a variety of contaminants, but also from a variety of background electrolyte matrices for use in electro-oxidation with BDD anodes.

2. Materials and Methods

2.1 Electrochemical Oxidation System Using a BDD Anode

This electrochemical oxidation setup utilized a 10 L reservoir with a BDD anode in an electrode flow cell designed and manufactured by ADT (Diamonox™ Model 40 Monopolar Electrochemical Cell, ADT, Romeoville, IL). Local tap water, representing a realistic water that might be contaminated by emergency situations, was dechlorinated by passage through granulated activated carbon, and then was supplemented with approximately 10 mg L⁻¹ of contaminants (listed in Table S1) and experimentally determined concentrations of Na₂SO₄, NaH₂PO₄, NaNO₃, Na₂CO₃, NaCl, and Na₂B₄O₇·12H₂O electrolytes. After mixing for 10 minutes, this solution was recirculated over the 40 cm² electrode with an applied current of 4.4 amperes (~13 volts) at 8–10 liters per minute, except for a few samples treated at 8.8 amperes for comparison. Most experiments were carried out for two hours, with samples collected for LC-MS/MS analysis at 0, 3, 10, 20, 40, 60, 90, and 120 minutes. A few longer time period experiments were performed (24 and 72 hours) with samples collected throughout the experimental period. Toxicity tests were performed on a pre-selected subset of these samples (see below).

2.2 Analytical Methods

The N,N-diethyl-p-phenylenediamine (DPD) method for free chlorine, based on Standard Methods 4500-Cl G (2014), and an adapted DPD method with 0.25 µL of 1 g L⁻¹ horseradish peroxidase added to allow for hydrogen peroxide measurement were utilized to monitor oxidant presence. Samples were quenched with sodium thiosulfate where necessary and adjusted to neutral pH prior to analysis.

A direct-inject liquid chromatograph with tandem mass spectrometer (LC-MS/MS) was used to quantify concentrations of target contaminants using an AB SCIEX 5500 QTrap (SCIEX, Framingham, MA) or Thermo TSQ quantum MS/MS (Thermo Fisher Scientific, Waltham, MA) with a Dionex Ultimate LC system (Dionex, Sunnyvale, CA). The method included monitoring two multiple reaction monitoring (MRM) transitions for each analyte (see Table S2). Perfluorooctanoic acid (PFOA) was analyzed using a direct inject LC-MS/MS method

using a Quatro Premier mass spectrometer (Waters Corporation, Milford, MA) monitoring the ions noted in Table S2.

2.3 Toxicity Measurements

Samples (175 mL, in triplicate) of non-contaminated drinking water (control), untreated contaminated drinking water (Time 0), and EAOP-treated contaminated drinking water (120 minutes) were placed in respirometer (Model WB1000-SB, N-CON, Crawford, GA) reaction vessels used for aeration throughout the test. Ammonia concentrations in these samples were adjusted to approximately 45 mg L^{-1} . Mixed liquor was collected daily from a local WWTW and allowed to settle. Settled sludge flocs (175 mL) were added to each sample vessel, and the ammonia nitrogen concentration was measured both before and after two hours of aeration. Ammonia concentrations were determined by the Salicylate Method(2015) using Amver™ Diluent Reagent High Range Test 'N Tube™ vials, and a DR/2000 spectrophotometer all from HACH® (Loveland, CO). The NI test was considered complete when the ammonia concentration of the control decreased by 25%.

The Microtox® toxicity assay used the Microtox® Model 500 (Modern Water Inc., New Castle, DE). Differences in light output above 10% are attributed to toxic effects of the sample according to ISO 11248–2007 (Sánchez et al., 2014). Samples were analyzed in duplicate after 0, 10, 40, 90, and 120 minutes of EAOP treatment for two-hour trials and at extended intervals for longer experiments.

3. Results and Discussion

3.1 Selection of BDD Electrolytes

3.1.1 Effect of Electrolyte Concentration and Toxicity—Initial batch experiments examined the suitability of six electrolytes for electro-oxidation using a BDD anode and microbial toxicity testing. The Microtox® test was utilized as a screening tool because it is the more sensitive of the two toxicity assays utilized (Dalzell et al., 2002). Microtox® toxicities of electrolyte solutions of 0.05 N, 0.1 N and 1.0 N Na_2SO_4 , NaH_2PO_4 , NaNO_3 , Na_2CO_3 and NaCl were tested to determine initial background toxicities of these potential electrolyte matrices. Solutions of 0.05 N, 0.1 N, and 0.2 N $\text{Na}_2\text{B}_4\text{O}_7$ were utilized due to solubility constraints.

Higher normality electrolyte solutions tended to yield higher Microtox® toxicities. The NaH_2PO_4 , Na_2CO_3 and $\text{Na}_2\text{B}_4\text{O}_7$ electrolytes exhibited Microtox® inhibitions of 86% or greater at all normalities tested. The elevated observed pH values (pH 8 for $\text{Na}_2\text{B}_4\text{O}_7$ and pH 11–12 for Na_2CO_3) and the buffering capacity of NaH_2PO_4 may have contributed to this observed toxicity. The other electrolytes exhibited less than 3% inhibition at both 0.01 N and 0.1 N concentrations. Background Microtox® toxicities were investigated using full blank trials with only NaCl , NaNO_3 , Na_2SO_4 , or NaH_2PO_4 with pH correction prior to toxicity testing to investigate toxicity, solubility constraints, and pH considerations.

3.1.2 Impacts of Electrolytes on Solution pH—Changes in pH affect electrochemical oxidation via contaminant and oxidant speciation, so pH changes during treatment are an important electrolyte selection criterion. Increases up to approximately pH

12 in NaNO₃, NaCl, and Na₂SO₄ blank experiments suggest electrolyte interactions within the electrochemical system. Na₂SO₄ trials exhibited the highest pH and greater increases in pH for higher electrolyte normalities. The NaH₂PO₄ was the only electrolyte that yielded fairly stable and lower (pH 4.3 to 5.7) pH values throughout trials, as expected given its buffering capacity. The buffering capacity of the NaH₂PO₄, as well as the high pH values of the other electrolytes, can pose operational challenges with pH neutralization, which will be necessary to eliminate toxicity to sludge and/or receiving water.

Changes in pH are expected during electro-oxidation using a BDD anode, because the electrochemical production of hydroxyl radicals (Eq. 1) produces H⁺, thereby decreasing the pH of treated waters (Uranga-Flores et al., 2015). Further, hydroxyl radicals may then combine to form hydrogen peroxide (Eq. 2), which may subsequently decay (Eq. 3), yielding oxygen and more H⁺ (Uranga-Flores et al., 2015).

However, because the NaNO₃, NaCl, and Na₂SO₄ electrolytes all exhibited different amounts of pH increase, these reactions are not sufficient to explain the observed pH differences, indicating that more specific interactions with each electrolyte are likely occurring. Indeed, the production of secondary oxidants via reactions between electrolytes, the electrodes, and/or hydroxyl radicals have been reported to affect H⁺ and OH⁻ concentrations, thereby affecting the solution pH. For example, chloride from the NaCl electrolyte may react to form chlorine (Eq. 4) and then, in an alkaline medium, consume OH⁻ to produce hypochlorite (Eq. 5), thereby lowering the pH (Sirés et al., 2014).

Further, the sulfate from the Na₂SO₄ electrolyte has been reported to react through two mechanisms to ultimately produce peroxodisulfate. The first involves direct oxidation of sulfate at the electrode (Eq. 6) (Uranga-Flores et al., 2015; Jalife-Jacobo et al., 2016). If the solution pH is such that the sulfate is protonated, the HSO₄⁻ can also react, yielding H⁺ and decreasing the pH (Eq. 7) (Uranga-Flores et al., 2015). However, the second mechanism produces OH⁻ through indirect hydroxyl radical mediated reactions (Eqs. 8 and 9), which would be expected to increase the pH (Uranga-Flores et al., 2015; Jalife-Jacobo et al., 2016).

Likewise, phosphate is also reported to undergo direct (Eq. 10) (Brillas and MartínezHuitle, 2015) and indirect hydroxyl radical mediated (Eq. 11) reactions to produce peroxodiphosphate, as well as other peroxophosphates, which are also affected by the pH and whether or not they are protonated (Sirés et al., 2014).

Unlike the other electrolytes, the nitrate electrolyte is not expected to undergo oxidation reactions. Rather, under some conditions, nitrate reduction may occur at the cathode (Eq. 12), yielding OH^- formation and increases in pH, as well as transformation and removal of nitrogen species through off-gassing (Eq. 13) (Lévy-Clément et al., 2003; Martin de Vidales et al., 2016).

Another possible explanation for the observed increases in pH may result from off gassing of hydrogen gas produced via reduction of water at the cathode (Eq. 14) (Brillas and MartínezHuitle, 2015).

Some combination of these reactions, favoring those that lead to the observed pH increases, are likely occurring in the system presented in this study. Complex interactions have been reported with the utilization of BDD anodes for electro-oxidation (Cui et al., 2009; Faouzi Elahmadi et al., 2009; Ratiu et al., 2010) impacting the pH. In this study, usage of 0.05N NaNO₃ electrolyte impacted pH less than the other electrolytes.

3.1.3 Minimizing Impacts of Secondary Oxidants—In addition to pH concerns, another potential microbial toxicity concern is that electrolyte interactions can form secondary oxidants, which may exhibit toxicity and require oxidant quenching. Secondary oxidants, including persulfates, percarbonates, perphosphates, chlorine, and even chlorate and bromate can be produced on many anodes, (Panizza and Cerisola, 2009; Sirés et al., 2014) complicating electrolyte selection in a given application by confounding data interpretation during system implementation. For example, the NaCl electrolyte produced oxidant(s) measuring up to 330 mg L⁻¹ as active chlorine during the two-hour treatment time of the 1.0 N NaCl blank trial. These DPD-measurable oxidants were readily quenched with sodium thiosulfate. Toxic effects were observed at the highest electrolyte concentrations of 0.5–1.0 N NaCl, but Microtox® toxicity remained below 20% for the lower electrolyte concentrations.

Because chloride salts are widely available and might be used despite toxicity concerns, further investigation of the oxidant(s) detected at very high levels using the NaCl electrolyte may be necessary. Two test compounds were chosen, one that reacts readily with chlorine and another that does not. Experiments were performed to degrade either BPA or tris(2-chloroethyl) phosphate (TCEP) utilizing an electro-oxidation with a BDD anode, comparing the NaCl or the NaNO₃ electrolytes. The results are summarized in Figure 1. TCEP, which is not expected to react readily with active chlorine, was degraded at a similar rate regardless of which electrolyte was used. BPA, which is expected to react readily with active chlorine, was degraded in less than three minutes of treatment using the NaCl electrolyte, even with very little time for the chlorine concentration to build. The reaction progressed much more slowly in the presence of NaNO₃, which is not expected to participate in the reaction or produce reactive chlorine. Therefore, this electrochemical oxidation using a BDD anode, in the presence of the NaCl electrolyte, likely produces large concentrations of active chlorine, which may contribute to the degradation of contaminants, similar to reports with other electrodes (Murugananthan et al., 2011; Saylor et al., 2012). Although not directly measured in this study, the formation of organochlorinated intermediates, as well as chlorate, may present further concerns when using the NaCl electrolyte (Sirés et al., 2014).

Prior to electro-oxidative treatment using the BDD anode, the DPD test did not indicate the presence of oxidants for the Na₂SO₄ electrolyte solutions. However, after treatment, the presence of persistent oxidants was observed. The 0.5 N solution produced oxidants equivalent to up to 103 mg L⁻¹ as Cl₂ almost two months after sample generation. Further trials with 0.05 N Na₂SO₄ indicated that the DPD color change continued for 20 minutes or

more after DPD was mixed with the samples, as well as after quenching with sodium thiosulfate. This indicates that some portion of the oxidants formed react more slowly with DPD than chlorine, hydrogen peroxide, or chloramines and that they are not readily quenched by sodium thiosulfate. Indeed, persulfate reactions with sodium thiosulfate have been reported, but long reaction times may be necessary to achieve oxidant removal (Olmez-Hanci et al., 2014). Even after quenching, all concentrations of the Na_2SO_4 electrolyte exhibited variable toxicities. Together, these factors render this electrolyte less applicable.

The NaNO_3 and NaH_2PO_4 electrolytes only measured up to 1.5 mg L^{-1} and 2.4 mg L^{-1} oxidant as Cl_2 , respectively. The NaNO_3 electrolyte yielded greater Microtox® toxicities for higher normalities. However, no discernible trend was found between NaH_2PO_4 electrolyte concentration and toxicity. These results indicate that NaNO_3 might be more inert than NaCl or Na_2SO_4 during electro-oxidation using a BDD anode and that, from a microbial toxicity standpoint, it could be advantageous over the other electrolytes at concentrations of approximately 0.05N.

3.2 Investigation of effect of electrolyte on toxicity and degradation

In light of the general greater toxicity and pH changes at higher normality, the 0.05 N electrolyte concentration was chosen for further trials with propanil as a model contaminant. The NaCl , NaNO_3 , Na_2SO_4 , and NaH_2PO_4 electrolytes were studied to determine their simultaneous effects on contaminant degradation, as well as on microbial toxicity. Propanil degradation and the corresponding Microtox® toxicities are presented in Figure 2 (note that analytical variability contributes to large fluctuation in C/C_0 when both values are large). After two hours of treatment, the Na_2SO_4 electrolyte exhibited 100% propanil degradation, followed by NaH_2PO_4 (73% degradation), and NaNO_3 (56% degradation). The NaCl electrolyte, frequently utilized in the literature and sometimes recommended by manufacturers, exhibited the slowest propanil degradation, with only 36% degradation after two hours of treatment. The propanil degradation was sensitive to electrolyte and followed the overall trend: $\text{Na}_2\text{SO}_4 > \text{NaH}_2\text{PO}_4 > \text{NaNO}_3 > \text{NaCl}$.

The Microtox® toxicity (Figure 2b), however, did not follow this trend with the final Microtox® toxicities reading: $\text{Na}_2\text{SO}_4 < \text{NaCl} < \text{NaH}_2\text{PO}_4$ (quenched with sodium thiosulfate) $< \text{NaNO}_3 < \text{NaH}_2\text{PO}_4$ (unquenched). The final Na_2SO_4 and NaCl samples did not exhibit Microtox® toxicities above the 10% toxicity threshold (Sánchez et al., 2014), with final toxicities of $5\% \pm 1\%$ and $11\% \pm 2\%$, respectively. The solution treated with the NaH_2PO_4 electrolyte exhibited $92\% \pm 1\%$ toxicity after two hours of treatment, though once quenched, the final toxicity decreased to $23\% \pm 1\%$. This toxicity was not observed in the blank and may indicate some secondary oxidant formation/reactions contributing to microbial toxicity. The NaNO_3 exhibited a slightly greater toxicity to that of the quenched NaH_2PO_4 with $32 \pm 1\%$ inhibition after the two-hour treatment time. Interestingly, in Figure 2b, the NaNO_3 samples showed increased toxicities within the first 10 minutes of treatment, then a subsequent decrease in toxicity.

In spite of exhibiting lower contaminant degradation compared to several other electrolytes, 0.05 N NaNO_3 electrolyte was chosen for the majority of further trials due to lack of demonstrated toxicity and other process concerns such as inertness and buffering capacity.

The NaNO_3 electrolyte has been reported to be inert during electro-oxidation with BDD anodes, meaning that the electrolyte does not participate in reactions nor produce secondary oxidants, so the majority of the resulting contaminant degradation would likely result only from reactions with hydroxyl radicals (Murugananthan et al., 2011). Further, the NaNO_3 avoids several pitfalls of other electrolytes such as the potential for producing chlorinated byproducts as with NaCl , along with the toxicity and pH adjustment issues related to the buffering capacity of NaH_2PO_4 . In addition, the nitrate electrolyte itself is not expected to adversely impact biological processes and many utilities already have processes in place for its removal because it is a common nutrient. Since electrolytes are not expected to be present in many of the contaminated waters arising from incident response situations, waters may need to be amended with the nitrate electrolyte prior to electrochemical treatment with BDD anodes.

3.3 Treatment Performance and Toxicity for a Variety of Classes of Contaminants

A concentration of 0.05 N NaNO_3 electrolyte was used to investigate the ability of electro-oxidation using a BDD anode to degrade a variety of contaminants. As detailed in Table S1, these contaminants include herbicides and pesticides such as propanil, carbofuran, aldicarb, atrazine and cyanazine; flame retardants such as PFOA, diethyl methyl phosphonate (DEMP) and TCEP; and pharmaceuticals/contaminants of interest such as BPA, carbamazepine, and phenylephrine. These contaminants were selected to cover a range of reported hydroxyl radical reaction rates and chemical structures (listed in Table S1), as well as potential contamination incident concerns. Contamination concentrations ranged up to 10 mg L^{-1} , to represent concentrations that might be generated during some contamination scenarios.

Contaminant degradation and the corresponding Microtox® toxicity for these contaminants are presented in Figure 3. Contaminant degradation profiles for phenylephrine and aldicarb are not presented in Figure 3a due to analytical detection issues. Contaminants that consistently fell below the 10% Microtox® toxicity threshold, including TCEP, cyanazine, DEMP and PFOA, are not shown in Figure 3b (to yield a more readable figure). Data in Figure 3 demonstrate that the extent of electro-oxidation using a BDD anode is very contaminant-dependent, under the conditions tested. For example, carbofuran was nearly completely degraded, with 95% degradation in the two-hour treatment time, whereas PFOA and DEMP exhibited very little degradation with 13% and 15% degradation, respectively.

Figure 3b demonstrates a variety of microbial toxicity behaviors that do not necessarily follow the corresponding contaminant degradation data. In particular, carbofuran, the contaminant with near complete degradation, also exhibited the highest Microtox® toxicity by the end of the two-hour treatment time. These results for carbofuran suggest that degradation intermediates are more toxic than the parent compound and, coupled with its near complete degradation, these intermediates may have been produced in quantities large enough to exhibit Microtox® toxicity. Accordingly, it is not unreasonable that some other compounds have toxic degradation intermediates as well, but either the parent compounds were refractory enough during the two-hour treatment time or that the intermediates were

degraded quickly enough that the intermediates were not present in sufficient quantity to exhibit toxic effects.

Several compounds in this study, like BPA and propanil, showed measurable degradation that did not correspond to similar reductions in Microtox® toxicity. In contrast, other contaminants like DEMP and PFOA exhibited very little degradation but were consistently below the toxicity threshold. Microtox® toxicities for carbofuran, carbamazepine, atrazine, propanil increased during treatment. These multi-contaminant degradation and toxicity results demonstrate that parent contaminant degradation alone is not an adequate measure of treatment, and that Microtox® toxicity could be an important tool for understanding the effectiveness and implications of electro-oxidation of contaminated waters using a BDD anode.

While the Microtox® assay may be a useful indicator of ecotoxicity, it has been reported to be a poor indicator of microbial toxicity for activated sludge microbes due to its sensitivity (Dalzell et al., 2002). NI results, presented in Table 1, better indicate potential effects of treatment on activated sludge organisms for this study. A 50% inhibition benchmark for NI is used by some utilities to indicate a level of concern warranting further testing. This benchmark is based on research studying inhibition by heavy metals (Juliastuti et al., 2003; Hartmann et al., 2013). These toxicity thresholds are operational and can be defined at various levels based on the toxicity test and the individual situation. These inhibition results are generally categorized from 20% to 50% inhibition for similar activated sludge test methods (Juliastuti et al., 2003). Results show that only the pre-EAOP treatment sample containing propanil exhibited toxicity within its error of the 50% inhibition benchmark. Many of the pre- and post-treatment NI toxicity results are not significantly different from each other at the 95% confidence interval. Further, observed negative inhibition results indicate that, in some cases, EAOP-treated contaminated waters promoted nitrification in activated sludge. These results suggest that activated sludge is fairly resilient to contaminant loading, as well as to impact by EAOP-treated effluent. These results generally demonstrate low NI toxicity and should bolster the confidence—but not eliminate all concerns—of wastewater treatment works in accepting a variety of contaminated waters.

4 Conclusions

This study provides systematic information about the impacts of background electrolytes on pH, potential secondary oxidant formation, contaminant degradation, and microbial toxicity upon electro-oxidation using BDD anodes. This study is particularly valuable for practical applications of EAOPs due to its systematic evaluation of toxicity resulting from various electrolytes and contaminant classes. The optimal electrolyte for this study, nitrate, balances competing factors and is compatible with current nutrient removal treatment processes.

The extent of contaminant degradation alone is not enough to monitor reaction progress nor infer that effluents are less toxic to receiving waters, highlighting the importance of testing microbial toxicity. Further, although the Microtox® toxicity test may be a good screening tool for some contaminants, its results may not be indicative of activated sludge behavior. Overall, in spite of incomplete contaminant degradation, observed NI results may bolster the

confidence of wastewater utilities in the resiliency of their activated sludge processes to a variety of contaminants of concern, including effluents from EAOP treatment using BDD anodes.

This study demonstrates the applicability of electro-oxidation using the BDD anode toward treatment of refractory organic compounds in waters generated by intentional and unintentional incidents. These results address immediate knowledge gaps and help provide decision makers with an additional treatment tool in a toolbox approach to address portable and incident/situation-specific goals. Studies comparing this electro-oxidation system using a BDD anode with O_3/H_2O_2 and an UV/H_2O_2 AOPs will be presented in a future publication.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1:
Degradation of tris(2-chloroethyl) phosphate(TCEP) and Bisphenol A(BPA) in an unbuffered electro-oxidation using a BDD anode with 0.05 N NaCl or NaNO₃ electrolytes and 4.4 A applied current.

Figure 2: Propanil degradation (a) and Microtox® toxicity (b) using unbuffered electro-oxidation using a BDD anode with 0.05 N electrolytes and 4.4 A or 8.8 A (higher current) applied current.

Figure 3:
 Degradation (a) and Microtox® toxicity (b) of various contaminants using unbuffered anodic oxidation using a BDD anode with 0.05 N NaNO_3 electrolyte and 4.4 A applied current.

Table 1:

Nitrification Inhibition Percentages upon Electro-Oxidation with a BDD Anode. Inhibitions above or within the error of the 50% threshold are bolded.

Compound	Pre-EAOP NI	% Error	Post-EAOP NI	% Error
<i>Carbamazepine</i>	−6%	2%	17%	8%
<i>Aldicarb</i>	3%	32%	7%	5%
<i>Phenylephrine</i>	4%	5%	12%	5%
<i>BPA</i>	0%	12%	2%	4%
<i>Carbofuran</i>	6%	12%	23%	5%
<i>Atrazine</i>	−23%	30%	8%	25%
<i>Propanil</i>	42%	13%	29%	18%
<i>Cyanazine</i>	6%	7%	27%	9%
<i>DEMP</i>	8%	20%	17%	4%
<i>TCEP</i>	3%	6%	−9%	14%
<i>PFOA</i>	−25%	10%	22%	22%